

# AERC 2014

9th Annual European  
Rheology Conference

April 8 – 11, 2014  
Karlsruhe, Germany



organized by



German Rheological Society

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# Welcome to the AERC in Karlsruhe!

## Dear fellow rheologists,

As engineers, scientists, educators and researchers not only from Europe, but all over the world, we converge these days to share our ideas and advance our knowledge in rheology. Our subject is central to many technological pursuits in the areas of chemical engineering, biological systems and life science engineering. Fundamental aspects of polymer chemistry and soft matter physics are also prominent in rheological research. With the AERC 2014, we have made an effort to gather a wide range of advanced research in all areas of rheological matters.

This is the 9<sup>th</sup> AERC and meanwhile this European rheology meeting is well established in the international conference landscape. This year, 441 abstracts have been submitted, comprising 327 contributions from European colleagues and 114 abstracts submitted by fellows from 22 countries overseas. We have selected 250 oral contributions in six parallel sessions with no keynote lectures in order to give as many of our colleagues, especially the younger ones at the early stage of their careers, a chance to present their results and ideas. Beyond that, almost 200 posters will be on display for the duration of the conference. Furthermore, twelve companies will show their latest developments in rheological equipment and measuring techniques with experts at each table waiting for your questions and feedback.

Lots of work has been necessary to put all this together and on behalf of the organizing committee we would like to thank everyone who contributed to the AERC 2014 Karlsruhe. First of all, we have to thank the ESR for providing this European conference platform. We also would like to acknowledge all the sponsors and exhibitors for their generous financial support. Thanks also to the session chairs and the members of the scientific organizing committee for developing an ambitious scientific program. Last, but not least, we would like to express our deep gratitude to the members of our research groups and the local organizing committee including the DRG office in Berlin who did all the background work to make this event happen.

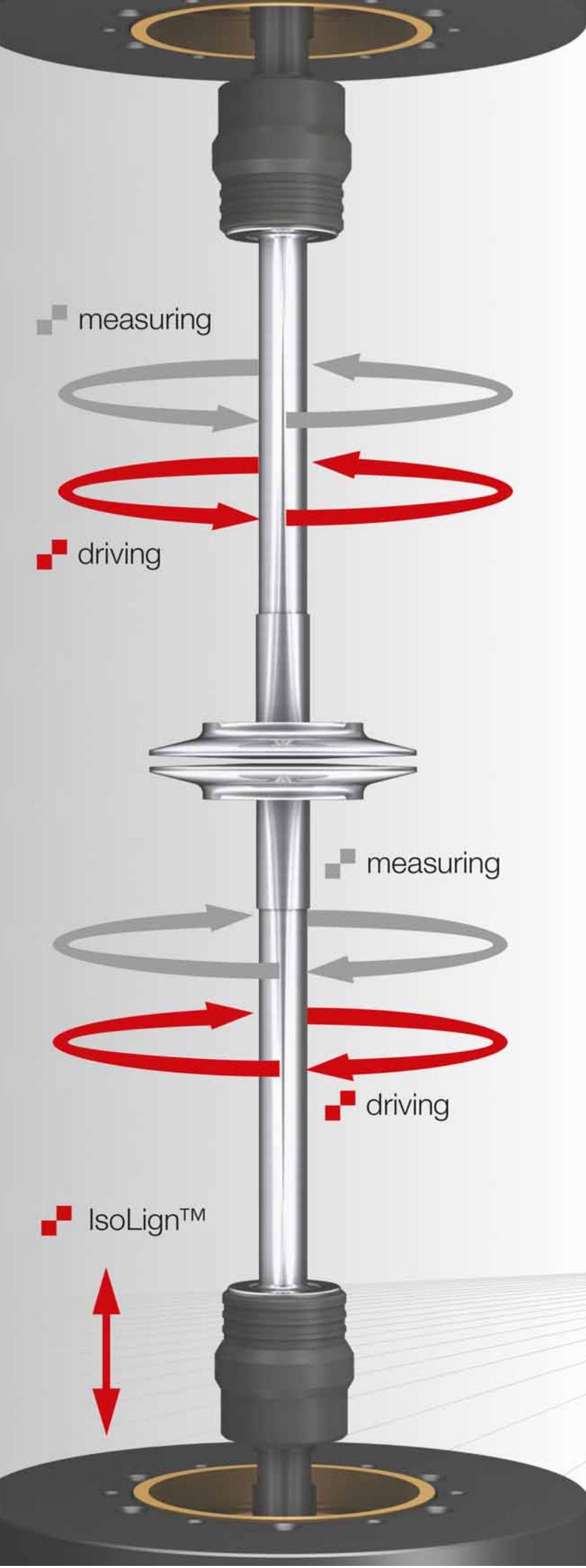
In the end, it is you who will make the conference a success. So give and enjoy superb talks, posters and exhibitions - and do not forget to take some time to explore the hidden beauties of Karlsruhe!



A handwritten signature in blue ink that reads "N. Willenbacher".

A handwritten signature in blue ink that reads "Manfred Wilhelm".

Norbert Willenbacher                      and                      Manfred Wilhelm  
- Chairmen Annual European Rheology Conference 2014 -



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# Into the Future – in Karlsruhe

## Business and hi-tech centre

Karlsruhe is well known as the city of researchers: Carl Benz, inventor of the automobile, was born here; while physicist Heinrich Hertz discovered electromagnetic waves at the city's university. Today, one of the most prominent think tanks is Karlsruhe Institute of Technology (KIT), a merger of Karlsruhe Research Centre and Karlsruhe University. And that is just one of the reasons why the city is at the heart of the Karlsruhe Technology Region, one of the most dynamic and successful economic regions in Europe. Over 2,500 companies are active in the IT and media sector alone.

## Home to art and culture

Visitors to Karlsruhe will not be disappointed by its cultural attractions. The city is home to a number of excellent museums. In addition to the Baden State Museum (Badisches Landesmuseum), located in the Karlsruhe palace, there is the State Art Gallery (Staatliche Kunsthalle), Municipal Gallery (Städtische Galerie) and Natural History Museum (Naturkundemuseum). Karlsruhe's ZKM | Centre for Art and Media – Germany's answer to France's Pompidou Centre – offers a unique cultural experience. As the world's first interactive museum, it invites visitors to join in and be amazed. Every year, the international art scene comes together for the art KARLSRUHE art fair.

## A green city with savoir-vivre

Karlsruhe combines urban flair with attractive parks and natural landscapes. Shoppers flock to the busy shopping streets and the largest indoor shopping centre in southern Germany. Just a few minutes away, green oases such as the municipal gardens (Stadtgarten) and the riverbanks along the Rhine are ideal for enjoying a walk or a quiet break. Lovers of good food will find plenty to tempt the palate in Karlsruhe. Renowned for their outstanding quality, restaurants specialising in the traditional cuisine of Baden offer dishes prepared with locally grown ingredients.



The pyramide on the market place is a popular meeting place in Karlsruhe right in the city center.

Photo by Stadt Karlsruhe

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- Applications in laboratories and small scale production
- The development of new products
- Testing the processing behavior for recipe development or incoming and final material inspection
- Quality control during production in combination with measuring heads
- Production of small tubes and profiles
- Production of blown and flat films
- On-line rheology combined with film inspection and haze and gloss measurement
- Determination of rheological properties of compounds under process conditions

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### Extrusion rheology for product quality specification

$$\tau = \frac{\Delta p \cdot R}{2 \cdot L} \text{ Pa}$$

$$\dot{\gamma} = \frac{4 \cdot \dot{V}}{\pi \cdot R^3} \text{ s}^{-1}$$

$$\eta = \frac{\tau}{\dot{\gamma}} \text{ Pa} \cdot \text{s}$$

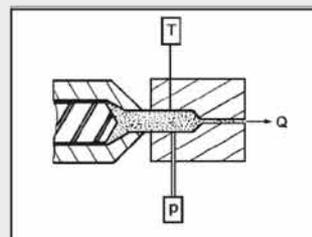
Evaluation of kinematic viscosity with a rheometric round capillary die head

$$\tau = \frac{\Delta p \cdot H}{2 \cdot L} \text{ Pa}$$

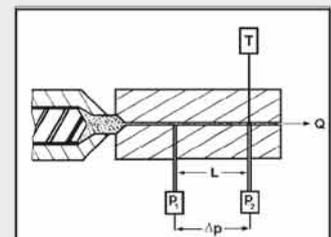
$$\dot{\gamma} = \frac{6 \cdot \dot{V}}{B \cdot H^2} \text{ s}^{-1}$$

$$\eta = \frac{\tau}{\dot{\gamma}} \text{ Pa} \cdot \text{s}$$

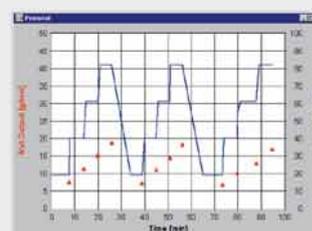
Evaluation of kinematic viscosity with a rheometric slot capillary die head



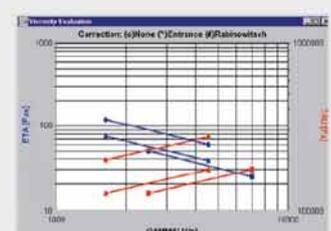
Schematic of a round capillary die head



Schematic of a slot capillary die head



On-line diagram



Flowcurve

# KIT – Unique in German Research



Karlsruhe Institute of Technology (KIT) is the merger of Forschungszentrum Karlsruhe GmbH and Universität Karlsruhe (TH). This merger on October 01, 2009, resulted in one of the largest science institutions in Europe. KIT bundles the missions of both precursory institutions: A state university with teaching and research tasks and a large-scale research center conducting program-oriented provident research. Within these missions, KIT is operating along the three strategic fields of action of research, teaching, and innovation.

## Research

Research at KIT is organized in seven centers. These centers give KIT research its profile and allow for its strategic planning. The following KIT centers have been established:

- Energy
- Materials, Structures, Functions
- Elementary Particle and Astroparticle Physics
- Climate and Environment
- Mobility Systems
- Information, Systems, Technologies
- Humans and Technology

## Teaching

Education and the promotion of young scientists are in the focus of KIT. During their studies the students are already familiarized with real research projects. The number of scientists and engineers available for teaching exceeds the average. KIT's doctoral students are integrated in an attractive environment with small working groups and access to large devices. This gives the opportunity to conduct independent research in internationally competitive teams. Offers to students are complemented by non-specific advanced training in general and career-relevant key qualifications. Teaching at KIT is organized in 11 departments: Architecture, Civil Engineering, Geo- and Environmental Sciences, Chemistry and Biosciences, Chemical and Process Engineering, Electrical Engineering and Information Technology, Humanities and Social Sciences, Informatics, Mechanical Engineering, Mathematics, Physics, Economics and Management.

## Innovation

KIT has taken responsibility for designing the cooperation of science and industry such that research results are transferred optimally to the market. KIT has specialized in the commercialization of inventions and know-how regarding new products, processes, or services. Innovation management extends from the counseling of inventors and patent applications to technology marketing, project initiation, to licensing and the support of spinoffs.

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Fresenius Kabi employs around 31,000 people worldwide. In 2012 the company reported sales of more than €4.5 billion. Fresenius Kabi AG is a wholly owned subsidiary of the Fresenius SE & Co. KGaA health care group.

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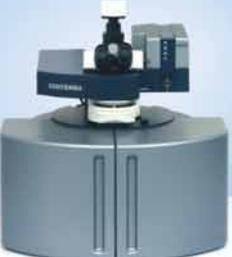
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# Industrial exhibition

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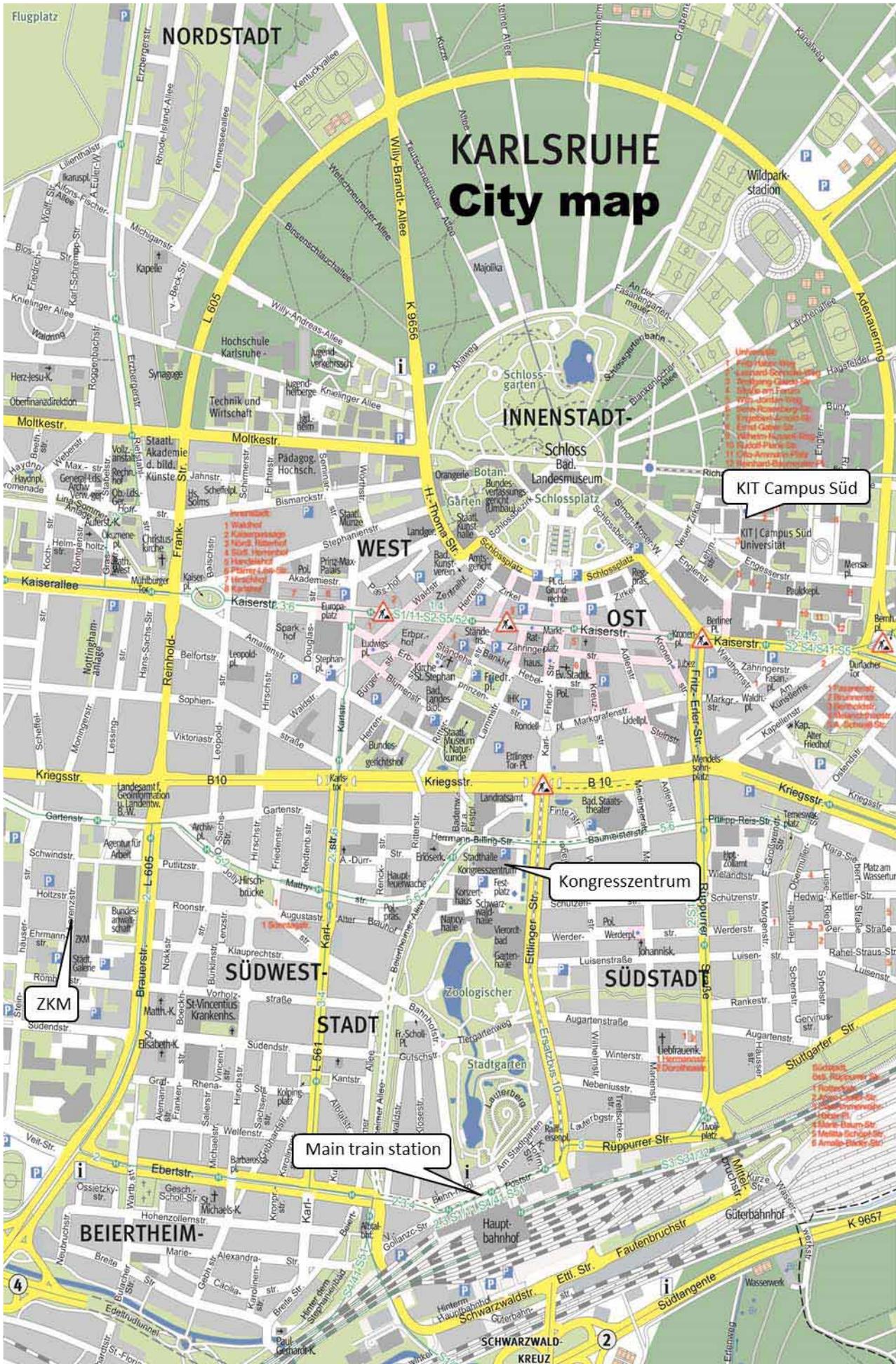
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# KARLSRUHE City map

KIT Campus Süd

Kongresszentrum

Main train station

ZKM

- 1. Hauptbahnhof
- 2. Karlsruher Schloss
- 3. Durlacher Tor
- 4. Schlossplatz
- 5. Schlossgarten
- 6. Zoo
- 7. Hauptbahnhof
- 8. Hauptbahnhof
- 9. Hauptbahnhof
- 10. Hauptbahnhof
- 11. Hauptbahnhof





## DRG – German Rheological Society

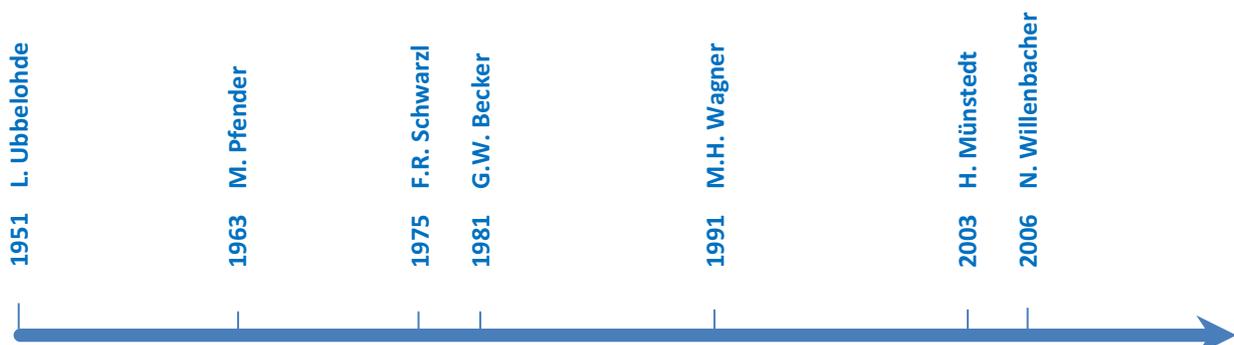
The German Rheological Society (DRG), founded in 1951, is **an association of experts from natural and engineering sciences** interested in all aspects of the deformation and flow of matter. The DRG attracts people from science, education and industry who aim to further the exchange of rheological expertise. The mission of the DRG is to promote and propagate rheology at all levels and build a tight network connecting academic and industrial partners.

**Annual meetings** facilitate exchange of latest developments regarding rheological aspects of process engineering, material design as well as new ideas dealing with experimental or theoretical aspects of rheology. In 2014 it is the AERC in Karlsruhe where members of the DRG as well as guests are welcome to present, share and discuss their ideas to a mutual benefit.

Today DRG has more than 200 members. With an annual fee of 12.50 Euro they support their network and also receive **various benefits** including a **reduced rate for the meetings and workshops** organized by the society and **a free copy** of six issues per year Applied Rheology. One of the main aims of the DRG to support young researchers. Therefore, DRG covers the conference fee for the PhD students participating in the AERC or ICR. More than 30 PhD students benefitted from **conference grants** within the last ten years. Moreover, every two years the DRG bestows the **Young Rheologists Award** to honor outstanding PD theses in the field of rheology.

Numerous internationally well recognized rheologists have served the executive board of the DRG during its more than 60 years of vivid history.

### Presidents of the DRG e. V.



# Organization

## Local Organizing Committee

@KIT, Karlsruhe

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Karolina Alibegovic (BAM, Berlin)  
Kerstin Bausch  
Nico Dingenouts  
Bernhard Hochstein  
Christopher O. Klein  
Claude Oelschlaeger  
Beate Oremek  
Sabine Weiland  
Jutta Willenbacher  
  
Manfred Wilhelm, conference chair  
Norbert Willenbacher, conference chair

## Scientific Committee

## Affiliation

---

Christian Friedrich	FMF, Freiburg
Ulrich Handge	HZG Geesthacht, Geesthacht
Christian Marotzke	BAM, Berlin
Christian Wagner	Universität des Saarlandes, Saarbrücken
Manfred H. Wagner	TU Berlin, Berlin

## Symposium

## Organizers

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Advances in Rheometry	Maik Nowak and Thomas Schweizer
Biopolymers, Active Fluids, and Food Rheology	Hans Wyss and Mats Stading
Colloids and Suspensions	Matthias Ballauff and Moshe Gottlieb
Fow-Induces Phase Transitions and Flow Instabilities	Christian Wagner and Sandra Lerouge
Non-Newtonian Fluid Mechanics and Flow Simulation	Pier L. Maffettone and Evan Mitsoulis
Industrial Rheology and Processing	Dick J. Dijkstra and Bettina Wolf
Polyelectrolytes, Associating Fluids, and Liquid Crystals	Christian Friedrich and Valery G. Kulichikin
Microfluidic and Microrheology	Monica Oliveira and Anke Lindner
Polymer Melts, Blends, Copolymers, and Nanocomposites	Ulrich Handge, Manfred Wagner, Dimitris Vlassopoulos, and Alexei Likhtman
Interfacial Phenomena, Surfactants, Emulsions, and Foams	Jan Vermant and Crispulo Gallegos
Viscoplasticity and Granular Media	Philippe Coussot and Igor Emri

## Symposium

## Shortname

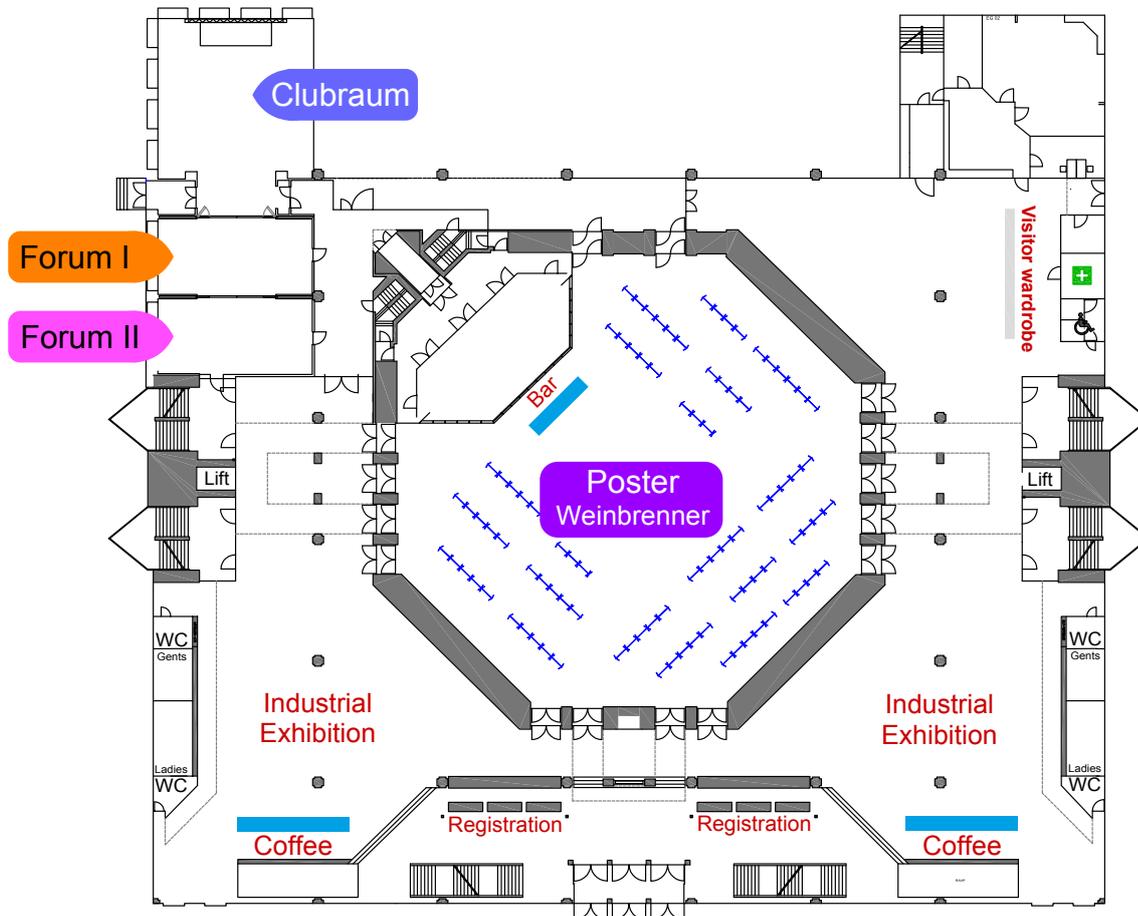
Advances in Rheometry	AR
Biopolymers, Active Fluids, and Food Rheology	BF
Colloids and Suspensions	CS
Flow-Induces Phase Transitions and Flow Instabilities	FI
Non-Newtonian Fluid Mechanics and Flow Simulation	FM
Industrial Rheology and Processing	IR
Polyelectrolytes, Associating Fluids, and Liquid Crystals	LC
Microfluidic and Microrheology	MR
Polymer Melts, Blends, Copolymers, and Nanocomposites	PM
Interfacial Phenomena, Surfactants, Emulsions, and Foams	SF
Viscoplasticity and Granular Media	VP

Tuesday, 8th of April						
17:00	Welcome Reception sponsored by Thermo Scientific (2 h)					
Wednesday, 9th of April						
8:30	Welcome at the AERC 2014 (20 min.), Hans-Thoma (Red)					
8:50	Plenary Lecture 1: Stephan Herminghaus (60 min.), Hans-Thoma					
9:50	Coffee Break sponsored by Fresenius (30 min.)					
	<b>Hans-Thoma</b> (Red, 660 seats)	<b>Johann-Peter-Hebel</b> (Yellow, 250 seats)	<b>Alfred-Mombert</b> (Green, 250 seats)	<b>Clubraum</b> (Blue, 145 seats)	<b>Forum I</b> (Orange, 75 seats)	<b>Forum II</b> (Pink, 73 seats)
10:20	PM1	PM43	CS1	BF1	SF1	LC1
10:40	PM2	PM44	CS2	BF2	SF2	LC2
11:00	PM3	PM45	CS3	BF3	SF3	LC3
11:20	PM4	PM46	CS4	BF4	SF4	LC4
11:40	PM5	PM47	CS5	BF5	SF5	LC5
12:00	Lunch Break (70 min.)					
13:10	PM6	PM48	CS6	BF6	SF6	LC6
13:30	PM7	PM49	CS7	BF7	SF7	LC7
13:50	PM8	PM50	CS8	BF8	SF8	LC8
14:10	PM9	PM51	CS9	BF9	SF9	LC9
14:30	PM10	PM52	CS10	BF10	SF10	IR1
14:50	Coffee Break (30 min.)					
15:20	PM11	PM53	CS11	BF11	SF11	IR2
15:40	PM12	PM54	CS12	BF12	SF12	IR3
16:00	PM13	PM55	CS13	BF13	SF13	IR4
16:20	PM14	PM56	CS14	BF14	SF14	IR5
16:40	PM15	PM57	CS15	BF15	SF15	IR6
17:00	Poster Session sponsored by Anton Paar (2h), Weinbrenner					
18:00	Public Meeting of the Committee of the European Society of Rheology (1h), Clubraum					

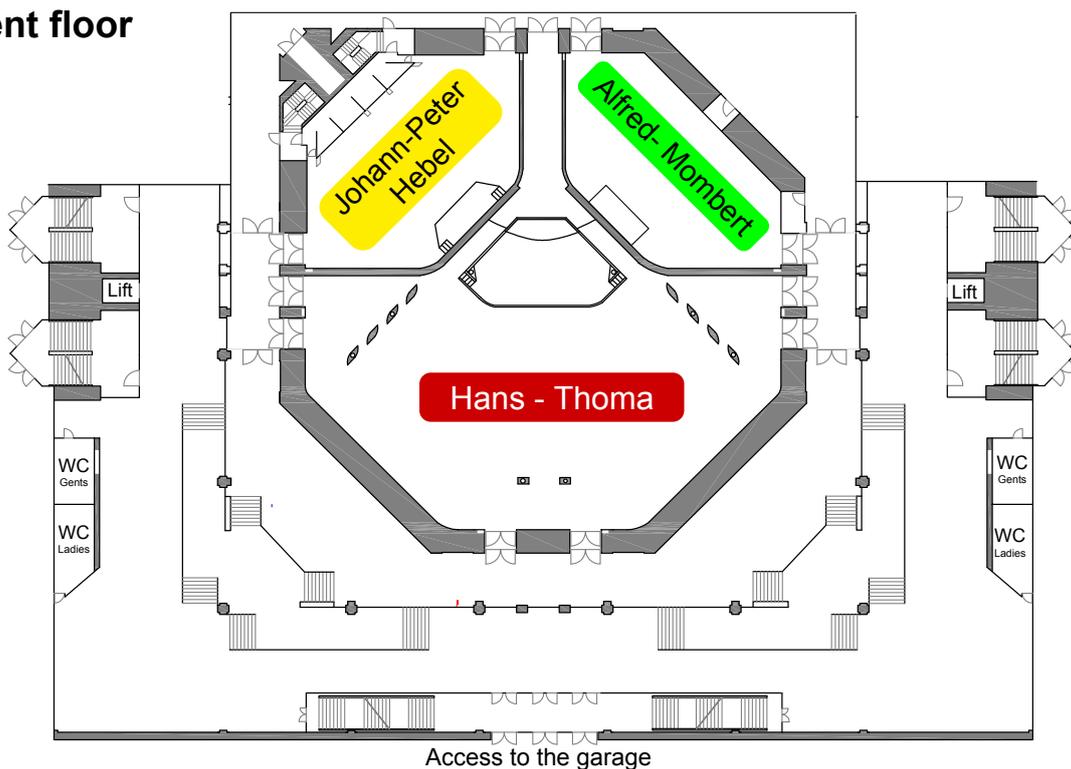
Thursday, 10th of April						
8:30	Plenary Lecture 2: Erich J. Windhab (60 min.), Hans-Thoma					
9:30	Short Break (10 min.)					
	<b>Hans-Thoma</b>	<b>Johann-Peter-Hebel</b>	<b>Alfred-Mombert</b>	<b>Clubraum</b>	<b>Forum I</b>	<b>Forum II</b>
9:40	PM16	FM1	CS16	BF16	SF16	IR7
10:00	PM17	FM2	CS17	BF17	SF17	IR8
10:20	PM18	FM3	CS18	BF18	AR1	IR9
10:40	Coffee Break sponsored by Fresenius (30 min.)					
11:10	PM19	FM4	CS19	BF19	AR2	IR10
11:30	PM20	FM5	CS20	BF20	AR3	IR11
11:50	PM21	FM6	CS21	BF21	AR4	IR12
12:10	PM22	FM7	CS22	BF22	AR5	IR13
12:30	Lunch Break (70 min.)					
13:40	PM23	FM8	CS23	VP1	AR6	IR14
14:00	PM24	FM9	CS24	VP2	AR7	IR15
14:20	PM25	FM10	CS25	VP3	AR8	IR16
14:40	PM26	FM11	CS26	VP4	AR9	IR17
15:00	PM27	FM12	CS27	VP5	MR1	IR18
15:20	Coffee Break (30 min.)					
15:50	PM28	FM13	CS28	VP6	MR2	IR19
16:10	PM29	FM14	CS29	VP7	MR3	FI1
16:30	PM30	FM15	CS30	VP8	MR4	FI2
16:50	PM31	FM16	CS31	VP9	MR5	FI3
17:10	PM32	FM17	CS32	VP10	MR6	FI4
18:30	Live music, dinner and art at the ZKM, doors open at 18:00					
19:15	Conference dinner sponsored by TA Instruments, ZKM Foyer					
Friday, 11th of April						
9:00	Plenary Lecture 3: Dimitris Vlassopoulos (60 min.), Hans-Thoma					
10:00	Handover of the poster prizes and presentation of the AERC 2015 (30 min.), Hans-Thoma					
10:30	Coffee Break (30 min.)					
	<b>Hans-Thoma</b>	<b>Johann-Peter-Hebel</b>	<b>Alfred-Mombert</b>	<b>Clubraum</b>	<b>Forum I</b>	<b>Forum II</b>
11:00	PM33	FM18	CS33	VP11	MR7	FI5
11:20	PM34	FM19	CS34	VP12	MR8	FI6
11:40	PM35	FM20	CS35	VP13	MR9	FI7
12:00	PM36	FM21	CS36	VP14	MR10	FI8
12:20	Lunch Break (70 min.)					
13:30	PM37	FM22	AR10	VP15	MR11	FI9
13:50	PM38	FM23	AR11	VP16	MR12	FI10
14:10	PM39	FM24	AR12	VP17	MR13	FI11
14:30	PM40	FM25	AR13	VP18	MR14	FI12
14:50	PM41	FM26	AR14	VP19	MR15	FI13
15:10	PM42	FM27	AR15	VP20	MR16	FI14
15:30	Farewell Coffee					

# KMK | Kongresszentrum – Stadthalle

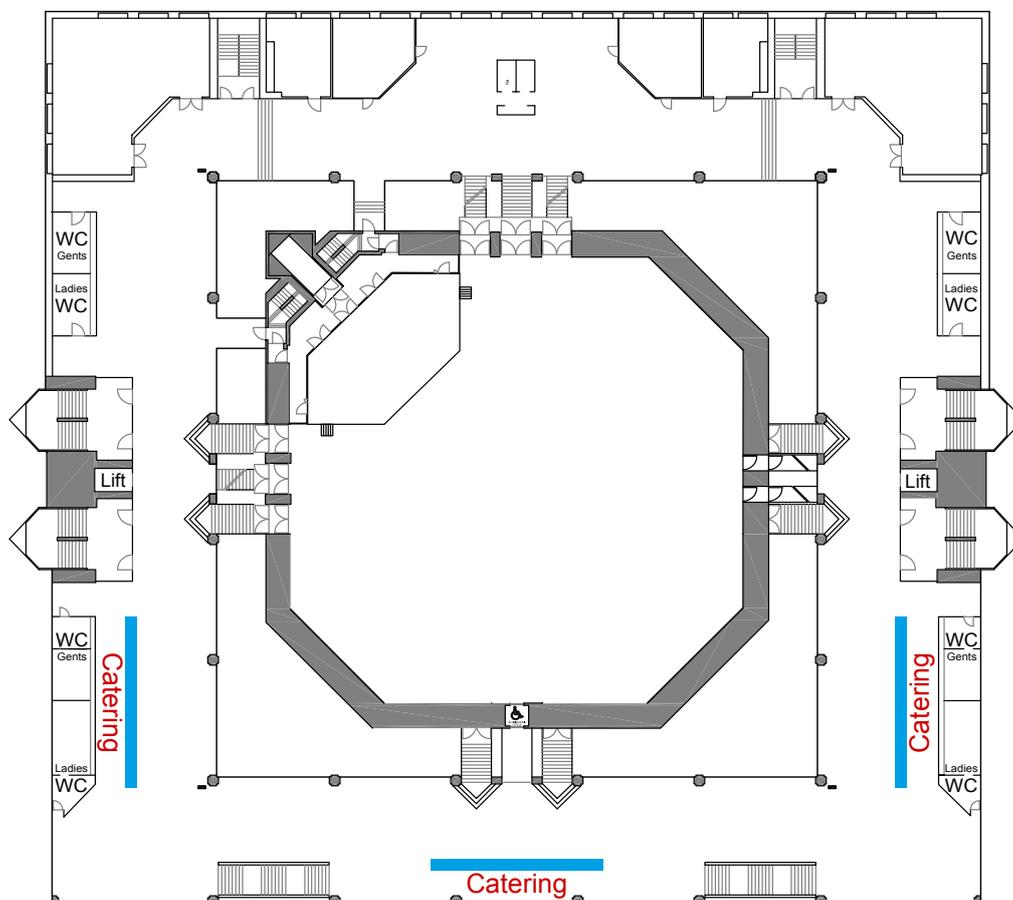
## Stadthalle Ground floor



## Stadthalle Basement floor



## Stadthalle Second floor



### Special agenda items and their location:

<b>Welcome Reception</b> (Sponsored by Thermo Scientific)	April 8, 2014 KMK, Stadthalle Foyer ground floor (Industrial Exhibition) 18:00 to 21:00
<b>Poster Session</b> (Sponsored by Anton Paar)	April 9, 2014 KMK, Stadthalle Weinbrenner Saal (ground floor) 17:00 to 19:00
<b>Conference Dinner</b> (Sponsored by TA Instruments)	April 10, 2014, from 18:00 ZKM – Center for Art and Media Lorenzstr. 19 76135 Karlsruhe
	18:30 to 19:00 Chamber concert in the ZKM Medientheater Doors open at 18:00
	19:15 to 24:00 Get-together and conference dinner in the Foyer of the ZKM
	20:30 to 22:00 Special opening of the ZKM interactive video art exhibition guided by museum scouts



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# Conference Dinner AERC 2014

April 10, 2014,  
from 18:30

ZKM - Center for  
Art and Media  
Lorenzstr. 19  
76135 Karlsruhe

The ZKM is a platform for **experimentation and discussion**, with a mission to participate actively in working towards the future and engage in the ongoing debate about the sensible and meaningful use of technology. Visitors appreciate its **extraordinary spacious ambiente** viewing public exhibitions, meeting up and enjoying events.



Photo by Stadt Karlsruhe

## PROGRAM OVERVIEW Dinner

- 18:30 to 19:00** Chamber concert in the ZKM Medientheater (doors open at 18:00)
- 19:15 to 24:00** Get-together and Conference Dinner in the ZKM Foyer
- 20:30 to 22:00** Special opening of the current ZKM interactive video art exhibition guided by museum scouts

## How to get there

### from the Kongresszentrum:

**By tram:** Take Bus 100 to Hauptbahnhof Vorplatz (main station), change to tram No. 2 (blue line). Get off at stop ZKM.

**By foot:** Cross Beiertheimer Allee than follow Alter Brauhof, proceed on Augustastraße and Roonstraße until you reach Brauerstraße. Cross Brauerstraße, turn left, after 120 m you will find the entrance to ZKM (1.6 km, approx. 20 min).

## Concert of the KIT chamber orchestra

Edvard Grieg:  
(1843 - 1907)

From the string quartet op. 27 g-Moll  
Un poco Andante - Allegro molto agitato, Romanze, Finale

Carl Maria von Weber:  
(1786 - 1826)

Overture to the opera "Der Freischütz"  
Adagio - Molto vivace



Photo by KIT chamber orchestra

**You may call them heroes.** In 2012, the **KIT chamber orchestra** won - for the seventh time in a row - the Deutsche Orchesterwettbewerb which takes place every four years. However, this time the KIT chamber orchestra set an unexpected highscore. The jury of the contest noted such an excellence in their presentation that they could not but giving the highest number of points to them that has ever been reached by an orchestra in this category. Additionally, the Deutsche Musikrat bestowed the title "**Orchestral Heroes**" upon them.



# BOOK OF ABSTRACTS

[www.aerc2014.kit.edu](http://www.aerc2014.kit.edu)



The scientific part of the abstract book has been designed and created by Christopher O. Klein.



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Tuesday, 8th of April						
17:00	Welcome Reception sponsored by Thermo Scientific (2 h)					
AERC 2014 Wednesday Morning, 9th of April						
8:30	Welcome at the AERC 2014 (20 min.), Hans-Thoma					
8:50	Plenary Lecture 1: Stephan Herminghaus, Complex fluids far from equilibrium (60 min.), Hans-Thoma					
9:50	Coffee Break sponsored by Fresenius (30 min.)					
	Hans-Thoma	Johann-Peter-Hebel	Alfred-Mombert	Clubraum	Forum I	Forum II
10:20	PM1 Hiroshi Watanabe Component relaxation times in entangled binary blends of linear chains: Reptation/CLF along partially or fully dilated tube	PM43 Giovanni Filippone Assembly of interfacially adsorbed plate-like nanoparticles in immiscible polymer blends	CS1 Stefan Egelhaaf Stress overshoots in concentrated colloidal dispersions and metallic glasses: A microscopic structural study	BF1 Ward Janssens Influence of urea on the rheology of gliadin solutions	SF1 Fabian C. Birbaum Interfacial rheology of particle at the water-air interface in the LAOS regime	LC1 Florian J. Stadler NIPAM-based polymers with dopamine-functionalities – versatile building blocks for self-healing hydro- and organogels with tunable rheological properties
10:40	PM2 Manfred H. Wagner A Unifying Model for Elongational Flow of Polymer Melts and Solutions Based on the Interchain Tube Pressure	PM44 Kangsheng Liu 'Disentanglement' of polyethylene chains in the presence of graphene	CS2 Tatjana Sentjabrskaja Glasses of binary colloidal mixtures under shear	BF2 Thomas H. S. van Kempen Why blood clots don't break: Nonlinear viscoelastic properties of fibrin	SF2 Caroline Balemans The Influence of Interfacial Rheology on the Drainage and Dewetting of Thin Liquid Films	LC2 Fabien Dutertre Rheological properties of sticky rods formed by self-assembled comb-like amphiphilic copolyelectrolytes
11:00	PM3 Thomas Schweizer Non-linear rheology of melts of dendronized polymethacrylate polymers with varying length and generation	PM45 Gerald J. Schneider From the Chain Conformation and Dynamics in Polymer at the Micro and Mesoscale to the Macroscopic Properties of Nanocomposites	CS3 Marco Laurati Microscopic investigation of creep in colloidal glasses	BF3 Giovanna Tomaiuolo Clinical evaluation of Cystic Fibrosis patients by mucus viscoelastic properties	SF3 Peter Fischer Interfacial rheology of bacterial biofilms at air/water and oil/water interfaces	LC3 Hayder a Abdulbari Flow behavior of non-Newtonian anionic polymer-surfactant mixtures in pipes
11:20	PM4 Alexei Likhtman The tube axis and entanglements in polymer melts	PM46 Hadi Goldansaz Anomalous Rheological Behavior of Polymeric Nanoparticle/Linear Polymer Blends	CS4 Miriam Siebenbürger Transient Rheology of Colloidal Suspensions - Shear Reversal	BF4 Francois Caton The elasticity of blood	SF4 Dirk W. Schubert A Novel Simple Approach for Spreading Dynamics of Polymeric Fluids	LC4 Catalin Gainaru Rheological signature of supramolecular structures in hydrogen-bonded liquids
11:40	PM5 Giovanni Ianniruberto Convective Constraint Release Revisited	PM47 Sam Krop Filled polycarbonate; the sum of its parts?	CS5 Michel Cloitre Internal stress in soft particle glasses	BF5 Anke Lindner Microfluidic flows of E. coli suspensions	SF5 Leonard Sagis Nonlinear rheology of fluid-fluid interfaces with a complex microstructure	LC5 Tetsuharu Narita Linear and non linear viscoelastic properties of chemically crosslinked associating polymer gels: separability of strain and time effects governed by sticky Rouse mode
12:00	Lunch Break (70 min.)					

**AERC 2014 Wednesday Afternoon, 9th of April**

	Hans-Thoma	Johann-Peter-Hebel	Alfred-Mombert	Clubraum	Forum I	Forum II
<b>13:10</b>	PM6 Qian Huang Bridging the Gap between Semidilute Polymer Solutions and Polymer Melts	PM48 Anton Santamaría The enigma of the apparently vanishing long chain branches in nanocomposites elaborated with irradiated polypropylene	CS6 H. Henning Winter Powerlaw relaxation with positive exponent for the colloidal glass transition and negative exponent for gelation	BF6 Andre Braun Using rheological methods to measure biological responses of living cells to hydrodynamic stresses	SF6 Job Thijssen Interfacial Rheology of Model Particles at Liquid Interfaces	LC6 Claudia Schmidt Shear Banding in a Lyotropic Lamellar Phase Studied by Nuclear Magnetic Resonance Diffusometry and Velocimetry
<b>13:30</b>	PM7 Maksim Shivokhin Understanding the effect of constraint release environment on the end-to-end vector relaxation time of linear chains	PM49 Zdenek Starý Elongational rheology of carbon black filled polymethylmethacrylate	CS7 Alessio Zaccone Linking self-assembly, relaxation and rheology at the colloidal gel transition	BF7 Simon J. Haward Synovial Fluid Hyaluronate Analysis using Stagnation Point Flow	SF7 Heinz Rehage Deformation, orientation and bursting of microcapsules in simple shear flow: Wrinkling processes, tumbling and swinging motions	LC7 Pavlik Lettinga 3-D reorientational motion in sheared nematic platelet dispersions
<b>13:50</b>	PM8 Christos Tsenoglou Nonlinear viscoelasticity of Commercial Low Density Polyethylenes: the Effect of Long Chain Branching in the Presence of Entanglements	PM50 Ievgeniia Ivaneiko Multiscale approach to dynamic-mechanical behavior of reinforced elastomers	CS8 Esmaeel Moghimi Structural Modification of Colloidal Gels by Shear	BF8 Hector Matias Lopez Viscosity reduction due to the activity of Escherichia Coli	SF8 Dario Donnarumma Morphology and Flow Properties of Multilamellar Structures in Surfactant Solutions	LC8 Ruud van der Sman Stability of thin foams films stabilized with surfactants investigated by Lattice Boltzmann phase field method
<b>14:10</b>	PM9 Mahdi Abbasi Characterization of Long Chain Branched Topologies of Industrial Polyethylenes by Molecular Stress Function (MSF) Theory	PM51 Lukas Schwab Nonlinear behavior of heterogeneous elastomer samples investigated by means of Fourier Transform Rheology	CS9 Clara Weis Fluidization of highly concentrated crystalline dispersions	BF9 Domenico Gabriele Stabilisation of oil-based food suspensions through organogelation	SF9 Lazhar Benyahia A Droplet as a mini-rheometer to evaluate interfacial viscoelasticity of solid particles-laden liquid/liquid interfaces	LC9 Nino Grizzuti Time-dependent rheology and microstructure of fresh cement-based mortars
<b>14:30</b>	PM10 Pavlos S. Stephanou Multi-scale modeling of high-MW polymer melt viscoelasticity starting from the atomistic level	PM52 Mykhailo Semkiv Two-scale model for the elasto-viscoplastic behavior of silica-filled rubber	CS10 Fangfang Chu Dynamics of thermosensitive core-shell dumbbells	BF10 Guy Della Valle Envisioning wheat flour dough as a triphasic medium to predict bubbles structure stability	SF10 Philippe Coussot Measuring the Surface Tension of Yield Stress Fluids	IR1 Katja Klimke High Melt Strength Polypropylene (HMS-PP) from the Borealis Daploy™ HMS process: Process optimisation, characterisation techniques and applications
<b>14:50</b>	<b>Coffee Break (30 min.)</b>					
<b>15:20</b>	PM11 Efren Andablo-Reyes Non-linear shear flow behavior of disentangled ultra-high molecular weight polyethylene	PM53 Bastian Walter A Thermodynamically Consistent Model to Predict the Magneto-Rheological Behaviour of Magneto-Sensitive Elastomers	CS11 Thomas Voigtmann Channel flow of glass-forming fluids: combining microscopic theory with macroscopic simulation	BF11 Timo Faber Engineering cheese sensory-texture: computations and rheology on a semi-solid	SF11 Jan Vermant Dilatational rheometry using a circular through	IR2 Joachim Kaschta Elongational Flow Properties Of Long-Chain Branched Poly(Ethylene Terephthalate)
<b>15:40</b>	PM12 Debjani Roy Reentanglement Kinetics of sheared modified Polyisobutylene	PM54 Kamran Riazi Polystyrene comb architectures as a model for the investigation of spinnability of branched polymers	CS12 Fabian Frahsa Memory effects in colloidal rheology: A schematic mode coupling Model	BF12 Fausto Calderas Rheology of chocolate-flavored, reduced-calories coating as a function of conching process	SF12 Gerald G. Fuller Rheotaxis: The Sensing and Migratory Response of Microvascular Endothelial Cells to Local Wall Shear Stress Profiles	IR3 Maria Josefina Carbone Extensional behavior of Poly (lactic acid)
<b>16:00</b>	PM13 Evelyne van Ruymbeke Dynamic dilution effect in binary blends of linear polymers	PM55 Gale A. Holmes Rheological Evidence for Cure Retardation in Epoxy Clay Hybrid Nanocomposites	CS13 Samruddhi Kamble Ascertaining Universal Features of Yielding of Soft Materials	BF13 Noemi Baldino Rheological optimization of pasta dough mixing by large-deformation properties in uniaxial extension	SF13 Bettina Wolf Food emulsion interfaces to manipulate digestive behaviour	IR4 Oliver Steinhof Extensional flow properties of lubricating grease and the effect of tackiness additives
<b>16:20</b>	PM14 Ludovica Hengeller The effect of nematic interactions in uniaxial extension of polymer blends	PM56 Johannes Steinhaus Correlation of dynamic viscosity and dielectric ion viscosity of resins used for nano-hybrid dental composites and the effects of resin composition, temperature and filler content	CS14 Emmanuelle Abisset-Chavanne On the introduction of size effects in the mesoscopic description of microstructured suspensions via the use of high order approaches	BF14 Mats Stading Food Oral Design	SF14 Danila Gaudino Dynamic rheological response of entangled worm like micellar solutions	IR5 Damien Chaveroux Influence of polymer structure on the rheological behaviour and the shear stress stability of lubricants
<b>16:40</b>	PM15 Dimitrios G. Tsalikis Conformational dynamics and topological analysis for polymer rings via atomistic molecular dynamics simulations and comparison with experimental data	PM57 Emanuel Ionescu Rheological modeling of ceramic nanocomposites in creep	CS15 Jan Domurath Viscosity amplification in dilute suspensions of spherical particles with a non-Newtonian matrix fluid	BF15 Crispulo Gallegos Rheokinetics of salivary alpha-amylase catalysed hydrolysis of starch: effect of inhibitors	SF15 Antonio Perazzo Emulsion morphology evolution by phase inversion method	IR6 Alexandros D. Gotsis Bubble growth in a strain hardening polymeric fluid
<b>17:00</b>	<b>Poster Session sponsored by Anton Paar (2h), Weinbrenner</b>					
<b>18:00</b>	<b>Public Committee Meeting of the European Society of Rheology (1h), Clubraum</b>					

**AERC 2014 Thursday Morning, 10th of April**

**8:30** Plenary Lecture 2: Erich J. Windhab, Rheology in Oro-Gastro-Intestinal Structure Engineering (60 min.), Hans-Thoma

**9:30** Short Break (10 min.)

	Hans-Thoma	Johann-Peter-Hebel	Alfred-Mombert	Clubraum	Forum I	Forum II
<b>9:40</b>	PM16 Luigi Grassia Resolution of the local segmental mode in amorphous polymers	FM1 Yannis Dimakopoulos Effect of RBC migration phenomena on the hemodynamics in stenotic microvessels under pulsating flow conditions	CS16 Rossana Pasquino Alignment of spheres in confined geometries	BF16 Hasan Haj Ahmad Rheological Examination of Chicken Meat Restructuring	SF16 Jennifer Kübel Application of FT-rheology to the Characterization of Beer Foam	IR7 Abel Jerez Rheological behaviour of thin PVOH films for industrial applications
<b>10:00</b>	PM17 Vito Speranza Simultaneous measurements of rheology and crystallization of an isotactic polypropylene	FM2 Alexander Rüttgers 3D multiscale FENE dumbbell simulations on massively parallel multi-GPU clusters	CS17 Jooyoung Lee Effect of attractive nanoparticles on the gelation of bimodal suspension	BF17 José F. Solanilla Rheological properties of Costa Rican guava ( <i>Psidium friedrichsthalianum</i> (O. Berg) Niedenzu) pulp	SF17 Valery Kulichikhin The new interfacial rheometer: study of spreading phenomena on water surface	IR8 Sanjay Rastogi Unprecedented high-modulus high-strength tapes and films of Ultra High Molecular Weight Polyethylene via solvent-free route
<b>10:20</b>	PM18 Stefano Piccarolo Nodular morphology of melt solidified iPP suggests crucial role of melt before solidification	FM3 Francisco Chinesta PGD-based parametric solutions of double-scale Fokker-Planck equations: application to suspensions involving aggregates of rods	CS18 Monica Schneider Capillary Suspensions- A New Formulation Route for Printable Electronics	BF18 Amélie Banc Structuration and Rheological Properties of Gels made from Gluten Proteins	AR1 Victor H. Rolón-Garrido Transition from ductile to cohesive fracture of photo-oxidated LDPE	IR9 Huong-Lan Nguyen Process Rheology Of Extruded Wood-PVC-Composites

**10:40** Coffee Break sponsored by Fresenius (30 min.)

<b>11:10</b>	PM19 Hiroshi Watanabe Dielectric Relaxation of Entangled Monodisperse Polyisoprene: Contribution of Constraint Release	FM4 Filipe A. Cruz Influence of channel aspect ratio on the onset of elastic instabilities in three-dimensional cross-slots	CS19 George Petekidis Rheology, structure and dynamics of concentrated colloidal suspensions and glasses during start-up shear and cessation	BF19 Patrick A. Rühls Rheology of hagfish slime – a marine biopolymer	AR2 Robert Powell Direct Measurement of Rheological Properties of Viscoplastic Fluid in Laminar Hagen Poiseuille Flow Using Different Measurement Techniques	IR10 Steinar Ouren Viscoelastic behaviour of Polymer modified Bitumen at low temperatures
<b>11:30</b>	PM20 Yumi Matsumiya Rheo-Dielectric Responses of Entangled cis-Polyisoprene under Uniform Steady Shear and LAOS	FM5 Gaetano D'Avino Non-linear dynamics of an ellipsoid in a sheared viscoelastic fluid	CS20 Fabian Westermeier Combining coherent X-ray scattering with Rheology	BF20 Salvatore Costanzo Concentration effects on the sol-gel transition of HPC aqueous solutions	AR3 Fernando T. Pinho Extensional rheometry of magnetic dispersions	IR11 Paul Nommensen Controlled shear history in rheological characterization of cement- and gypsum-based construction materials
<b>11:50</b>	PM21 Mohamed Yousfi Highlighting the role of ionic liquids in the control of the morphology of immiscible polymer blends by interfacial tension assessment	FM6 Massimiliano M. Villone Simulations of the behavior of a spherical elastic particle in Newtonian and viscoelastic fluids under confined shear flow	CS21 Florence Gibouin Coupled measurements for local rheogram construction	BF21 Deepa Agarwal Rheological Properties of highly refined Cellulose: Carboxymethylcellulose Mixtures compared to other commercially available Fibres	AR4 Fábio A. Cardoso Pressure distribution evolution during squeeze-flow of cement-based mortars	IR12 Maximilian Pospischil Paste Rheology as Key to a Successful Development of an Industrial Dispensing Process for Solar Cell Metallization
<b>12:10</b>	PM22 Michael Langeloth Dynamics of linear polymer chains in a binary melt	FM7 John Tsamopoulos On the abrupt increase of the rise velocity of a deformable bubble in viscoelastic solutions	CS22 A. Kate Gurnon Rheology and microstructure of concentrated, near hard-sphere colloidal dispersions under steady shear and LAOS	BF22 Sharadwata Pan Unravelling the dynamics of Semi-dilute Polymer Solutions using DNA Rheology	AR5 Ingo F.C. Naue Applying a High Sensitive Force Measurement to a Commercially Available CaBER for Measuring Elongational and Tack Properties	IR13 Tinne Monteyne Continuous Pharmaceutical Melt Granulation: Rheology as a predictive Tool to determine processability of the Formulation

**12:30** Lunch Break (70 min.)

AERC 2014 Thursday Afternoon, 10th of April

	Hans-Thoma	Johann-Peter-Hebel	Alfred-Mombert	Clubraum	Forum I	Forum II
13:40	PM23 Kurt Kremer Coarse grained models for polyurethanes	FM8 Martien A. Hulsen Simulations of deformable systems in fluids under shear flow using an arbitrary Lagrangian Eulerian technique	CS23 Anni Sorvari Optical coherence tomography combined with rheological characterization of microfibrillated cellulose suspensions	VP1 Marjan Zare Buoyancy effects on micro-annulus formation in primary cementing of oil and gas wells	AR6 Aloyse Franck Orthogonal superposition (OSP) of small strain oscillation shear on steady or oscillation shear in a rotational rheometer	IR14 Matthias Kruse Influence of polymer extrusion on linear-viscoelastic properties of poly(ethylene terephthalate)
14:00	PM24 Helmut Münstedt Rheological Investigations of the Gelation of Polyvinylbutyral Solutions by Tetrabutyl-Orthotitanate	FM9 Michael F. Webster High-Weissenberg number predictions for contraction-expansion flow and micellar fluids	CS24 Jonathan E. Seppala Shear-induced irreversible breakdown of shear thickening fluids	VP2 Edson J. Soares Challenges on measuring the yield-stress of waxy crude oils	AR7 Jörg Läger An enhanced rotational rheometer system with two motors	IR15 Dietmar Lerche Interrelationship between rheological behavior of continuous phase and phase separation of dispersed nano- and micro-particles
14:20	PM25 Barry W. Fitzgerald Coarse Grained Computer Simulations of Star Polymer Melts	FM10 Robert J. Poole Symmetry-breaking bifurcations in T-channel flows: effects of fluid viscoelasticity	CS25 Victor Keniti Sakano Evaluation of consolidation of different cement paste by Vicat, oscillatory rheometry and isothermal calorimetry	VP3 Rafael Mendes Flow Behavior of Waxy Oils: from Local Rheology to Pipelines	AR8 Carlos Gracia Fernández Advances in the Rheological Characterization of ER Fluids	IR16 Haticé Mercan Numerical Investigation of Film Blowing Process
14:40	PM26 Christos Tzoumanekas Primitive path dynamics, Constraint Release and Contour Length Fluctuations in a model Polyethylene melt: A first principles, atomistic simulation study	FM11 Joana M. Malheiro Time-dependent secondary flows of FENE-CR fluids in a curved duct of square cross-section	CS26 Roberto Cesar de Oliveira Romano Monitoring of transition from fluid to solid state of cementitious suspensions with bauxite residue	VP4 Martin Boisy General aspects of yield stress fluids – Terminology and definition of viscosity	AR9 Herbert Mucha Advanced Dynamic Mechanic Thermal Analysis (DMTA) an interdisciplinary tool in industry and research	IR17 Peter Kunzelmann Semi-empirical equations for the description of Rheotens experiments
15:00	PM27 Livia Moreira Equilibration and rheological properties of high molecular-weight polymer melts	FM12 Arjen Bogaerds Fiber spinning under filament pull-out conditions: a stability analysis	CS27 Martin Bombrowski Negative first normal stress differences and microstructure in flocculated kaolin suspensions	VP5 Michael F. Webster Numerical modeling of thixotropic and viscoelastoplastic materials in complex flows	MR1 Tetsuharu Narita High frequency dynamics of a liquid crystalline, cyanobacterial, sulfated polysaccharide studied by DLS/DWS microrheology	IR18 Christian Clasen Dispersy and spinnability: Why highly polydisperse polymer solutions are desirable for electrospinning
15:20	<b>Coffee Break (30 min.)</b>					
15:50	PM28 Alexander Malkin A new approach for pressure drop calculations in flow of viscoelastic fluids through short channels	FM13 Mônica F. Naccache Finite element simulations of the displacement of a thin blade in an elasto-viscoplastic medium	CS28 Guillaume Ovarlez Shear-induced migration in noncolloidal suspensions	VP6 Jeremy Bleyer Simulations of yield stress fluid flows : a novel optimization technique	MR2 Mathias Reufer Recent trends in diffusing wave spectroscopy based microrheology	IR19 Joao Maia In-Situ Characterization of Model Thermoplastic Polyurethane Systems using Rheo-FTIR
16:10	PM29 Frédéric Bossard Chain Conformation and Thermal Annealing of Electrospun Polystyrene Fibers: A Small Angle Neutron Scattering Study	FM14 Sérgio Frey A numerical investigation of the flow of thixotropic elasto-viscoplastic materials through a planar sudden expansion	CS29 Roger Tanner Non-colloidal Suspensions: The Relation Between Theory and Experiment in Shearing Flows	VP7 Teodor Burghlea Why do some simple flows of Carbopol gels remain elusive?	MR3 Manlio Tassieri Measuring the solutions' relative viscosity with optical tweezers without Fourier transform	F11 Dietmar Auhl Flow-induced crystallisation kinetics of polylactid-acids from large amplitude shear rheology compared to optical and thermal analysis
16:30	PM30 Loic Hilliou PHA obtained from mixed microbial cultures fed with food industry by-products: thermorheological characteristics and benchmarking with commercial PHA	FM15 Rudy Valette Theoretical and numerical analysis of shear banding instabilities in thixotropic fluids	CS30 Wolfgang Gleissle Autolubricated Flow and Transient Flow Phenomena	VP8 Markus Hütter Suitability of the Ree-Eyring approach to describe yielding of polymer glasses	MR4 John Duffy Using optical microrheology and microfluidic flows to extend the rheological characterization of complex fluids into high frequency and high shear rate regimes	F12 Peter C. Roozemond Shear-induced crystallization of polypropylene: a rheological study with in-situ DSC and WAXD
16:50	PM31 Chen-Yang Liu The Rheological Behaviors of Polyethylene oxide in Ionic Liquids	FM16 Evan Mitsoulis Rheology of Poly lactides: Experiments and Simulations	CS31 Abdoulaye Fall Interplay Between Discontinuous Shear Thickening and Migration in Concentrated Cornstarch Suspensions	VP9 Caroline Hanotin Viscoelasticity of vibrated granular suspensions	MR5 Zahra Fahimi Deformation-dependent viscoelastic properties and inhomogeneity in physically cross-linked hydrogels by combining micro- and macro-rheology	F13 Natalie Germann Improved constitutive model for shear-banding wormlike micellar fluids and comparison with rheology & microstructure experiments
17:10	PM32 Wim Briels Brownian dynamics of self-assembly and rheology of stiff pi-stacking polymers	FM17 Ida Karimfazli Active control of convective heat transfer using electrorheological fluids	CS32 Gabriela Araujo Valencia Study of maximum volume fraction of particles of inert suspensions	VP10 Kasper van der Vaart Breaking Size-Segregation Waves in Granular Avalanches	MR6 Bruke Daniel Jofore Thin Film shear Rheology of P(NIPAM-co-AA) Microgels	F14 Dirk Sachsenheimer Capillary Thinning and Elongation Induced Structure of Wormlike Micelles Solutions
18:30	Live music, dinner and art at the ZKM, doors open at 18:00					
19:15	Conference dinner sponsored by TA Instruments, ZKM Foyer					

**AERC 2014 Friday Morning, 11th of April**

9:00

Plenary Lecture 3: Dimitris Vlassopoulos, Molecular rheology of entangled branched polymers using combs (60 min.), Hans-Thoma

10:00

Handover of the poster prizes and presentation of the AERC 2015 (30 min.), Hans-Thoma

10:30

Coffee Break (30 min.)

	Hans-Thoma	Johann-Peter-Hebel	Alfred-Mombert	Clubraum	Forum I	Forum II
11:00	PM33 Paula Moldenaers The effect of pressure on the viscosity of miscible polymer blends: relation between free volume and pressure coefficients	FM18 Edtson Emilio Herrera Valencia Continuous Squeeze Flow Film Of A Structured Fluid: Non-Newtonian Effects	CS33 Frank Aangenendt Shear-thinning of soft core-shell particles	VP11 Ranjini Bandyopadhyay Scaling behaviour in convection-driven Brazil nut effect	MR7 Erwin K. Reichel Parallel Plate Resonators for Shear-Wave Rheometry of Viscoelastic Fluids	F15 David Hoyle Extensional necking instabilities in complex fluids and soft solids
11:20	PM34 Frank Snijkers A rheological study of vitrimers	FM19 Thomas A. Hunt Periodic boundary conditions for the simulation of uniaxial extensional flow	CS34 Sunhyung Kim Direct observation of the formation of microstructure in drying colloidal films with in-situ vertical small angle X-ray scattering	VP12 Thomas Weinhart Coarse-grained local and objective continuum description of 3D granular flows down an inclined surface	MR8 Laura Casanellas Elastic instabilities in the microflow of viscoelastic fluids	F16 Sita Drost Contraction flow instabilities in nematic polymer solutions
11:40	PM35 Matthias Mihalic Assessing the phase structure of molten polymer blends using a generalized Gramespacher-Meissner model	FM20 Ramon Silva Martins Comparison between objective and non-objective kinematic flow classification criteria	CS35 Dimitri Merger Microstructural origins and nonlinear signatures of yielding in heterogeneous nanoemulsion colloidal gels	VP13 Dionysios Photeinos On the increase of the Mean Rise Velocity of a Bubble in a Viscoplastic Fluid Induced by an Oscillating Pressure Field	MR9 Konstantinos Zografos Flow of power-law fluids in microfluidic bifurcating networks designed using biomimetic principles	F17 Mathias Bechert Influence of the inlet velocity on the onset of draw resonance in fiber spinning
12:00	PM36 Didier R. Long Phase separation dynamics in polymer blends close to T <sub>g</sub> : aging and rejuvenation	FM21 Mario Minale Use of rheology to validate a new theory for the flow through a porous medium	CS36 Ehsan Farno Rheology of municipal anaerobic digested sludge: Effect of temperature on composition	VP14 Fiacre Ahonguio Influence of surface properties on the creeping flow of a yield stress fluid around spheres	MR10 Rosa D'Apolito Microfluidic interfacial tensiometry of confined droplets in elongational flow	F18 Roland Kádár Local dynamics and first normal stress difference during extrusion flow in high sensitivity slit die via the 'hole effect'

12:20

Lunch Break (70 min.)

**AERC 2014 Friday Afternoon, 11th of April**

	Hans-Thoma	Johann-Peter-Hebel	Alfred-Mombert	Clubraum	Forum I	Forum II
<b>13:30</b>	<p>PM37 Huagui Zhang Nonlinear Rheology of Interphase: Relaxation after a Step Strain, Startup Shear and Uniaxial Extension of PMMA/PVDF Compatible Multilayers</p>	<p>FM22 Chongyoup Kim Theoretical and experimental studies on the contact line motion of second-order fluid</p>	<p>AR10 Corneliu Balan Influences of patterned surface in rheometry of complex fluids</p>	<p>VP15 Mathilde Maillard Viscoplastic dip-coating: experiments and simulations</p>	<p>MR11 Pierre Ballesta Elastic-driven flow instability of polymeric suspension under oscillatory flow perturbations</p>	<p>FI9 Sandra Lerouge Elastic turbulence in the flow of wormlike micellar solutions</p>
<b>13:50</b>	<p>PM38 Khalid Lamnawar Understanding of the compatibilization effect of the multifunctionalized epoxy in PLA/PBAT biopolymer blends: linear and non-linear rheology, morphology and interfacial properties</p>	<p>FM23 Ahmed Talhaoui Numerical Simulation of two miscible fluids within a static mixer</p>	<p>AR11 David Konigsberg Correcting for Shear Strain in an Oscillatory Squeeze Flow Rheometer</p>	<p>VP16 Günter K. Auernhammer Experiments on wet granular matter: Tracing the motion of single particles and drops</p>	<p>MR12 Anne Kowalczyk Visualization of micro-scale inhomogeneities in acrylic thickener solutions: a multiple particle tracking study</p>	<p>FI10 Jordi Ortín Vortex ring formation in oscillatory pipe flow of wormlike micellar solutions</p>
<b>14:10</b>	<p>PM39 Abdulwahab S. Almusallam Large Amplitude Oscillatory Shear of Immiscible Polymer Blends and Comparison to Predictions of Droplet and Anisotropy Models</p>	<p>FM24 Dmitry A. Fedosov Dense semiflexible polymer brushes in flow: a model for glycocalyx layer in blood vessels</p>	<p>AR12 Ricardo Andrade High strain extensional rheometry of polymer melts</p>	<p>VP17 Antoine Marchal Influence of the yield stress on the evolution of a bubble population in a viscoplastic fluid</p>	<p>MR13 Giovanna Tomaiuolo Microconfined flow-based imaging methods to study red blood cell membrane viscoelastic properties</p>	<p>FI11 Marco Ellero Transition to elastic turbulence and mixing in a periodic array of cylinders confined in a channel</p>
<b>14:30</b>	<p>PM40 Chloé Epinat Analysis of phase inversion composition and rheological behavior of PA6/HDPE reactively compatibilized blends</p>	<p>FM25 David J. C. Dennis Organisation of large-scale motions in turbulent pipe flow of a dilute polymer solution</p>	<p>AR13 Karl-Friedrich Rätzsch Low-field NMR as a new in-situ combined method for shear rheology</p>	<p>VP18 Catherine Barentin Capillary rise of Yield Stress Fluid</p>	<p>MR14 Chaouqi Misbah Rheology of a confined blood model</p>	<p>FI12 Annie Colin Elastic instability in straight channel for shear thinning fluids induces a genuine drag reduction</p>
<b>14:50</b>	<p>PM41 Reza Salehiyan Characterization of compatibilized Polypropylene/Polystyrene blends via nonlinear rheological properties under large amplitude oscillatory shear (LAOS) flow</p>	<p>FM26 Richard D. Whalley Hibernating Turbulence in Newtonian Fluids and Dilute Polymer Solutions</p>	<p>AR14 Volker Rätzsch Rheometry, NMR and Combined RheoNMR of TiO<sub>2</sub>-Filled Poly(n-alkyl methacrylates) and t-Polyisoprenes to Investigate Molecular Dynamics of Composite Materials</p>	<p>VP19 Johan Paiola Yield stress fluid flow in simple model porous media</p>	<p>MR15 Haider Dakhil Viscoelastic behavior of cells measured in a rotational rheometer</p>	<p>FI13 Chérif Nouar On the nature of the first bifurcation in shear-thinning Taylor-Couette flow</p>
<b>15:10</b>	<p>PM42 Michael Kempf Non-linear Rheology of Well-Defined Comb Polymer Architectures with a Low and Controlled Degree of Long-Chain Branching</p>	<p>FM27 Roger Khayat Free-surface jet of a power-law fluid near channel exit</p>	<p>AR15 Marius Mermét-Guyennet LAOS: The strain softening/strain hardening paradox</p>	<p>VP20 Thibaud Chevalier The specificity of yield stress fluid flows through porous media</p>	<p>MR16 Thomas John Microrheology in biological active fluids on the basis of sedimenting beads</p>	<p>FI14 Chong Li Onset of the Rayleigh-Bénard convection in a yield stress in relation with rheological properties close to the solid-liquid transition</p>
<b>15:30</b>	<b>Farewell Coffee</b>					



# Wednesday Morning

## Welcome at the AERC 2014 in Karlsruhe

Wednesday 8:30 Hans-Thoma

Welcome and greetings

M. Wilhelm and N. Willenbacher, conference chairs

Dr. F. Mentrup, Mayor of the city of Karlsruhe

Prof. Dr. D. Löhle, Vice President for Research and Information, Karlsruhe Institute of Technology

## Plenary Lecture 1

Wednesday 8:50 Hans-Thoma

PL1

### Complex fluids far from equilibrium

Stephan Herminghaus\*<sup>1</sup>

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Max Planck Institute for Dynamics and Self-Organization (MPIDS), Göttingen, Germany

Although many complex fluids of practical relevance (such as, e.g., biological matter) are intrinsically non-equilibrium systems, the corresponding model systems used in science are most of the time at (or close to) equilibrium, as it is the case for colloidal suspensions or polymer melts. We will discuss several complex fluids which can be tuned far off equilibrium, but are still simple enough to serve as model systems accessible to fundamental research. It is shown that granular matter exhibits phase transitions very much akin to their equilibrium counterparts, but with unusual critical exponents. The simplicity of its dissipation mechanisms allows for systematic studies of the influence of non-equilibrium on collective phenomena in general. Similarly, the swarming behaviour of self-propelling droplets in so-called 'active emulsions' may be within the same universality class (if this exists at non-equilibrium), but as well serve as a model system for circadian dynamics in marine plankton, the largest biomass system on earth. It is discussed how important aspects of the microscopic 'activity' of the emulsion can be assessed by purely rheological means.

## Polymer Melts, Blends, Copolymers, and Nanocomposites - PM

Organizers: Ulrich Handge, Manfred Wagner, Dimitris Vlassopoulos, and Alexei Likhtman

Wednesday 10:20 Hans-Thoma

PM1

### Component relaxation times in entangled binary blends of linear chains: Reptation/CLF along partially or fully dilated tube

Hiroshi Watanabe\*<sup>1</sup>, Yumi Matsumiya<sup>1</sup>, Evelyne van Ruymbeke<sup>2</sup>

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Recent dielectric analysis suggested that entangled linear cis-polyisoprene (PI) chain in monodisperse bulk reptates, in the terminal relaxation regime, along a partially dilated tube with its diameter being determined by the constraint

<sup>1</sup>\* = Corresponding Author, Name = Presenting Author

release (CR)-activated tension equilibration along the chain backbone [Matsumiya et al., *Macromolecules* 2013, 46, 6067]. In relation to this finding, we have re-examined the terminal relaxation times of components in linear PI blends having various component molecular weights and volume fractions,  $M_i$  and  $v_i$  ( $i = 1$  and  $2$  for the short and long components). In entangled blends with  $M_2 \gg M_1$  and large  $v_2$ , the relaxation time  $\tau_{2,b}$  of the long chain decreases with decreasing  $v_2$  but stayed considerably larger than  $\tau_{2,soln}$  of the same long chain in a solution having the same  $v_2$ . This result suggested that the CR-activated tension equilibration retards the reptation of the long chain in such blends. A simple "solution model" considering this retardation due to the CR relaxation of short-long entanglements was formulated. Utilizing data for the CR relaxation time  $\tau_{dil-2,CR}$  of dilute long chains, the model well described the  $\tau_{2,b}$  data in the blends. Nevertheless, this model could not apply to the cases where  $M_2$  and  $M_1$  are rather narrowly separated and the short-long entanglements considerably survive in the time scale of the long chain relaxation. For this case, a "blend model" was formulated to consider self-consistently, though in an approximate way, the CR relaxation of all species of entanglements (short-short, short-long, long-short, and long-long entanglements) thereby mimicking coupled relaxation of the long and short chains. The component relaxation times deduced from this model (again on the basis of the  $\tau_{dil-2,CR}$  data) were surprisingly close to the data, not only for the PI/PI blend having narrowly separated  $M_2$  and  $M_1$  but also for those with  $M_2 \gg M_1$  as well as for polystyrene blends.

Wednesday 10:40 Hans-Thoma

PM2

### A Unifying Model for Elongational Flow of Polymer Melts and Solutions Based on the Interchain Tube Pressure

Manfred H. Wagner\*

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Berlin Institute of Technology (TU Berlin), Polymer Engineering / Polymer Physics, Berlin, Germany

A substantial difference in the elongational viscosity of polymer solutions and melts is observed experimentally: With increasing strain rate, the elongational viscosity of polymer solutions first decreases and then suddenly increases when the strain rate approaches the inverse Rouse stretch relaxation time. In contrast, the elongational viscosity of well-entangled polymer melts shows a continuously decreasing trend with a scaling of approximately at higher strain rates. A consistent model of the rheology of polymer melts and solutions is presented, based on the idea that the pressures exerted by a polymer chain on the walls of an anisotropic confinement are anisotropic [Doi and Edwards (1986)]. In a tube model with variable tube diameter, chain stretch and tube diameter reduction are related, and at deformation rates larger than the inverse Rouse time, the chain is stretched and its confining tube becomes increasingly anisotropic. Tube diameter reduction leads to an interchain pressure in the lateral direction of the tube [Marrucci and Ianniruberto (2004)]. We argue that chain stretch is balanced by interchain tube pressure in the lateral direction, which is proportional to the 3rd power of stretch, and by a spring force in the longitudinal direction of the tube, which is linear in stretch. Permanent dilution of the polymer by a solvent does not change the relative interchain tube pressure. Quantitative agreement between highly nonlinear viscoelastic experiments in elongation [Qian et al. (2013a,b)] and predictions for melts and solutions is obtained based exclusively on the relaxation modulus of the polymer melt, the volume fraction of polymer in the solution and the time-temperature shift caused by the reduction of the glass transition temperature  $T_g$  of the polymer in solution relative to  $T_g$  of the melt.

Wednesday 11:00 Hans-Thoma

PM3

### Non-linear rheology of melts of dendronized polymethacrylate polymers with varying length and generation

Thomas Schweizer\*<sup>1</sup>, Hao Yu<sup>1</sup>, Baozhong Zhang<sup>1</sup>, A. Dieter Schlüter<sup>1</sup>, Dimitris Vlassopoulos<sup>2</sup>

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Dendronized polymers represent a special class of macromolecules with properties strongly differing from ordinary thermoplastics. Their rheological behaviour can be largely influenced by changing the degree of polymerisation, the generation (number of branching points from the core to the shell) and the functionalization of the shell. Due to the bottle-brush-like architecture, the backbone is stiffened and the possible functionalization of the shell allows for strong intermolecular interaction. Whereas the linear viscoelastic behaviour has been studied for different generations of equal degree of polymerisation, nothing is known about the non-linear behaviour.

In this presentation, viscosity data and both normal stress differences are shown for three samples of a dendronized polymethacrylate polymer PG1, differing in degree of polymerisation from  $P_n = 50$  (PG1-50) to  $P_n = 500$  (PG1-500) and  $P_n = 1100$  (PG1-1100). For a constant degree of polymerisation  $P_n = 500$ , generations 1-4 have also been

compared. The non-linear rheology has been measured using an MCR302 with a double partitioned plate cell CPP3, developed at ETH Zurich. The diameters of the two partitions are 6 and 12 mm, so that the shear stress and both normal stress differences can be determined with 70-80 mg of sample and a 6° cone. The most striking result is: The molecules show a strong intermolecular interaction, possibly via hydrogen bonds (HB). This is expressed by the fact that PG1-50 already shows strong normal force signals for Weissenberg numbers around one. Without the strong HB interactions, these stiff molecules would certainly not be entangled and show any normal stress effects. It is therefore questionable whether the concept of an entanglement network is applicable to dendronized polymers of lowest generation at all. At lower shear rates, the HB interactions lead to gel-like response in PG1-50 and PG1-500. With PG1-1100, interactions are so strong, that a steady state cannot be achieved, neither at constant shear rate, nor in creep.

Wednesday 11:20 Hans-Thoma

PM4

### **The tube axis and entanglements in polymer melts**

Alexei Likhtman\*, M. Ponmurugan

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Although the tube theory is very popular and successful, the tube concept remains evasive and ill defined. In the first part of this talk I'll describe a simple computer algorithm to construct the tube axis as a center line of the cloud of chain configurations at different moments of time. We test this algorithm on trajectories generated from simulations of concatenated well entangled ring polymers, thus avoiding all disentanglement processes. We find that entanglements are clearly manifested through the curvature of tube axis, and we can successfully identify binary and ternary entanglements in molecular dynamics simulations. Several quantitative characteristics of entanglements are reported and discussed. The second part of this talk will discuss a definition of entanglements as persistent contacts between the mean paths of polymer chains. This definition will be tested in molecular dynamics simulation of linear melts. We trace the dynamics of individual entanglements and study their lifetime, distribution along the chain and the way they are created or destroyed.

Wednesday 11:40 Hans-Thoma

PM5

### **Convective Constraint Release Revisited**

Giovanni Ianniruberto\*, Giuseppe Marrucci

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University Federico II, Department of Chemical Engineering, Materials, and Industrial Production, Naples, Italy

The molecular mechanism known as Convective Constraint Release, CCR for short, is here revisited to account for the fact that in fast flows topological entanglements decrease in number, as recently shown by the molecular dynamics simulations of Baig et al. [2], and even before by the Brownian simulations of Yaoita et al. [3]. Based on the same Brownian dynamics code, Furuichi et al. (2010) suggested that the time-strain separability in step strain relaxation is influenced by the entanglement density dynamics, an idea previously explored by Archer et al. [1]. The model that is here proposed is therefore tested against literature data of stress relaxation following large step strains, where the time-strain separability is approached in a time much longer than the expected Rouse time, a mystery that has long remained unsolved.

[1] Archer et al., *Macromolecules* 35, 10216-10224 (2002)

[2] Baig et al., *Macromolecules* 43, 6886-6902 (2010)

[3] Yaoita et al., *J. Chem. Phys.* 128, 154901 (2008)

## Polymer Melts, Blends, Copolymers, and Nanocomposites - PM

Organizers: Ulrich Handge, Manfred Wagner, Dimitris Vlassopoulos, and Alexei Likhtman

Wednesday 10:20 Johann-Peter-Hebel

PM43

### Assembly of interfacially adsorbed plate-like nanoparticles in immiscible polymer blends

Giovanni Filippone\*, Andrea Causa, Martina Salzano de Luna, Luigi Sanguigno, Domenico Acierno

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The assembly of clay nanoparticles in a PS/PMMA immiscible blend is studied combining morphological investigations and rheological analyses. A reference system based on pure PS allows to highlight the role of a preferred polymer-polymer interface on the dynamics and structures of the filler in the melt. The blend exhibits a drop-matrix morphology, and the particles preferentially adsorb at the polymer-polymer interface. As a result, flocculation phenomena are hindered and the viscoelastic behaviour of the blends at low filler content is not affected by the particles. Once the available polymer-polymer interface is saturated, any further addition of particles causes an increase of elasticity during time, which reflects the rearrangement of the lamellae in the melt and their eventual assembly in a space-spanning network. The marked elastic connotation of such a superstructure exceeds the interfacial contribution of the drops, and the viscoelasticity of the filled blend can be described irrespective of the presence of the dispersed polymer phase. The network exhibits a peculiar structure, which embeds and connects single and clustered droplets. Assuming it as a collection of fractal flocs, fractal models conceived for colloidal gels are used to elucidate the space arrangement of the particles. The analysis reveals that the PMMA drops hinder the free growth of the flocs and provides them additional elasticity. The flocs, stronger than those which form in the homogeneous PS, are interconnected through weak links based on lamellae not constrained at the drop surface.

Wednesday 10:40 Johann-Peter-Hebel

PM44

### 'Disentanglement' of polyethylene chains in the presence of graphene

Kangsheng Liu<sup>1</sup>, Eflen Andablo-Reyes<sup>1</sup>, Sara Ronca<sup>1</sup>, Sanjay Rastogi<sup>1,2</sup>

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Graphene sheets have attracted much attention in both academia and industry, due to their extraordinary physical, mechanical and thermal properties and the promising potential for modifying properties of polymeric materials [1,2]. Due to difficulties in scale up of graphene preparation, thermal reduction of graphene oxide is widely used to obtain reduced graphene oxide (rGON), which has similar structure and properties to graphene. rGON fillers possess extremely high aspect ratio, as the mono- or few stacked layers have areas in the range of a few square micrometers, and thickness of one or few atoms. We investigated the influence of rGON on composites with polyethylene, namely HDPE/rGON and UHMWPE/rGON [3], by means of rheology and differential scanning calorimetry (DSC). For the low concentration of fillers our rheological results indicate a decrease in complex viscosity of the composites. The decrease in viscosity at the low concentrations may be attributed to decrease in the entanglement density of the polymer network due to the attachment of long chain components with the high-aspect-ratio filler. The chain attachment to graphene has been further supported by NMR and has influence on the crystallization kinetics from melt as observed by DSC. The drop in complex viscosity for both rGON filled HDPE and UHMWPE at various frequencies, is a rarely reported phenomenon in practical soft matter [4]. This study presents a possible crucial effect to facilitate their processing.

[1] Novoselov, K. S. et al; Nature; 2004; 306; 666

[2] Stankovich, S. et al; Nature; 2006; 442; 282

[3] Rastogi, S. et al; Nat Mater; 2005; 4; 635

[4] Li, Y. et al; PRL; 2012; 109; 118001

Wednesday 11:00 Johann-Peter-Hebel

PM45

**From the Chain Conformation and Dynamics in Polymer at the Micro and Mesoscale to the Macroscopic Properties of Nanocomposites**

Gerald J. Schneider\*, Dieter Richter

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Intense research has led to substantial progress towards understanding polymer melts and nanocomposites. For that purpose, knowledge of the single chain dynamics is of particular interest. It is important for modeling or predicting the macroscopic material response needed for the target oriented engineering of new hybrid materials starting from the single molecule. Furthermore, it is useful to resolve apparent contradictions raised by experimental results of different techniques. Finally, it may lead to optimized materials ranging from the classical car tire to battery or fuel cell applications.

In composites, hard impenetrable walls impose constraints on polymer melts, by limiting the accessible regions. As will be shown in the talk, such a confinement significantly affects the polymer dynamics when the interparticle distances and the dimensions of the embedding polymer chains are comparable, which is crucial for polymer processing and technology.

The talk presents results on model nanocomposites well suited to act as interlink between a theoretical understanding and the technical application. Measurements, such as rheology are introduced that represent the typical macroscopic material behavior. Then the usefulness of neutron scattering experiments for obtaining a detailed picture of the microscopic and mesoscopic situation is presented. In particular, the advantage of recording a dynamic correlation function with a high spatial resolution is shown. Finally, the importance of a combined analysis of the results of different techniques enhances the understanding of our knowledge on polymer melts and composites, in particular the relationship between the fundamental parameters and the material behavior.

Wednesday 11:20 Johann-Peter-Hebel

PM46

**Anomalous Rheological Behavior of Polymeric Nanoparticle/Linear Polymer Blends**Hadi Goldansaz<sup>1</sup>, Vahid Karimkhani<sup>2</sup>, Fatemeh Goharpey<sup>2</sup>, Faramarz Afshar-Taromi<sup>2</sup>, Il Kim<sup>3</sup>, Florian J. Stadler\*<sup>4</sup>, Evelyne van Ruymbeke\*<sup>1</sup>

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<sup>1</sup>Université catholique de Louvain, Bio and soft matter, Louvain-La-Neuve, Belgium, <sup>2</sup>Amirkabir University of Technology, Polymer Engineering & Color Technology, Tehran, Iran, <sup>3</sup>Pusan National University, The WCU Centre for Synthetic Polymer Bioconjugate Hybrid Materials, Pusan, Korea, <sup>4</sup>Chonbuk National University, School of Chemical Engineering, Jeon-ju, Korea

We study the effects of the addition of soft dendritic polyethylene (dPE) nanoparticles on the rheological properties of a linear polystyrene (PS) matrix. Several systems are investigated, containing different amount of dPE - each from 0 v% to 20 v%.

Their viscosity is found to exhibit non-monotonic dependence on the dPE concentration. In particular, with the addition of 1% dPE nanoparticles, we already observe a drastic reduction (more than one order of magnitude) in the terminal viscosity of the PS polymer. To the best of our knowledge, such a large decrease in viscosity (more than 90%) resulting from the addition of nanoparticles has never been reported. With increasing volume fraction of loaded dPE nanoparticles, viscosity is found to increase, and eventually becomes larger than the viscosity of pure PS. Furthermore, the addition of nanoparticles not only influences the terminal relaxation times of samples, but affects their whole relaxation spectra.

Homogeneity of blends is assured based on the ratio criteria between radius of gyration of PS and radius of dPE nanoparticles, and is confirmed by Atomic Force Microscopy (AFM) measurements. While confinement and free volume caused by nanoparticles fail to describe this unexpected viscosity reduction mechanism, it is believed that conformational changes of the entangled chains on the surface of nanoparticles - which generate an early relaxation mode and consequently affect the reptation dynamics of the entangled linear chains - are responsible for this behaviour.

Wednesday 11:40 Johann-Peter-Hebel

PM47

**Filled polycarbonate; the sum of its parts?**

Sam Krop, Lambert C.A. van Breemen\*, Han E.H. Meijer

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Since polymers play an increasingly important role in both structural and tribological applications, understanding their intrinsic mechanical response is key [1]. Therefore, much effort has gone into the development of models, such as the Eindhoven Glassy Polymer (EGP) model [2], which capture the polymers' response quantitatively. In practice, however, these polymers are filled, e.g. with colorants and impact modifiers.

To characterize the effect of filler particles on the intrinsic mechanical response, model systems of polycarbonate filled with either hard ( $\text{TiO}_2$ ) or soft (MBS) particles are tested in uniaxial compression. Since experimentally only macroscopic effects are probed, simulations are needed to reveal the effects at the inter-particle level. Therefore, representative volume elements (RVEs) are constructed, where the matrix material is modeled with the EGP model and the fillers with their individual mechanical properties. Comparing the simulated response of the RVEs with the experiments shows that the macroscopic response is captured well. Only at large deformations the simulations fail to capture the response of the hard-filled system. Moreover, the simulations clearly show that all the rate-dependence originates from the polymer matrix; fillers only change the magnitude of stress.

In the simulations it is assumed that the particles perfectly adhere to the matrix. In reality, for the hard-filled system, this interface or the polymer itself will fail at some point; the local strains significantly exceed the macroscopic applied deformation. But since the local deformations are now available quantifying the onset of failure is within reach. Subsequently, this method proves to be beneficial as a design tool too: different scenarios, e.g. altering or even combining filler properties, are easily tested without the need of tedious experiments.

[1] Van Breemen et al., *Wear* 2012, 274-275, 238-247[2] Van Breemen et al., *J. Mech. Phys. Solids* 2011, 59(10), 2191-2207**Colloids and Suspensions - CS**

Organizers: Matthias Ballauff and Moshe Gottlieb

Wednesday 10:20 Alfred-Mombert

CS1

**Stress overshoots in concentrated colloidal dispersions and metallic glasses: A microscopic structural study**Marco Laurati<sup>1</sup>, Kevin Mutch<sup>1</sup>, Christian Amann<sup>2</sup>, Matthias Fuchs<sup>2</sup>, Thomas Voigtmann<sup>2</sup>, Matthias Ballauff<sup>3</sup>, Miriam Siebenbürger<sup>3</sup>, Stefan Egelhaaf\*<sup>1</sup>

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We investigate the link between variations in the microscopic structure and stress overshoots in concentrated colloidal dispersions. The microstructure of the colloidal system at different times after application of shear is determined using confocal microscopy. We find shear-induced cage deformation, i.e. structural anisotropy [1,2]. When this is maximal, the stress overshoot in the rheological response occurs and a super-diffusive regime is observed in the single-particle dynamics. In addition to this anisotropic deformation of the cage, we also observe a local isotropic compression which might be related to particle migration, similar to what observed for shear banding phenomena [3]. Moreover, the anisotropic deformation is composed of a quadrupolar angular distortion but also a higher order term: The first is consistent with predictions of plasticity theories for the spatial structure around a plastic event (based on Eshelby calculations), while the latter is observed for the first time.

These findings, which are in agreement with MCT predictions and simulations, are expected to improve the understanding of the microscopic origin of stress overshoots in metallic glasses, since using MCT the stress-strain curves of these systems can be mapped onto those of concentrated colloidal dispersions [3].

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[3] C. P. Amann et al. (2013) arxiv:1302.2030.

Wednesday 10:40 Alfred-Mombert

CS2

**Glasses of binary colloidal mixtures under shear**

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We investigate yielding during step rate experiments on glasses of binary colloidal hard sphere mixtures with large size asymmetry (size ratio 1:5) [1,2]. The variation in the magnitude of the stress overshoot observed at yielding, as a function of shear rate, indicates the existence of two regimes: one at small shear rates where Brownian motion significantly contributes to the restructuring of the material; a second one at large shear rates where collisions dominate the shear-induced rearrangements [3]. The results of rheology are compared to measurements of the dynamics of particles under shear. The super-diffusion typically associated with stress overshoots [4] becomes more pronounced for mixtures in which the dynamics are increasingly arrested. In addition we observe cage constriction effects, i.e. an increase of the localisation of particles under shear. In the mixtures they occur at Peclet number values considerably smaller than in one-component systems. Moreover, we observe different degrees of shear-induced constriction depending on mixing ratio, which closely follow changes in the magnitude of the stress overshoot.

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Wednesday 11:00 Alfred-Mombert

CS3

**Microscopic investigation of creep in colloidal glasses**Tatjana Sentjabrskaja<sup>1</sup>, Pinaki Chaudhuri<sup>2</sup>, Wilson Poon<sup>3</sup>, Jürgen Horbach<sup>2</sup>, Stefan Egelhaaf<sup>1</sup>, Marco Laurati\*<sup>1</sup>

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Using colloidal glasses, the microscopic origin of the rheological creep response is investigated by confocal microscopy and numerical simulations. Upon application of a step stress, the single-particle dynamics is found to be subdiffusive in the case of creep and diffusive in the case of steady flow. In both cases, dynamical heterogeneities, namely regions of enhanced activity, are observed. During creep, these active regions remain localised. In contrast, during the onset of steady flow, the active regions grow. This is reflected in a transient superdiffusive regime in the particle dynamics and a related rapid increase in the bulk strain. The macroscopic rheological response can thus be understood based on the microscopic spatially-resolved single-particle dynamics.

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Wednesday 11:20 Alfred-Mombert

CS4

**Transient Rheology of Colloidal Suspensions - Shear Reversal**Miriam Siebenbürger\*<sup>1</sup>, Fabian Frahsa<sup>2</sup>, Matthias Fuchs<sup>2</sup>

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At low deformations, colloidal glasses exhibit first a linear deformation, followed by a stress overshoot and the sheared steady state [1]. In this transition range from solid to fluid the reversal of the shear deformation can spend insights in the dynamics of the underlying structural transformations. Experimental investigations are performed by model suspension of thermo-sensitive colloids, consisting of a poly(styrene) core and a poly(N-isopropylacrylamide) shell. By a set of shear reversal experiments the aging effect often observed in experimental systems can be discussed separately from the structural transformations due to the shear. Experiments show that the 'shape' of the overshoots depends on the waiting time, independent of the deformation at or below the stress maximum. Whereas

the height and the position of the minimum of the undershoots in the reversed shear flow is correlated with the deformation at the start of the shear reversal. All results for different shear rates and waiting times will be compared to the Mode Coupling Theory (MCT) and simulations, which show good agreement compared to the experimental results [2].

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Wednesday 11:40 Alfred-Mombert

CS5

### Internal stress in soft particle glasses

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Many glassy materials have the capacity to store mechanical stresses when they solidify. Internal stress is known to have a great impact on the mechanical behavior and the long-term evolution of materials. For instance the relaxation of internal stress upon flow cessation is often invoked to explain the unusual slow dynamics or the spontaneous motion that sometimes occurs without forced flow in colloidal glasses and biological materials. However, the physical origin of internal stresses and the relation between its amplitude and material properties and/or processing conditions are still open questions.

In this talk we identify the microscopic origin of internal stresses that build up when suspensions of soft and deformable particles above close-packing are suddenly brought to rest from steady shear flow. Our approach uses experiments on concentrated microgel suspensions and particle scale simulations based on a microscopic model which consider that jammed particles are in contact and interact via elasto-hydrodynamic repulsive forces [1]. We find that the stress exhibits a two-step relaxation after flow cessation. First, there is a rapid relaxation through ballistic particle motion, where the number of particles in contact and the particle radial distribution quickly returns to equilibrium. This is followed by a second relaxation requiring cooperative motion of particles, where the angular distortions of the pair distribution function decay very slowly. It is this second process that causes the long-time persistence of the internal stress [2]. The microscopic mechanisms are reflected in scaling expressions which relates the amplitude of the internal stress and the characteristic time of the initial relaxation to material properties and processing conditions.

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## Biopolymers, Active Fluids, and Food Rheology - BF

Organizers: Hans Wyss and Mats Stading

Wednesday 10:20 Clubraum

BF1

### Influence of urea on the rheology of gliadin solutions

Ward Janssens<sup>1</sup>, Mathieu Meerts<sup>1</sup>, Bert Lagrain<sup>2</sup>, Jan A. Delcour<sup>2</sup>, Ignace Verpoest<sup>3</sup>, Peter Van Puyvelde<sup>\*1</sup>

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Increased attention for environmentally friendly materials have stimulated the research on protein based bioplastics. One important protein in this respect is the storage protein gluten, which consists of gliadin and glutenin. The former have a molecular weight between 30 and 80 kDa, the latter between 80 kDa and several million Da. Gluten is difficult to process because of the high molecular weight of the glutenin component. Therefore, in this work, the focus is on gliadin solutions. Gliadins are extractable in for example water mixed with alcohol [1] or urea [2]. In literature, often recurring compositions are aqueous solutions of gliadin with varying concentration and with 8 M urea and 1 % (w/w) sodium sulfite [3]. Usually, urea and sodium sulfite concentrations are kept constant. However, Zhang et al. [4] showed that urea has a drastic effect on the viscosity of soybean protein solutions. Hence, in this work, we investigated the influence of varying urea and protein concentration on the rheological properties of gliadin solutions.

The viscosity and intrinsic viscosity of samples with varying urea and gliadin concentration are determined and the influence of urea on the overlap concentration is discussed. It was shown that urea does not have an influence on the viscosity below the overlap concentration, whereas above it urea reduces the effect of higher protein concentration on viscosity. This shows that urea has no effect on the intramolecular interactions, but opposes intermolecular interactions.

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### Wednesday 10:40 Clubraum

BF2

#### **Why blood clots don't break: Nonlinear viscoelastic properties of fibrin**

Thomas H. S. van Kempen<sup>\*1</sup>, Gerrit W. M. Peters<sup>2</sup>, Frans N. van de Vosse<sup>1</sup>

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Blood clots form to prevent blood loss, but often develop within a blood vessel leading to occlusion with potentially dramatic consequences. The mechanical properties of the clot are important for its functioning but complicated due to the many components that play a role. Therefore constitutive models are being developed to study the mechanical properties of blood clot formation.

The main structural component of the blood clot is fibrin, a fibrous network that forms within the clot. Fibrin provides strength to the clot and is therefore of pivotal importance for its mechanical properties. The remarkable nonlinear viscoelastic properties of fibrin are expected to be important for its physiological functioning but current constitutive models do not capture these nonlinear phenomena. In this study, a constitutive model is developed for the nonlinear viscoelastic behavior of fibrin.

Based on large amplitude oscillatory shear (LAOS) experiments, three nonlinear features are modeled. Fibrin shows strain stiffening that originates from fiber rearrangements and intrinsic nonlinearities of the fibers during large deformations, which is modeled using a strain dependent shear modulus. A second feature is softening observed upon multiple deformation cycles. It has been hypothesized that fibers plastically elongate during successive deformation cycles, leading to this thixotropic behavior. By analyzing the transient LAOS data, this effect is quantified and incorporated using a network disintegration parameter that governs the decrease of the shear modulus based on the deformation history. A third nonlinear feature is an increase of the viscous dissipation during a deformation cycle, incorporated using a strain dependent viscous contribution.

The model is able to describe the rich nonlinear viscoelastic behavior of the fibrin network. Given its relative simplicity, the model is suitable for numerical simulations of blood clot formation in blood vessels.

### Wednesday 11:00 Clubraum

BF3

#### **Clinical evaluation of Cystic Fibrosis patients by mucus viscoelastic properties**

Giovanna Tomaiuolo<sup>\*1,2</sup>, Giulia Rusciano<sup>3</sup>, Sergio Caserta<sup>1,2</sup>, Antonio Carciati<sup>1</sup>, Vincenzo Carnovale<sup>4</sup>, Pasquale Abete<sup>4</sup>, Antonio Sasso<sup>3</sup>, Stefano Guido<sup>1,2</sup>

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Cystic fibrosis (CF) is the most frequent life-limiting genetic disease in Caucasian populations, among whom it occurs in approximately 1 in 3000 birth[1]. In CF patients airways mucus shows an increased viscoelasticity due to the concentration of high molecular weight components. Such mucus thickening eventually leads to bacterial overgrowth and prevents mucus clearance[2]. The altered rheological behavior of mucus results in chronic lung infection and inflammation, which causes most of the cases of morbidity and mortality, although the cystic fibrosis complications affect other organs as well. From the rheological point of view, mucus is a dense, viscoelastic gel-like material, characterized by the presence of a large number of entanglements between glycoproteins and other mucosal components, stabilized by hydrogen bonding and electrostatic and hydrophobic interactions[3]. Here, we present a quantitative study on the correlation between cystic fibrosis mucus viscoelasticity and patients clinical status. In particular, a new diagnostic parameter based on the correlation between CF sputum viscoelastic properties and

the severity of the disease has been developed. By using principal component analysis, we show that the types of bacterial colonization are significantly correlated to the elastic modulus, and that the latter can be used for CF severity classification with a high predictive efficiency (88%). The data presented here show that the elastic modulus of airways mucus, given the high predictive efficiency, could be used as a new clinical parameter in the prognostic evaluation of cystic fibrosis[4].

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### Wednesday 11:20 Clubraum

BF4

#### The elasticity of blood

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While the viscosity of blood has long been recognized as a marker for many pathologies and has therefore been studied for many decades, the viscoelasticity of blood has received very little attention. While this fact may seem surprising, it stems mainly from the large experimental difficulties associated with measuring the viscoelasticity of a low viscosity material (ca. 4 mPa\*s at 10 s<sup>-1</sup>) which sediments quite rapidly, may have a very low yield stress and may even be thixotropic. On top of this, blood presents a large biological variability, both in terms of protein concentrations, erythrocytes concentration and physical properties.

In order to decrease as much as possible the biological variability, we used model blood consisting in washed erythrocytes resuspended at varying volume fractions in a buffer supplemented with various concentrations of the main plasma proteins (fibrinogen, albumin, immunoglobulins). To avoid the central problem of erythrocytes sedimentation, we used Optimal Fourier Rheometry which is the fastest possible small amplitude oscillation technique as well as avoids the superposition problems of FTMS.

Results first show that the elastic modulus of blood is surprisingly high, and can actually be as large or larger than the viscous modulus, depending on conditions. We will discuss the origin of this elasticity and its links with both the protein content as well as the microstructure of blood. Finally, we will discuss the implications of these findings on the (micro)circulation of blood and its potential influence on cardiovascular pathologies.

### Wednesday 11:40 Clubraum

BF5

#### Microfluidic flows of E. coli suspensions

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The non-Newtonian character of complex suspensions is due to flow-induced orientation, rearrangement, or deformation of microscopic objects suspended in simple fluids. In particular, suspensions of microswimmers show new hydrodynamic phenomena, as for example collective motion or an uncommon viscosity and have attracted a large number of theoretical and numerical studies. Experimental work is however still scarce and, in particular, linking the microstructure on the particle level to the macroscopic response under flow remains an open challenge. Here, we study the flow of E. coli suspensions in well chosen microfluidic geometries allowing this link to be established. First, we employ a Y-channel, a powerful rheometer for measuring shear viscosities, to study the non-Newtonian viscosity of these active suspensions. Then, we investigate the individual and collective dynamics of E. coli bacteria under flow, taking advantage of a direct visualization of fluorescently labeled bacteria in microfluidic channels. The combination of these two observations is a first step to directly link the microstructure on the bacteria level to the measured effective non-Newtonian viscosity.

## Interfacial Phenomena, Surfactants, Emulsions, and Foams - SF

Organizers: Jan Vermant and Crispulo Gallegos

Wednesday 10:20 Forum I

SF1

### Interfacial rheology of particle at the water-air interface in the LAOS regime

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One approach to reduce the usage of natural material resources is to create a foamed product. Foams are instable structures and therefore stabilizers such as surfactants, proteins, and particles are used. Particles have some special features such as high adsorption energy making them interesting candidates for the production of ultra-stable foams [1 - 4]. Investigating interfacial properties of the particle adsorption layer is crucial to understand their stabilizing behavior. Foams are often further processed with high shear forces. Therefore investigating particle behavior in the nonlinear response region is important.

Different hydrophobic silica particles were chosen to probe different particle penetration into the interface [5]. Further two particles of the same hydrophobicity but with different interaction properties were investigated to understand the influence of particle network at the interface. To measure the interfacial properties a biconus geometry attached to a Physica MCR 501 was used. All particles showed a viscoelastic behavior. They differ in absolute values in  $G'$  and  $G''$  depending on particle hydrophobicity and showed a weak strain overshoot [6]. A different behavior in the LAOS regime could be detected for the different networking properties. All measured particles showed an oscillation in Lissajou-plots for high frequencies and amplitudes.

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Wednesday 10:40 Forum I

SF2

### The Influence of Interfacial Rheology on the Drainage and Dewetting of Thin Liquid Films

Caroline Balemans<sup>1</sup>, Saad Bhamla<sup>2</sup>, Gerald G. Fuller\*<sup>2</sup>

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Insoluble layers protect thin liquid layers against instability and dewetting. An important examples from the human body is the tear film that protects the corneal epithelium. Experiments are presented on the drainage and dewetting of aqueous layers draining from hemispherical, hydrogel contact lens surfaces where those layers are laden with insoluble surfactants. These experiments are carried out as a function surface pressure, which controls the surface viscoelasticity of the surfactant films. The apparatus used to measure the drainage dynamics utilizes an interferometer that measures the aqueous layer thickness above contact lenses as the lenses are elevated through insoluble layers. Data are offered for bovine meibum and DPPC phospholipid films where the interfacial viscoelasticity has been measured as functions of surface pressure. It is found that enhancing the surface rheology has two dramatic consequences: the thickness of the aqueous layers that are captured by the lenses are increased and the time scale for drainage of the layers is strongly increased. Both effects are beneficial to the stability of thin films, such as the tear film. These experimental results are compared against theoretical calculations that qualitatively predict the experimental trends where the interfacial rheology is captured through the Boussinesq number, which is the ratio of interfacial stresses to bulk stresses.

Wednesday 11:00 Forum I

SF3

**Interfacial rheology of bacterial biofilms at air/water and oil/water interfaces**Patrick A. Rühs<sup>1</sup>, Lukas Böni<sup>1</sup>, Lukas Böcker<sup>1</sup>, Gerald G. Fuller<sup>2</sup>, Fredrik Inglis<sup>3</sup>, Peter Fischer\*<sup>1</sup>

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Biofilms are highly complex biological assemblies composed of bacterial cells embedded in an extracellular polymeric matrix. Biofilms are ubiquitous and can cause severe environmental and health problems. Therefore it is intriguing to understand the influence factors on the formation and the destruction of bacteria biofilms [1, 2]. In this contribution, we study the initial kinetics of bacterial attachment as well as the transient biofilm formation of model bacteria at both the air/water and oil/water interface through interfacial rheology and tensiometry. Electrophoretic mobility measurements and bacterial adhesion to hydrocarbons (BATH) tests were performed to characterize selected bacteria. To validate interfacial rheology and tensiometry measurements, we monitored biofilm formation utilizing both confocal laser scanning microscopy and light microscopy. Using this combination of techniques, we were able to observe the elasticity and tension development over time, from the first bacterial attachment up to biofilm formation. Interfacial rheology proved to be a valuable tool for studying biofilms as the influence of temperature, media type, bacterial strain, pH and surfactant concentration could be observed successfully during biofilm formation [3].

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Wednesday 11:20 Forum I

SF4

**A Novel Simple Approach for Spreading Dynamics of Polymeric Fluids**Dirk W. Schubert\*, Michael Härth

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The spreading of an axisymmetric drop on partially and completely wetted substrates is investigated from the theoretical and experimental point of view. Novel physical models considering the capillary force, the gravitational force and a viscous friction force simultaneously, are derived. The models enable the analytical mathematical description of the drop radius as a function of the spreading time, which is useful for practical applications. The construction of a master curve is proposed. The theoretical models are experimentally verified, using different hydrophobic and hydrophilic polymer films as substrates and polydimethylsiloxanes of different viscosities as liquids. The comparison shows that theory and experiment are consistent.

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Wednesday 11:40 Forum I

SF5

**Nonlinear rheology of fluid-fluid interfaces with a complex microstructure**Leonard Sagis\*<sup>1,2</sup>

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When fluid-fluid interfaces have a complex microstructure (e.g. a 2d gel, 2d glass, or 2d liquid crystalline structure), their response to dilatational deformations is often nonlinear even at small deformations. This behavior is a result of structural rearrangements induced by the applied deformation, and can be observed in interfaces stabilized by proteins, polymers, or colloidal particles [1]. The data analysis commonly used by profile analyzing tensiometers (PAT) for the determination of surface dilatational properties cannot adequately describe nonlinear responses of complex interfaces [1]. Here we discuss how Lissajous curves and a generalized form of the Laplace equation can be used to obtain more meaningful measures for the dilatational properties of complex interfaces. As an example we present dilatational data for fluid-fluid interfaces stabilized by oligosaccharide-fatty acid esters, protein fibrils,

and protein-polysaccharide complexes. At high deformation amplitudes the Lissajous curves of surface pressure versus deformation of these interfaces show remarkable asymmetries between the compression and extension part of the cycle. For example, air-water interfaces stabilized by oligosaccharide-fatty acid mono-esters display strain-thinning behavior in extension, and strain-hardening in compression. A possible explanation for this behavior is that during compression the interface is compressed to a 2D soft glassy state. Oil-water interfaces stabilized by semi-flexible protein fibrils display a highly elastic response upon compression, and a more viscous response upon extension. These interfaces may be undergoing an isotropic-to-nematic transition during compression. We analyze the Lissajous curves for these interfaces with a scheme recently introduced by Ewoldt et al. [2].

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## Polyelectrolytes, Associating Fluids, and Liquid Crystals - LC

Organizers: Christian Friedrich and Valery G. Kulichikin

Wednesday 10:20 Forum II

LC1

### NIPAM-based polymers with dopamine-functionalities – versatile building blocks for self-healing hydro- and organogels with tunable rheological properties

Florian J. Stadler<sup>1,2</sup>, Saud Hashmi<sup>1,3</sup>, Mohammad Vatankhah-Varnoosfaderani<sup>1,4</sup>, Amin GhavamiNejad<sup>1</sup>

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Copolymers of NIPAM and dopamine methacrylate can establish reversible, self-healing 3D-networks when the dopamine functionality is active above pH=7.5. Classically, dopamines are used for supramolecular crosslinking via metal-ligand supramolecular interactions, which can be tuned by selecting proper multivalent metal-cations. Such hydrogels can vary in modulus within 2 orders of magnitude, depending on choice of ion. Furthermore, the nonlinear and self-healing characteristics are also tunable, e.g. Fe<sup>3+</sup> has a significantly higher modulus than B<sup>3+</sup> and is self-healing even after 10000 % deformation. The solvent additionally influences the properties. While a solution of the copolymer in dimethylformamide is stiff and not self-healing, the presence of a tiny amount of water leads to softening and self-healing. In aprotic solvents, the same copolymer forms gels based on hydrogen bonding. The reactivity and hydrogen bonding formation of catechol groups in copolymer chains were studied via UV-Vis and <sup>1</sup>H-NMR spectroscopy, while self-healing properties and the reversibility between sol and gel were tested rheologically. The produced, reversible organogel can self-encapsulate physically-interacted or chemically-bonded solutes, such as drugs, due to the thermo-sensitivity of the co-polymer. This system offers dual-targeted and controlled drug delivery and release.

Wednesday 10:40 Forum II

LC2

### Rheological properties of sticky rods formed by self-assembled comb-like amphiphilic copolyelectrolytes

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Comb-like amphiphilic copolyelectrolytes (polysoaps) based on styrene (hydrophobic unit) and N,N dimethylalkyl(vinylbenzyl)ammonium chloride (surfactant like unit) have been studied in aqueous solutions. For a composition of 80mol% surfactant-like unit, polymer chains self-assemble within cylinders [1]. The presence of hydrophobic patches at the surface of the micelles induces connection between cylinders which result in the formation of networks displaying viscoelastic properties. The relaxation process of a macroscopic strain was attributed to the break-up/recombination of the junctions. Varying the length of the alkyl grafts allows tuning the nature of the hydrophobic patches and then the strength of the junctions. In the same way, the addition of a neutral surfactant which covers the hydrophobic patches tremendously decreases the relaxation time of the gels.

[1] Limouzin-Morel, C., F. Dutertre, W. Moussa, C. Gaillard, I. Iliopoulos, D. Bendejacq, T. Nicolai, and C. Chasse-nieux, One and two dimensional self-assembly of comb-like amphiphilic copolyelectrolytes in aqueous solution. *Soft Matter*, 2013. 9(37): p. 8931-8937.

## Wednesday 11:00 Forum II

LC3

**Flow behavior of non-Newtonian anionic polymer-surfactant mixtures in pipes**

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Transporting liquids in strategic pipelines is considered as one of the most power consuming sectors in the industry due to the turbulent mode these liquids are transported within. The addition of minute quantities of polymeric additives was proven to have huge effect in reducing the power dissipation and increasing the flow. These polymers have low resistance to high shear forces and usually it loses its drag reduction ability after certain distance. Combining surfactants and polymers with two opposite polarities can modify the mechanical properties of the polymers and its resistance to shear force. In the present work, a novel approach of combining polymeric additive and surfactant from the same species (anionic) is conducted to investigate the real mechanism behind the cross bridging phenomena suggested for the normal combination procedure. Sodium Polystyrene Sulfonate (NaPSS) and sodium Alkylbenzene sulfonate were chosen to be the anionic polymer and anionic surfactant to be investigated with different addition concentrations ranged between 200 to 1000 ppm. The drag reduction ability of the individual and mixed additives was investigated using Rotating Disk Apparatus (RDA) designed and fabricated especially for this work. The shear resistance of the solutions was investigated with different rotation speeds ranged between 50 to 3000 rpm. The experimental results showed that the drag reduction performance of the investigated polymer was enhanced by 42% when combined with the surfactant additive at addition concentration of 400 ppm for both additives. A new mechanism for the polymer performance enhancement was suggested. This mechanism suggests that the repulsive forces between the two anionic additives will result in a compression effect that will squeeze the polymer molecules and the surfactant micelles formed in the solution.

## Wednesday 11:20 Forum II

LC4

**Rheological signature of supramolecular structures in hydrogen-bonded liquids**Catalin Gainaru<sup>1</sup>, Roxana Figuli<sup>2</sup>, Tina Hecksher<sup>3</sup>, Bo Jakobsen<sup>3</sup>, Jeppe Dyre<sup>3</sup>, Manfred Wilhelm<sup>2</sup>, Roland Böhmer<sup>1</sup>

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Our work demonstrates experimentally that liquids composed of small alcohol molecules can display rheological behavior otherwise typical for oligomeric chains. This identification of supramolecular polymeric behavior was made possible by combining rheological experiments in which we cover more than seven decades in frequency and more than five decades in intensity at temperatures much lower than previously attained. As small-molecule systems we deliberately chose monoalcohols because (i) they can be viewed as model systems for liquid water and (ii) like water they display strong, but surprisingly poorly understood effects of hydrogen bonding. With water and various peptide-bonded substances, these alcohols share the so-called Debye electrical absorption [1], which, e.g., for water is exploited in the microwave oven. The microscopic understanding of this phenomenon is still so much in its infancy because there is a general belief that the Debye process manifests itself only in a single type of (electrical) experiments [2]. Our rheological results show that this view is untenable and opens up a number of exciting new perspectives: One can now benefit from the reach theoretical basis of polymer science to explore and ultimately understand the anomalous physical behavior of a wide range of hydrogen-bonded liquids. In this work we performed first steps in this direction [3].

[1] L-M. Wang, R. Richert, *J. Chem. Phys.*, 121, 11170, 2004.

[2] D. Fragiadakis, C. M. Roland, and R. Casalini, *J. Chem. Phys.* 132, 144505 (2010).

[3] C. Gainaru, R. Figuli, T. Hecksher, B. Jakobsen, J. C. Dyre, M. Wilhelm, R. Böhmer, arXiv:1305.4341 [cond-mat.soft]

Wednesday 11:40 Forum II

LC5

**Linear and non linear viscoelastic properties of chemically crosslinked associating polymer gels: separability of strain and time effects governed by sticky Rouse mode**Koichi Mayumi, Alba Marcellan, Guylaine Ducouret, Costantino Creton, Tetsuharu Narita\*

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We have prepared highly deformable poly(vinyl alcohol) gels having simultaneously covalent crosslinks (glutaraldehyde) and reversible crosslinks (borate ion) with a well identified life time. This PVA "dual crosslink" gel is a simple physical model of both an associative polymer solution and a mechanically reinforced tough chemical gel.

The breakage of transient crosslinks dissipates strain energy and enhances the fracture toughness and extensibility of the dual crosslink gels. We performed systematic studies on large strain mechanical properties of the dual crosslink gels over 4 orders of magnitudes of strain rates. We propose a new analysis method showing that the strain can be separated into strain- and time-dependent terms. The strain-dependent term is predicted by the classical rubber elasticity theory (neo Hookian) and the time-dependent term is found identical to the relaxation modulus measured by small amplitude oscillatory shear measurements.

Linear rheological properties were studied by microrheology based on diffusing-wave spectroscopy in order to compare dual crosslink gels with corresponding chemical gels and physical gels at exactly the same condition. We show that the shear modulus of the dual crosslink gel can be represented as a sum of the modulus of the chemical network and that of the physical network. The contribution of the physical crosslinks in the dual crosslink gel show particular dynamics as  $G' = G'' \sim \omega^{0.5}$ , attributed to sticky Rouse mode (slowed down Rouse mode due to the physical crosslinks). It has been shown theoretically that the sticky Rouse mode can be found between the dissociation time of the physical association and the terminal time of the polymer chains. Our dual crosslink gel with chemical crosslinks has no terminal time, the sticky Rouse mode can be easily observed.

# Wednesday Afternoon

## Polymer Melts, Blends, Copolymers, and Nanocomposites - PM

Organizers: Ulrich Handge, Manfred Wagner, Dimitris Vlassopoulos, and Alexei Likhtman

Wednesday 13:10 Hans-Thoma

PM6

### Bridging the Gap between Semidilute Polymer Solutions and Polymer Melts

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Entangled polymer solutions and melts have been shown to behave differently in extensional flow, when the stretch rate is higher than the inverse Rouse time [1, 2]. However, the current tube model cannot capture the different nonlinear rheological responses, even with the mechanisms of chain stretch and convective constraint release. Recent experiments by Huang et al. [3] on concentrated polystyrene solutions and melts showed that the finite chain extensibility may provide part of the explanation. But at the same time the authors also demonstrated that other mechanisms are needed for a full explanation. In a follow-up work [4], Huang et al. proposed a hypothesis that one of the other mechanisms could be nematic interactions among the polymers and between polymer and solvent. The current tube model only works when the nematic interactions are shielded.

To further test this hypothesis, we consider the influence of solvent volume fractions on the nonlinear rheological responses of polymer solutions in extensional flow. We prepared five polystyrene (PS) solutions with different concentrations of the same PS polymer (with the molecular weight  $M_w = 545k$ ), diluted with the same oligomeric styrene (with  $M_w = 4k$ ). We test the influence of nematic interactions as a function of solvent volume fraction. If the hypothesis holds, then the nonlinear rheological responses of polymer solutions should be close to the predictions of the current tube model at a critical solvent volume fraction.

[1] P. K. Bhattacharjee et al., *Macromol.* 35: 10131-10148 (2002)

[2] A. Bach et al., *Macromol.* 36: 5174-5179 (2003)

[3] Q. Huang et al., *Macromol.* 46: 5026–5035 (2013)

[4] Q. Huang et al., *ACS Macro Lett.* 2: 741-744 (2013)

Wednesday 13:30 Hans-Thoma

PM7

### Understanding the effect of constraint release environment on the end-to-end vector relaxation time of linear chains

Maksim Shivokhin\*<sup>1</sup>, Rok Kocen<sup>1</sup>, Evelyne van Ruymbeke<sup>1</sup>, Nikos Hadjichristidis<sup>2,3</sup>, Christian Bailly<sup>1</sup>

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Effect of constraint release (CR) on relaxation of end-to-end vector in monodisperse linear and binary blends of short/long chains has been addressed by many authors (E. Pilyugina et al. (2012); Y. Matsumiya et al. (2012); T. Glomann et al., (2011)) but no clear picture has yet emerged.

In this study we validate the slip-spring model (A. E. Likhtman, 2005) by comparison with experimental small amplitude oscillatory shear measurements of prepared in “specific” way binary and ternary mixtures of linear chains (Polybutadiene) with well separated molecular weights. By preparing these mixtures we vary complexity of CR “environment” of the probe chain. In particular, we study three different CR environments: 1. single probe chain in a “gel”; 2. single probe chain in a “diluted gel”, and 3. probe chain entangled with other probe chains in a binary blend. Next, from the slip-spring simulations of these systems we extract dynamics of end-to-end vector of the probe chain affected by different CR environments and analyze the results in the frame of the tube model.

Based on analysis of effective friction coefficient in the fat tube (D. J. Read et al. 2012) we discuss effect of

enhanced relaxation mechanism of the chain on accelerating relaxation dynamics of the tube in which this chain is constrained. The longest relaxation time of the end-to-end vector is determined via competition between accelerated tube relaxation and reptation of the probe chain in a "gel". Analysis of these systems allows us to derive analytical equations predicting the longest end-to-end vector relaxation time in different CR environments with a wide range of molecular weights of short and long chains and their different ratios.

Wednesday 13:50 Hans-Thoma

PM8

### **Nonlinear viscoelasticity of Commercial Low Density Polyethylenes: the Effect of Long Chain Branching in the Presence of Entanglements**

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For a series of well characterized, randomly long chain branched, commercial LDPE melts, step-strain stress relaxation experiments are used to measure the shear strain  $\gamma$ , dependent damping function  $h(\gamma)$ , under large deformations. In the context of constitutive equations with a memory function obeying the principle of time-deformation separability (K-BKZ separable),  $h(\gamma)$  quantifies the strain "thinning" character of the fluid;  $h(\gamma)$  along with the linear stress relaxation modulus  $G(t)$ , is essential in calculating stress response under all types of shear deformation histories. A milder nonlinear viscoelastic behaviour for these branched polymers is observed in comparison with linear polymers, as seen before. This is due to their particular molecular architecture which contains an  $x$  fraction of internal (double crosslinked) strands that remain elastically active, longer.

Molecular theory arguments are employed to construct a novel  $h(\gamma, x)$  expression that successfully explains the experimental evidence; its derivation accommodates the fact that while external branches freely and swiftly shed entanglements by equilibration, right after deformation, internal branches maintain part of their segmental stretching and orientation, being less flexible to move.

Acknowledgement: This research has been co-financed by the European Union (ESF) and Greek national funds (OPELL-NSRF) through the program THALES COVISCO.

Wednesday 14:10 Hans-Thoma

PM9

### **Characterization of Long Chain Branched Topologies of Industrial Polyethylenes by Molecular Stress Function (MSF) Theory**

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The long chain branched (LCB) topologies of different types of industrial polyethylenes, hyper-branched low-density polyethylenes (LDPE) and sparsely branched metallocene polyethylenes (m-PE), were studied by gel permeation chromatography coupled with multi angle laser light scattering (GPC-MALLS) as well as rheological methods. Rheological behaviors were investigated by small amplitude oscillatory shear (SAOS), large amplitude oscillatory shear (LAOS) and extensional methods. Molecular stress function (MSF) theory [1] was then used to quantify the rheological behavior of these polyethylenes by two nonlinear material characteristics,  $\beta$  and  $f_{max}$ . Theoretically,  $\beta$  represents the ratio of the molar mass of the branched polymer to the molar mass of the backbone. It means that linear polymers have  $\beta = 1$  and model comb topologies have a  $\beta \leq 2$ , while hyper-branched topologies, e.g. Cayley tree, have higher values of  $\beta$ , which depends on the level of Cayley tree structure [2]. The parameter  $f_{max}$  indicates the maximum stretching of the polymer chains in flow [1-4]. Our results showed that the parameter  $\beta$  was sensitive to the presence of sparsely LCB in m-PEs, while it had a constant value of 1.8 for LDPEs produced in tubular reactors [3]. The value of  $\beta$  for autoclave LDPEs was between 1.6 and 2.5, however LDPEs synthesized in CSTR reactor had higher values i.e. 2.5 and 4.0. The other nonlinear material parameter,  $f_{max}$ , was dependent on strain rate for autoclave and CSTR LDPEs, while this dependency was not observed for tubular LDPEs. These results showed that MSF model is an appropriate constitutive equation for quantification of LCB topology in polyolefins.

[1] Wagner M, Yamaguchi M, Takahashi M, J Rheol 47:779-793 (2003)

[2] Abbasi M, Golshan Ebrahimi N, Nadali M, Khabazian Esfahani M, Rheol Acta 51:163-177 (2012)

[3] Abbasi M, Golshan Ebrahimi N, Wilhelm M, " J Rheol 57:1693-1714 (2013)

[4] Mahi H H, Abbasi M, Wilhelm M, Rodrigue D, J Rheol 57:881-899 (2013)

Wednesday 14:30 Hans-Thoma

PM10

### Multi-scale modeling of high-MW polymer melt viscoelasticity starting from the atomistic level

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At the heart of the reptation theory for the description of entangled polymer melt dynamics is the concept of the primitive path (PP), namely of the shortest path that connects the two ends of the chain without violating any topological constraints along the chain. From this, one can obtain all linear viscoelastic (LVE) properties of a polymer melt in a rather straightforward manner. Guided from this, we have designed a computational approach that allows one to obtain the LVE properties of a high-MW polymer melt starting from detailed atomistic simulations for a given polymer chemistry and polymer architecture. Our work contains the following steps:

1) We first map atomistic trajectories from the atomistic MD simulations onto trajectories of PPs for moderately entangled polymers of the given chemistry. The latter are used to compute the PP segment survival probability function  $\psi(s,t)$  for moderately entangled melts of the given polymer chemistry [Stephanou et al., J. Chem. Phys., 132, 124904 (2010)].

2) The computed curves are used next to parameterize a reliable tube model for polymer dynamics on the basis of the reptation theory, accounting for constraint release and contour length fluctuation mechanisms [Stephanou et al., Macromol. Theory Simul., 20, 752–768 (2011); *ibid* J. Non-Newton. Fluid Mech., 200, 111–130 (2013)]. The comparison suggests changes to the functional form of the model or to its boundary conditions.

3) The refined tube model is finally employed to predict the LVE properties of the same polymer chemistry but of significantly higher MW. We will present results from such a hierarchical computational approach for the cases of a mono- and bi-disperse cis-1,4-polybutadiene melt [Stephanou and Mavrantzas, Soft Matter, submitted (2013)]. A detailed comparison with independently measured experimental data available in the literature for the MW dependence of the zero-shear viscosity and the functions  $G'(\omega)$  and  $G''(\omega)$  of this polymer will also be presented.

Wednesday 15:20 Hans-Thoma

PM11

### Non-linear shear flow behavior of disentangled ultra-high molecular weight polyethylene

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Characterizing the non-linear rheological response of highly entangled polymer melts is a challenging task and at the same time important for their processing. In this work we test the efficiency of two different fashion of shear flow experiments, start-up shear and non-linear oscillatory shear deformations (strain controlled mode), on Polyethylene entangled melts. For this purpose we used high-density polyethylene (HDPE) with weight average molecular weight  $M_w$  below one million g/mol and ultra-high molecular weight polyethylene (UHMWPE) with  $M_w$  above one million g/mol. The influence of the steep increase in viscosity from HDPE to UHMWPE melt on the non-linearity is investigated. The stress waveforms obtained from oscillatory tests are contrasted with the results obtained at constant shear rate during the star-up flow experiments. The UHMWPE employed in this work is specially synthesized to contain reduced number of entanglements, know also as "disentangled" UHMWPE. On melting this polymer a non-equilibrium state is observed, which in time relaxes to the stable thermodynamic equilibrium state. Non-linear oscillatory deformations are used to investigate the differences between non-equilibrium and equilibrium states of the UHMWPE melt. The stress response is analyzed using Fourier-transform method to calculate the first three harmonics components in order to characterize the intrinsic nonlinearity of materials [1,2].

To evaluate the analysis of experimental results, different flow conditions are simulated using the Rolie-Poly constitutive equation [3]. To simulate the non-equilibrium state of the "disentangled" UHMWPE we suppose the polymer behaves like a entangled polymer melt with lower molecular weight.

[1] Hyun K, Wilhelm M. Macromolecules 42, 411–22 (2009).

[2] Hyun K. Progress in Polymer Science 36, 1697–1753 (2011).

[3] Likhtman A. E. Graham R. S. J. Non-Newtonian Fluid Mech. 114, 1-12 (2013).

Wednesday 15:40 Hans-Thoma

PM12

### Reentanglement Kinetics of sheared modified Polyisobutylene

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The rheological properties of a polyisobutylene (PIB) having a molecular weight five times its entanglement molecular weight were measured, along with interrupted shear flow experiments to quantify the time required for structural recovery following steady state shearing in the non-Newtonian regime. The reentanglement kinetics was substantially slower (by more than an order of magnitude) than expectations based on the linear rheology of the fully entangled material. This result is in accord with published interrupted shear flow results for concentrated polymer solutions. With increasing shear rate, the degree of disentanglement increases ("shear-thinning"). We measured the time required for recovery of the overshoot in the transient viscosity as a function of the shear rate and temperature. We find that the time for recovery of the stress overshoot is independent of the shear rate, thus, the kinetics of reentanglement are not affected by the degree of disentanglement. The activation energies for entanglement recovery and the linear dynamic properties were equivalent. A practical significance of the persistence of the disentangled state is the retention of a low viscosity and reduced elasticity over an extended time. Such "shear modified" materials offer improved processibility in high molecular weight polymers, without any change in their ultimate, equilibrium properties.

Wednesday 16:00 Hans-Thoma

PM13

### Dynamic dilution effect in binary blends of linear polymers

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We investigate and model the viscoelastic properties of binary blends composed of linear chains with widely separated molecular weights and different concentrations. These systems are indeed very suitable to test the validity and the limit of the constraint release (CR) process and dynamic tube dilution, and to determine the value of the dynamic dilution exponent. We first focus on binary blends composed of barely entangled short chains. In such a case, we show that the tension equilibration process needs to be taken into account and is correctly described by considering a CR-activated contour length fluctuation (CLF) process, which takes place along the fully dilated tube and is governed by the intrinsic Rouse time of a long-long entanglement segment. We also show that this CR-activated CLF process speeds up the relaxation of the long chains, which naturally leads to an effective dilution exponent equal to 4/3, despite the fact that the modeling is based on an alpha value of 1. This result is in agreement with the experimental data.

Then, we analyze the rheological behavior of binary linear blends composed of entangled short chains. In such a case, we show that the CR-activated CLF process also takes place, but with a delay time being necessary for the long chain to explore the dilated tube and move along it.

This approach is tested for several binary blends, showing an improved quality of the predictions compared to previous tube modeling on the same blends. By accounting for this tension equilibration process, we also show that the Graessley number above which the long chains reptate in a fully dilated tube is equal to 1, as it was initially proposed.

Wednesday 16:20 Hans-Thoma

PM14

### The effect of nematic interactions in uniaxial extension of polymer blends

Ludovica Hengeller<sup>1</sup>, Qian Huang<sup>1</sup>, Nicolas J. Alvarez<sup>1</sup>, Andriy Dorokhin<sup>2</sup>, Kristoffer Almdal<sup>2</sup>, Ole Hassager\*<sup>1</sup>

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Industrial polymers are largely polydisperse systems. One step towards understanding polydisperse polymers is the characterization of bi-disperse blends. Even though linear viscoelastic properties of bi-disperse polystyrene

blends have been investigated thoroughly both theoretically and experimentally in recent years [1], both nonlinear shear and extensional flow properties are lacking. In a recent study on solvent effects in monodisperse concentrated polymer solutions, Huang et al. (2013) [2] introduced a hypothesis that there exists nematic interactions between solvent-polymer and polymer-polymer molecules. However, this hypothesis needs further testing and is still an open question. The purpose of the present study is to investigate the existence of nematic interactions, namely polymer-polymer, in strong elongational flow using two bi-disperse polystyrene blends of 95 K and 545 K Mw with different weight ratios. We present both uniaxial extension and stress relaxation experiments to determine if orientation and extension of long PS chains induce orientation and extension in shorter chains (whose orientation should be unaffected by the flow).

[1] Nielsen J. K.; Rasmussen, H. K.; Hassager O., and McKinley G. H., "Elongational viscosity of monodisperse and bidisperse polystyrene melts", *J. Rheol.* 2006, 50, 453-476.

[2] Huang, Q.; Alvarez, N. J.; Matsumiya Y.; Rasmussen, H. K.; Watanabe H. and Hassager O. "Extensional Rheology of Entangled Polystyrene Solutions Suggests Importance of Nematic Interaction", *ACS Macro Lett.* 2013, 2, 741-744.

Wednesday 16:40 Hans-Thoma

PM15

### Conformational dynamics and topological analysis for polymer rings via atomistic molecular dynamics simulations and comparison with experimental data

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The experimental measurements of Kapnistos et al. [*Nature Materials*, 2008] have shown that the rheological response of a polystyrene ring melt contaminated with linear chains can differ significantly from that of the corresponding pure ring system. Motivated by this, we have started a new research project aiming at a detailed molecular understanding of dynamics and topological constraints in model ring-linear blends through atomistic molecular dynamic simulations [Tsalikis et al., *Reactive and Functional Polymers*, 2013]. We have focused on ring-linear polyethylene oxide (PEO) blends with molecular weight similar to those addressed experimentally. We will present results about the conformational and viscoelastic properties of these systems, as a function of the weight fraction of the linear component. We will also present results from a detailed topological analysis on selected configurations from the MD simulations which reveals significant threading of the cyclic PEO molecules by the linear chains.

## Polymer Melts, Blends, Copolymers, and Nanocomposites - PM

Organizers: Ulrich Handge, Manfred Wagner, Dimitris Vlassopoulos, and Alexei Likhtman

Wednesday 13:10 Johann-Peter-Hebel

PM48

### The enigma of the apparently vanishing long chain branches in nanocomposites elaborated with irradiated polypropylene

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Uniaxial elongational viscosity results were used to investigate the presence of long chain branching (LCB) in polypropylene/carbon nanotubes (CNT) nanocomposites. Long chain branching was triggered by irradiation using the following two protocols: a) Nanocomposites are prepared by melt mixing and submitted to irradiation (Protocol A) and b) Polypropylene is submitted to irradiation and nanocomposites based on this matrix are prepared by melt mixing (Protocol B). Dynamic viscoelastic results, supported by TEM microscopy analysis, indicated that CNTs were better dispersed in the case of Protocol B. As consequence, a lower rheological percolation threshold was found for this protocol, than for Protocol A. Elongational viscosity results showed strain-hardening behavior in the case of Protocol A, allowing estimating the level of LCB according to the irradiation dose. But, surprisingly enough, the nanocomposites of Protocol B did not show strain-hardening, although the irradiated matrix had LCBs (as detected by GPC/SEC measurements) and strain-hardening behavior. To disclose the enigma of what happened to long chain

branches in Protocol B, rheological measurements were carried out with samples taken at the different stages of the elaboration process.

Wednesday 13:30 Johann-Peter-Hebel

PM49

### **Elongational rheology of carbon black filled polymethylmethacrylate**

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The rheological behaviour of polymer composites under shear is extensively studied in the last decades; however, the studies dealing with elongational rheology of filled polymers are rather rare [1]. Nevertheless, such investigations are of great interest as the elongational flow is involved in the most of polymer processing techniques. In this work the behaviour of the polymethylmethacrylate (PMMA) filled with carbon black was systematically investigated in uniaxial elongation in the molten state using a Münstedt tensile rheometer in strain- and stress-controlled experimental modes.

As expected, the flow properties of the neat PMMA and the composite with carbon black concentration below percolation threshold are independent on the strain rate or stress applied. However, reaching a percolation threshold a systematic shift to lower viscosity values with increasing strain or stress is observed. This effect is explained as a consequence of the flow induced destruction of the structures formed by filler particles. The experiments performed confirm that the stress is the decisive parameter governing the behaviour of the composites containing developed particle structures. The results from elongational measurements are compared to those obtained in shear and thoroughly discussed.

[1] H.A. Barnes, Rheology Reviews 2003, 1-36

Wednesday 13:50 Johann-Peter-Hebel

PM50

### **Multiscale approach to dynamic-mechanical behavior of reinforced elastomers**

Ievgeniia Ivaneiko\*<sup>1</sup>, Vladimir Toshchevnikov<sup>1</sup>, Klaus-Werner Stöckelhuber<sup>1</sup>, Marina Saphiannikova<sup>1</sup>, Gert Heinrich<sup>1,2</sup>

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The main goal of present work is to develop a physically based multi-scale approach for description of the viscoelastic properties of reinforced elastomers for tire tread applications, in particular those based on a solution-polymerized styrene butadiene rubber. Rubber compounds with different fillers such as fumed silica with three different surface modifications, precipitated silica in three different grades and carbon black are investigated. For all samples we observe four distinct frequency regimes on the master curves constructed for the small strain storage  $E'(\omega)$  and loss  $E''(\omega)$  moduli at a chosen reference temperature (0 °C): 1) At very high frequencies, non-polymer relaxation modes due to rotational and vibrational motions inside the monomer can be identified. 2) For frequencies in the rubber-glass transition region, a semiflexible chain behaviour is observed with a typical scaling exponent of 3/4 for  $E'(\omega)$  for unfilled rubber and it decreases upon the filler addition. 3) For lower frequencies, the Rouse-like 1/2 exponent is clearly seen in the case of unfilled rubber. For filled rubbers we assume that mobile network chains and localised polymer chains due to the presence of filler contribute with exponents 1/2 and 3/8, respectively. 4) For even lower frequencies, we find a power-law behaviour with smaller values of the exponent. This can be explained with the entangled dangling chain concept for randomly cross-linked rubbers. To fit the master curves for unfilled and filled rubbers in the whole range of frequencies over 20 decades, we propose a multiscale approach based on the continuity of the logarithmic spectral density function  $H(\tau)$ . This approach is implemented in a fully automatic software, developed by us, and helps to identify the structural parameters, which show quantitative differences between the elastomers reinforced with different fillers.

Wednesday 14:10 Johann-Peter-Hebel

PM51

**Nonlinear behavior of heterogeneous elastomer samples investigated by means of Fourier Transform Rheology**Lukas Schwab<sup>1</sup>, Manfred Wilhelm\*<sup>1</sup>, Jean L. Leblanc<sup>2</sup>

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In this work the nonlinear behavior of unvulcanized SBR filled with different amounts of carbon black (cb) as well as the behavior of thermoplastic elastomers (TPEs) is investigated by means of Fourier Transform Rheology. TPEs are a class of materials which combine the good processability of thermoplastics with the high elasticity of vulcanized rubber materials. They are biphasic systems consisting of both hard segments with a high glass transition temperature (e.g. styrene) and soft, rubbery segments (e.g. isoprene, butadiene).

The intensity of the relative third higher harmonic,  $I_{3/1}$ , of the filled SBR samples shows a pronounced increase at medium shear amplitudes as soon as the filler content exceeds 12 vol%. This is attributed to the formation of a filler-filler network above the percolation limit. The increase of the complex modulus in the linear regime can not be explained with the empirical Guth-Gold equation for those highly filled systems, which is a further indication for a filler-filler network. For the first time  $I_{3/1}$  of highly filled SBR could be measured even at strain amplitudes below 10 % by using a very sensitive rubber rheometer with a closed die. A maximum of  $I_{3/1}$  could be detected at low amplitudes, whose origin may be in the heterogeneity of the polymer matrix. This peak vanishes after storing the samples for more than half a year at room temperature, indicating a change in the sample structure.

TPEs made of styrene-block-isoprene-block-styrene-copolymers, with a morphology of styrene spheres in an isoprene matrix, are used as simplified model systems for filled rubbers. With this material we can also find a maximum of  $I_{3/1}$  at low strain amplitudes. This strengthens our assumption of its origin in the biphasic structure of the polymer matrix. By ex-situ SAXS measurements, the shear induced orientation of the microphases can be observed.

Wednesday 14:30 Johann-Peter-Hebel

PM52

**Two-scale model for the elasto-viscoplastic behavior of silica-filled rubber**

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A dynamic two-scale model for describing the mechanical behavior of silica-filled elastomers is developed. The closed system of evolution equations is derived, consisting of evolution equations for the macroscopic momentum density, the temperature, the macroscopic deformation gradient and a mesoscale structure variable. The latter is given by the product of the number density of filler particles and the distribution function of particle-particle separation vectors. The system under consideration is strongly non-linear. The origins of non-linearity are the following: (i) the rubbery matrix, in which the particles are imbedded, expresses non-linear elastic effects; (ii) around the nanofillers, the matrix material forms glassy layers that overlap for sufficiently close particles, and consequently create temporary glassy bridges with a characteristic time scale that depends on the applied load (e.g. [1]). Extending earlier efforts to model nonisothermal and finite-deformation elasto-viscoplasticity [2, 3] with the GENERIC framework of nonequilibrium thermodynamics [4, 5, 6], we obtain the constitutive relation for the macroscopic stress tensor in terms of the filler-particle arrangement. Moreover, the filler-particle dynamics and the thermodynamic driving force for the breaking and recombination of the glassy bridges are derived. Finally, it is shown that the mesoscale dynamics can be cast into a stochastic differential equation in 6-dimensional space, amendable to Brownian dynamics-type simulations on the filler-particle level.

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Wednesday 15:20 Johann-Peter-Hebel

PM53

**A Thermodynamically Consistent Model to Predict the Magneto-Rheological Behaviour of Magneto-Sensitive Elastomers**Bastian Walter<sup>\*1</sup>, Prashant Saxena<sup>1</sup>, Joachim Kaschta<sup>2</sup>, Tobias Fey<sup>3</sup>, Dirk W. Schubert<sup>2</sup>, Paul Steinmann<sup>1</sup>

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Magneto-Sensitive Elastomers (MSEs) are smart materials composed of a non-magnetic, rubber-like polymeric matrix filled with magnetically permeable particles. On the application of an external magnetic field, magnetic dipoles are induced in the particles. Due to these dipole-dipole interactions, MSEs show a rapid, continuous and reversible change in their rheological and mechanical properties [1]. Therefore, MSEs are getting increasing interest in sensor, actuator and adaptive damping applications [2].

Focussing on isotropic model systems based on liquid silicone rubber filled with micro-meter sized carbonyl iron powder, well defined samples are investigated by means of a rheometer equipped with a magneto-rheological device (Anton Paar). The quality of dispersion below the percolation threshold, affected by the preparation conditions, is shown by  $\mu$ -CT and SEM imaging. The influence of material inhomogeneities on the experimental results is discussed. A material model, coupling the existing theories of viscoelasticity and the modelling procedure of magnetoelasticity, the latter recently developed by Dorfmann and Ogden [3], is successfully validated by means of oscillatory, quasi-static and transient shear experiments. In particular, relevant material parameters, e.g. a characteristic relaxation time and the elastic and viscous part of the shear modulus are obtained by fitting the experimental data of relaxation tests and shear experiments with and without an external magnetic field. Using these parameters the viscoelastic behaviour of MSEs in dynamic mechanical experiments under various experimental conditions can be successfully predicted for small deformations and low magnetic fields.

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Wednesday 15:40 Johann-Peter-Hebel

PM54

**Polystyrene comb architectures as a model for the investigation of spinnability of branched polymers**

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Polyolefins today have the most significant growth rate in filaments, staple fibers and nonwovens compared to all other synthetic fibers in textile industry. The existence of random long chain branching in commercial polymers like polyethylene (PE) has strong influences on the (non-)linear rheological properties of molten polymers during a melt spinning process [4]. Due to the unknown branching structure of the polymers, it is difficult to find quantitative correlations between topology and the rheological data of branched polymers. Therefore we synthesized model comb architectures using anionic polymerization of polystyrene resulting in well-defined backbone- and side chain length with low polydispersities ( $PDI < 1.1$ ) and a small amount of branches (0.1-1 mol % branches per backbone. Molecular weights were varied in the range between 15 and 42 kg/mol) [1-3].

Within this work, the linear and non-linear rheology of some comb homopolymer melts were studied in shear and elongation, which helps to better understand the influence of branching on the rheological properties of molten polymers. The effects of branching on spinnability and spinning stability of these polymer model combs were investigated by using capillary rheometer and rheotens. The obtained results of these experiments allow us to predict some important rheological properties related to the spinnability of commercial polymers during fiber formation.

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Wednesday 16:00 Johann-Peter-Hebel

PM55

**Rheological Evidence for Cure Retardation in Epoxy Clay Hybrid Nanocomposites**Gale A. Holmes<sup>\*1</sup>, Wayne Elban<sup>2</sup>, Mickey Richardson<sup>1</sup>

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The impact of nanoclay addition on the alpha-relaxation ( $T_g$ -peak) in montmorillonite (MMT)-filled epoxy systems has been the subject of debate, with some researchers reporting an increase in the glass transition temperature ( $T_g$ ), others a depression in  $T_g$ , while still others report no effect on the alpha-relaxation peak. In 2008, the Pearson research group reported the presence of two  $T_g$  in a diglycidyl ether of bisphenol-A (DGEBA) epoxy cured with piperidine and reinforced with an octadecylamine treated MMT clay. The lower  $T_g$  was attributed to the interphase near the surface of the clay layers. In this presentation, an epoxy blend consisting of DGEBA and the diglycidyl ether of butanediol (DGEED) is cured with meta-phenylenediamine (m-PDA) and reinforced with MMT clay treated with dimethyl benzyl hydrogenated-tallow ammonium (2MeBHT) chloride. By systematically varying the curing profile and monitoring the response of each system using frequency-temperature sweeps performed on an ARES-LS rheometer, a two  $T_g$  intercalated epoxy nanocomposite is formed with the lower  $T_g$  being caused by under-curing of the epoxy in the immediate vicinity of the clay nanoparticles. The implication of these results on epoxy nanocomposite formation will be discussed.

Wednesday 16:20 Johann-Peter-Hebel

PM56

**Correlation of dynamic viscosity and dielectric ion viscosity of resins used for nano-hybrid dental composites and the effects of resin composition, temperature and filler content**Johannes Steinhaus<sup>\*1,2,3</sup>, Thomas Haenel<sup>1,2,3</sup>, Bernhard Möglinger<sup>3</sup>, Berenika Hausnerová<sup>1,2</sup>

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Highly filled visible light-curing nano-hybrid composites play an important role in dental restoration applications. While the shear viscosity of the composites governs significantly the handling by the dentists, the curing behavior is controlled by the pure resin. As real-time measurements of the time dependent shear viscosity during the light-curing process are difficult to perform, the dielectric ion viscosity is an alternative to monitor and investigate the curing behavior. For resins based on the monomers BisGMA and TEGDMA, the initial dielectric ion viscosities and the corresponding shear viscosities were measured and investigated with respect to the effects of temperature, ratio of resin mixture, and filler content in order to find correlations. Both properties depend exponentially on temperature with the same value for the exponent coefficient. As the viscosities of BisGMA (800 Pa\*s) and TEGDMA (8 mPa\*s) differ significantly several mixture ratios BisGMA:TEGDMA were investigated. Qualitatively they showed a similar rheological and dielectric behaviour with respect to mixture ratios except the pure TEGDMA resin because of its low concentration of ions due to the high purity. However, the dependency of the dielectric ion viscosity on the filler content is rather linear for the investigated resins while the shear viscosity exhibits a strong non-linear increase.

Wednesday 16:40 Johann-Peter-Hebel

PM57

**Rheological modeling of ceramic nanocomposites in creep**Emanuel Ionescu<sup>1</sup>, Ralf Riedel<sup>1</sup>, Corneliu Balan<sup>\*2</sup>

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Rheology of nanocomposites materials brings value information not only about their mechanical behavior (normally under extreme conditions), but also on their chemical formulation and internal composition. In this work, dense monolithic polymer-derived ceramic nanocomposites (SiOC, SiZrOC, and SiHfOC) were synthesized via hot-pressing techniques and were evaluated with respect to their compression creep behavior at temperatures beyond 1000°C. The creep rates, stress exponents as well as activation energies were determined. The high-temperature creep in all materials discloses a viscoelastic flow process at extreme low rates, dependent on microstructure and phase

composition. The samples are modeled with the Jeffreys 3-constant constitutive relation; creep and recovery fittings prove the validity of the model. The viscosity and elastic modulus are computed and correlated with the phase composition and network architectures of the tested materials.

## Colloids and Suspensions - CS

Organizers: Matthias Ballauff and Moshe Gottlieb

Wednesday 13:10 Alfred-Mombert

CS6

### Powerlaw relaxation with positive exponent for the colloidal glass transition and negative exponent for gelation

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Experimental rheology can help to distinguish between gels and glasses. Two model systems of known linear viscoelasticity were chosen to exemplify the two material classes: (1) a crosslinking PDMS represents gelation (using chemical gelation instead of physical gelation) and (2) a concentrated colloidal suspension represents the soft glass transition. The longest relaxation time and the zero shear viscosity diverge for both materials, which look very similar in this way. However, the relaxation time spectrum  $H(\tau)$  and its expression as complex modulus, with components  $G'$  and  $G''$ , provide clear distinctions between gelation and the colloidal glass transition. While the long-time component of the relaxation time spectrum follows a powerlaw in time for both material types near LS-LST,  $H = H_0\tau^n$ , their powerlaw exponent  $n$  is of different sign (inverse behavior): negative  $n$  for the critical gel (material at the gel point) and positive  $n$  for the colloidal glass transition. The powerlaw spectrum is cut off by the diverging, longest relaxation time (called 'alpha relaxation time' for the glass) in the approach of the liquid-to-solid transition from the liquid side. Further examples will be shown in order to test the proposed distinction between chemical/physical gels and glasses (colloidal and molecular). In summary, relaxation data provide a clear distinction between these two classes of materials.

Wednesday 13:30 Alfred-Mombert

CS7

### Linking self-assembly, relaxation and rheology at the colloidal gel transition

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We propose a microscopic framework based on nonequilibrium statistical mechanics to connect the microscopic level of particle self-assembly with the macroscopic rheology of colloidal gelation. The method is based on the master kinetic equations for the time evolution of the colloidal cluster size distribution, from which the relaxation time spectrum during the gelation process can be extracted. The relaxation spectrum is a simple stretched-exponential for irreversible DLCA gelation, with a stretching exponent  $d_f/3$ , where  $d_f$  is the mass fractal dimension. As opposed to glassy systems, the stretched-exponential relaxation does not result from quenched-disorder in the relaxation times, but from the self-assembly kinetics in combination with the fractal character of the process. As the master kinetic equations for colloidal aggregation do not admit bond-percolation solutions, the arrest mechanism is driven by the interconnection among fractal clusters when excluded volume becomes active, i.e. at sufficiently high packing of clusters. The interconnections between rigid clusters decrease the soft modes of the system and drive a rigidity-percolation transition at the cluster level. Using the Boltzmann superposition principle, the aging and the full rheological response can be extracted for both irreversible and thermoreversible colloidal aggregation.

In the case of thermoreversible gelation, the attraction energy is finite and plays the role of the control parameter driving a nonequilibrium phase transition into a nonequilibrium steady-state (the gel). A power-law spectrum coexisting with a stretched-exponential cut-off is predicted leading to power-law rheology at sufficiently high frequency. Our theory is in good agreement with experimental data of different systems published by other authors, for which no theory was available.

Wednesday 13:50 Alfred-Mombert

CS8

**Structural Modification of Colloidal Gels by Shear**Esmaeel Moghimi<sup>1,2</sup>, George Petekidis<sup>\*1,2</sup>, Nick Koumakis<sup>3</sup>

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We studied the effects of oscillatory shear on the mechanical properties of a colloidal gel after shear rejuvenation. A model system of hard sphere colloids with the addition of non-adsorbing linear polymers, is used at an intermediate volume fraction allowing the quantification of the interplay between particle interactions and shear forces. Results reveal three main regimes depending on the strain amplitude. Large shear strains rejuvenate the gel which then evolves fast with time into a stronger solid while intermediate strains densify the gel and lead to weaker and more slowly evolving structures. Shaking the gel at even lower oscillatory shear strains again create stronger structures. These three regimes of shearing are reflect microscopic mechanisms of full rejuvenation and cluster breaking, cluster densification and over-aging due to gel coarsening.

Wednesday 14:10 Alfred-Mombert

CS9

**Fluidization of highly concentrated crystalline dispersions**

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We demonstrate that highly concentrated, crystalline colloidal dispersions can be fluidized by introducing weak attractive interactions. Polystyrene-butylacrylate model systems with 130nm particle radius and volume fractions between 0.55 and 0.65 have been studied. Depletion attraction forces were inferred by adding the non-adsorbing polyethylene oxide (PEO) with  $M_w = 20000$  or  $35000 \text{ g mol}^{-1}$ , corresponding to the polymer/particle size ratio of  $\zeta = 0.048$  and  $0.067$ , and concentrations between 1 and 10g/l. In addition to classical steady and oscillatory shear rheometry, a rectangular micro channel ( $\approx 30 \mu\text{m}$  height) has been used to study the flow behavior of these systems. Fluorescent particles have been used to determine the velocity profile in this flow cell, the accessible shear rate range is between 5 and  $20 \text{ s}^{-1}$ .

As expected the added polymer has a strong impact on the phase behavior of the suspensions and the liquid-crystalline coexistence region broadens significantly. Here we show for the first time, that this has a strong impact on the flow behavior of such concentrated dispersions. In analogy to the glass forming systems the addition of polymer leads to a drastic drop of the viscosity. The low shear viscosity goes through a deep minimum when an increasing amount of polymer is added. At a particle loading of 0.65 and  $\zeta = 0.048$  the viscosity at a shear rate of  $0.1 \text{ s}^{-1}$  drops by three orders of magnitude. Flow of concentrated crystalline dispersions without polymer in the rectangular channel is dominated by shear melting in the high shear rate regions close to the walls and plug flow in the channel center. In contrast, the dispersions including polymer show a strong growth of crystalline regions at the wall which finally leads to channel clogging. This unusual behavior also shows up in plate-plate rotational rheometry at gap heights  $< 500 \mu\text{m}$  and leads to an apparent increase of viscosity.

Wednesday 14:30 Alfred-Mombert

CS10

**Dynamics of thermosensitive core-shell dumbbells**Fangfang Chu<sup>1</sup>, Nils Heptner<sup>1</sup>, Miriam Siebenbürger<sup>1</sup>, Joachim Dzubiella<sup>1,2</sup>, Yan Lu<sup>1</sup>, Matthias Ballauff<sup>\*1,2</sup>

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We present a study of the dynamics of dumbbell-shaped colloids. The thermosensitive dumbbell-shaped microgels consist of a solid polystyrene core and a thermosensitive shell of cross-linked poly(N-isopropylacrylamide). These colloidal particles are nearly monodisperse as shown by cryogenic transmission electron microscopy. The aspect ratio  $L^*$  defined by the ratio of the center distance  $L$  and the diameter  $D$  can be varied between 0.24 and 0.3. The effective volume fraction can be varied by temperature and high volume fractions can be achieved easily because of the thermosensitive shell [1]. We observe the formation of a plastic crystal with Bragg-reflections in suspensions with volume fraction of about 0.5 as predicted by theory. The structure of plastic crystal and its structural evaluation under

shear are investigated via Rheo-SANS (small angle neutron scattering). For higher volume fraction a glassy state is formed. Moreover, oscillatory experiments in the linear viscoelastic regime and flow curves up to volume fractions of nearly 0.7 have been obtained. All data demonstrate that these particles present a novel model system for the study of the rheology of slightly anisotropic particles.

[1] F. Chu, M. Siebenbürger, F. Polzer, C. Stolze, J. Kaiser, M. Hoffmann, N. Heptner, J. Dzubiella, M. Drechsler, Y. Lu, M. Ballauff, Synthesis and Characterization of Monodisperse Dumbbell-Shaped Microgels, *Macromol. Rapid Comm.* 33 (2012) 104

Wednesday 15:20 Alfred-Mombert

CS11

### Channel flow of glass-forming fluids: combining microscopic theory with macroscopic simulation

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Glass-forming fluids show strongly non-Newtonian flow behavior. The interplay of slow microscopic structural relaxation with the mesoscopic flow field gives rise to shear thinning and yield-stress behavior. It furthermore causes pronounced flow-history effects. In a multiscale approach to the flow of glass-forming and in particular colloidal liquids, we perform mesoscopic simulations based on continuum-mechanics principles, augmented by suitable nonlinear, history-dependent constitutive equations that are derived starting from microscopic laws of motion. We first briefly present recent developments based on the mode-coupling theory of the glass transition (MCT) as an effort to derive such constitutive equations from a first-principles calculation of model colloidal suspensions. The theory captures the dependence of material properties on the past flow history, the appearance of residual stresses [1] and nonlinear creep phenomena [2]. We then present Lattice Boltzmann (LB) simulations of transient channel flow after application and removal of pressure drops based on a MCT-derived constitutive equation. The LB technique has been developed as an efficient method to solve the Navier-Stokes equations of Newtonian liquids in the low-Mach-number limit. We have extended this scheme to include the nonlinear integral-equation-constitutive laws that arise from the microscopic MCT description [3], in order to arrive at a multi-scale theory-and-simulation approach to the flow of dense liquids and glass formers.

[1] M. Ballauff et al, *Physical Review Letters* 110, 215701 (2013).

[2] M. Siebenbürger, M. Ballauff, and Th. Voigtmann, *Physical Review Letters* 108, 255701 (2012).

[3] S. Papenkort and Th. Voigtmann, arXiv:1310.7450 (preprint, 2013).

Wednesday 15:40 Alfred-Mombert

CS12

### Memory effects in colloidal rheology: A schematic mode coupling Model

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The viscoelastic properties of dense dispersions under time dependent flows provide insights into the slow structural dynamics close to the colloidal glass transition. Memory effects can be tested by already simple time dependences like start-up shear flow, flow reversal ('Bauschinger effect'), and shear cessation.

We present predictions from a schematic model of mode coupling theory (MCT) for these rheological protocols and compare them with experiments on model core-shell microgels, event-driven simulations of hard-disk mixtures, and molecular-dynamics simulations of hard-sphere mixtures [1,2,3]. The utilised schematic model is motivated by the microscopic ITT-MCT approach to the stress response of flow-driven systems and covers incompressible and homogeneous flows neglecting hydrodynamic interactions.

[1] C. P. Amann, F. Weysser, M. Fuchs, M. Siebenbürger, M. Krüger, and M. Ballauff, Overshoots in stress-strain curves: Colloid experiments and schematic mode coupling theory, *J. Rheol.* 57, 149 (2013).

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Wednesday 16:00 Alfred-Mombert

CS13

**Ascertaining Universal Features of Yielding of Soft Materials**Samruddhi Kamble<sup>1</sup>, Anurag Pandey<sup>1</sup>, Sanjay Rastogi<sup>2</sup>, Ashish Lele<sup>\*1</sup>

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Many metastable complex fluids, when subjected to oscillatory shear flow of increasing strain amplitude at constant frequency, are known to show a characteristic non-linear rheological response which consists of a monotonic decrease in the elastic modulus and a non-monotonic change in the loss modulus. In particular, the loss modulus increases from its low strain value, crosses the elastic modulus, and then decreases with further increase in the strain amplitude. Miyazaki et al. (Europhys Lett 75:915-921,2006) proposed a qualitative argument to explain the origin of the non-monotonic nature of the loss modulus and suggested that in fact this response could be universal to all complex fluids if they are probed in a certain frequency window in which the fluid is dominantly elastic in the small strain limit. In this letter, we confirm their hypothesis by showing that a wide variety of complex fluids, irrespective of their thermo-dynamic state under quiescent conditions, indeed show the aforementioned characteristic nonlinear response. We also show that the maximum relative dissipation during yielding occurs when the imposed frequency resonates with the characteristic beta relaxation frequency of the fluid.

[1] Miyazaki K et al (2006) Nonlinear viscoelasticity of metastable complex fluids. Europhys Lett 75(6):915

[2] Kamble S et al (2013) Ascertaining Universal Features of Yielding of Soft Materials. Rheol. Acta 52, 859-865.

Wednesday 16:20 Alfred-Mombert

CS14

**On the introduction of size effects in the mesoscopic description of microstructured suspensions via the use of high order approaches**Emmanuelle Abisset-Chavanne<sup>\*1</sup>, Julien Férec<sup>2</sup>, Gilles Ausias<sup>2</sup>, Francisco Chinesta<sup>1</sup>

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One of the trickiest issues of the microstructured suspensions modelling is the introduction of size effects in their mesoscopic description. Indeed, most of these approaches are based on the Jeffery's model and its phenomenological adaptations that do not introduce a micromechanical characteristic length in the kinematics and stresses. By the way, the rheological properties predicted are independent of the particles length. Consequently, new models are needed to enrich this Jeffery's kinematics in order to predict well the particles behaviour in the cases where the particles length is of the same order of magnitude as the flow characteristic dimensions, as in microfluidic flows or near a pipe wall. In this paper, we explore the introduction of high order gradient theories in the mesoscopic description of such suspensions. The work shows that the second order gradient does not modify the Jeffery's kinematics but introduces a relative velocity between the particle and the fluid. On the other hand, the third gradient introduces, more than this relative velocity, a modification of the Jeffery's kinematics. Finally, a simple test flow is used to illustrate the impact of such theories on the particles behaviour prediction and to compare their effects with the one of the use of closure relations.

Wednesday 16:40 Alfred-Mombert

CS15

**Viscosity amplification in dilute suspensions of spherical particles with a non-Newtonian matrix fluid**Jan Domurath<sup>\*1,2</sup>, Marina Saphiannikova<sup>1</sup>, Julien Férec<sup>2</sup>, Gilles Ausias<sup>2</sup>, Gert Heinrich<sup>1,3</sup>

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We performed a numerical study of a suspension based on a non-Newtonian matrix fluid and rigid spherical particles. In particular, we simulated an elongational flow of a Bird-Carreau fluid around a sphere and used numerical homogenization to obtain the effective viscosity of the suspension (i.e. by comparing energy) for different applied rates of deformation and different thinning exponents. In the Newtonian regime we obtained the well known Einstein result for the suspension viscosity:  $\eta = (1 + a\Phi)\eta_0$  with the amplification factor  $a=2.5$ .  $\Phi$  is the volume fraction of particles;  $\eta$  and  $\eta_0$  are the viscosities of the suspension and the matrix respectively. However in the transition region from Newtonian to non-Newtonian behavior we obtained lower values of the amplification factor  $a$ , which depend on

both the applied rate of deformation and the thinning exponent. In the power-law regime of the Bird-Carreau model, i.e. at high deformation rates, we found that the amplification factor  $a$  for the viscosity of the suspension depends only on the thinning exponent.

Analysis of the simulation results allowed us to propose a modification of the Bird-Carreau model for dilute suspensions with a non-Newtonian matrix fluid.

## Biopolymers, Active Fluids, and Food Rheology - BF

Organizers: Hans Wyss and Mats Stading

Wednesday 13:10 Clubraum

BF6

### Using rheological methods to measure biological responses of living cells to hydrodynamic stresses

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Living cell suspensions are often exposed to hydrodynamic stresses during biotechnological processes, such as fermentation or downstream applications, which may be beneficial or harmful to cells. When designing production processes, this shear sensitivity should be taken into account to guarantee high production yields. However, the optimization of processes with regard to the cell shear sensitivity is often done by trial and error instead of in a systematic way.

The goal of this study is to systematically investigate the biological answer of the cell to the hydrodynamics. Rheological methods are used to set up well-defined flow conditions and to study the effect of selected parameters on the cell. Such methods have already been used successfully to study red blood cells; we additionally focus on the heterogeneity of the cell population. The algae strain *Dunaliella Salina* is studied due to its lack of cell wall and its corresponding shear sensitivity. Furthermore, algae are easy to cultivate compared to other cell systems, e.g. animal cells. Rotational rheometry is used to set up small shear stresses. Capillaries are used to reach higher stresses by pumping the cells repeatedly through the capillary to guarantee a homogeneous stress history.

The results show that high shear stresses were necessary to reduce the cells viability. Below 140 Pa no cells died, above 140 Pa the survival rate decreased with increasing shear stress and number of passages. In all cases, the cell number decreased implying lysis. For shear stresses between 140 and 300 Pa only a part of the cell population is affected which emphasizes the importance of the population's heterogeneity with cells varying in state, size, or membrane thickness. For older cell populations, the survival rate is noticeably lower than for younger cells. Increasing the cell number had only a minor effect on the survival rate implying that the hydrodynamic stress instead of cell collisions leads to death.

Wednesday 13:30 Clubraum

BF7

### Synovial Fluid Hyaluronate Analysis using Stagnation Point Flow

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Piezo-actuated micropumps are used to generate an oscillatory stagnation point extensional flow field within a microfluidic cross-slot device in order to hydrodynamically stretch hyaluronic acid (HA) macromolecules in dilute solution. Measurements are made of the flow-induced birefringence at the stagnation point as the strain rate is precisely manipulated by controlling the frequency and amplitude of the piezo oscillation. The increase in birefringence beyond a critical strain rate allows the longest macromolecular relaxation times of the HA to be determined. The relaxation time is found to vary with molecular weight to the power of 1.8, consistent with a partially hydrated semi-flexible chain. Also, the value of the plateau birefringence at high strain rates is found to vary linearly with the HA concentration. By comparison, this information can be used to assess the concentration and relaxation time (hence relative molecular weight) of the HA contained in a diluted sample of physiological synovial fluid. Proof of concept is obtained using synovial fluid extracted from porcine tarsal (ankle) joint. It is demonstrated that this approach allows rapid HA analysis using microscopic synovial fluid samples (10-100  $\mu\text{L}$ ) and with quite minimal sample preparation being required. The method has potential as a microfluidic technique for rapid assessment of the health of synovial fluid in joint disease patients.

Wednesday 13:50 Clubraum

BF8

**Viscosity reduction due to the activity of Escherichia Coli**Hector Matias Lopez\*<sup>1</sup>, Jeremie Gachelin<sup>2</sup>, Eric Clement<sup>2</sup>, Carine Douarche<sup>3</sup>, Harold Auradou<sup>1</sup>

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Due to their importance in potential technological applications, such as bioremediation of soil, suspensions of swimming microorganisms (active fluids) are receiving increasing attention. Theoretical studies have predicted that the activity of bacteria results in a viscosity reduction at low shear rate.

We present, here, experimental measurements of the viscosity of Escherichia coli suspensions as a function of the shear rate. For shear rates larger than 10 Hz, the viscosity is constant and slightly above the viscosity of the suspended fluid. This behavior is similar to that expected for non-active particles. A second Newtonian plateau is observed for shear rates below 0.1 Hz. The viscosity value of this second plateau is significantly lower than that of the suspended fluid. We found that, in the range of our experimental conditions, the decrease is proportional to the bacteria concentration, suggesting that it is a result of the energy input of each microswimmer. Experiments performed at various temperatures give us information about the effect of bacterial activity on the viscosity reduction.

Wednesday 14:10 Clubraum

BF9

**Stabilisation of oil-based food suspensions through organogelation**Domenico Gabriele\*<sup>1</sup>, Francesca R. Lupi<sup>2</sup>, Noemi Baldino<sup>2</sup>, Lucia Seta<sup>2</sup>, Bruno de Cindio<sup>2</sup>

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Stabilisation of suspensions is a relevant issue in many industrial areas, including food processing. Water based systems are commonly stabilised by addition of hydrophilic structuring agents able to increase water phase consistency and, therefore, to reduce destabilising phenomena. When a similar solution is proposed for oil-based systems more difficulties arise owing to the lack of suitable structuring agents. Organogelation of the oil dispersing phase can be a potential solution to the stability issues currently observed in some practical applications. Organogelators are components (both polymeric or low-molecular weight agents) able to self-assemble into crystals and to promote solvent crystallisation yielding, as a final result, the formation of a three-dimensional crystalline network entrapping the residual liquid solvent and other potential particles dispersed in the oil phase.

In this work the stabilisation of oil-based meat suspensions was investigated by adding different edible organogelators (such as monoglycerides of fatty acids). The effects of proposed additives were analysed by destabilising the modified suspensions (by centrifugation) and comparing their rheological characteristics and oil loss to those of the unmodified systems (i.e. without addition of stabilisers). The obtained results confirm that organogelators can be successfully used to stabilise edible oil-based suspensions and that rheology is the most suitable tool to choose both the proper additive and concentration.

Wednesday 14:30 Clubraum

BF10

**Envisioning wheat flour dough as a triphasic medium to predict bubbles structure stability**Arnaud Turbin-Orger, Hubert Chiron, Laurent Chaunier, Guy Della Valle\*

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To determine the mechanisms of development of solid foams cereal, taken as model of baked goods, we have focused on the proofing stage, during which gas bubbles grow and interact, and finally lead to the cellular structure and crumb appearance. Elongational properties of starch / gluten matrix, and the kinetics of stability and porosity of different doughs during fermentation were determined at macroscopic scale by lubricated squeezing flow test and 2D image follow-up, respectively. The cellular structure of doughs and their evolution were determined by in situ X-ray microtomography (XRT). Resulting 3D images were analysed, to clarify the role of the volumic liquid fraction. Dough liquor (DL), taken as a model of the liquid phase separating bubbles, was extracted and its composition as well as its foaming and rheological properties were determined. The elongational properties of dough largely influenced its stability, the evolution of which was adjusted by an exponential decay; this result could not be explained by the

single bubble growth model. Porosity kinetics at macroscopic level were in good agreement with XRT results and both followed a Gompertz model. For highest dough porosity ( $> 0.5$ ), XRT showed that most bubbles are connected. The homogeneity of the cellular structure was defined from the size distributions of gas cells and walls; it was characterized by a critical thickness of walls ( $\approx 1\mu\text{m}$ ), below which the cells were separated by liquid films. The fermented dough could thus be considered as a three-phases medium: viscoelastic matrix / gas cell / liquid phase. The role of this 3rd phase, which behaves like a macromolecular solution, is taken into account by the DL surface tension ( $\approx 40\text{mN/m}$ ) and the presence of polysaccharides-proteins complexes at interfaces. Finally, the contributions of the different levels of matter organization were then integrated by defining a capillary number ( $\text{Ca} \approx 10^{-2}$ ), that ruled the overall behavior of the dough.

Wednesday 15:20 Clubraum

BF11

### Engineering cheese sensory-texture: computations and rheology on a semi-solid

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Cheese is a micro-structured food product, primarily consisting of water, protein, and fat. Cost price and caloric content drive cheese reformulation, which comes at the cost of deteriorated sensory-texture performance. New production processes or structuring routes are needed to decouple this relation between composition and cheese sensory-texture. For rational design of these processes there is a need for models that relate structure, composition and sensory-texture with each other.

The field of Material Science and Technology has a long history in the development and practical application of such models, which originate from the field of rheology. In this work the hybrid experimental-computational approach, developed at TU Eindhoven, is used in order to formulate constitutive models that couple microscopic (structure) to macroscopic (mechanical) properties of semi hard cheese. These constitutive models are used in simulations to design new cheese microstructures with texture properties that resemble full fat cheese.

We narrow down the broad concept of cheese sensory-texture to the attributes that become apparent at first touch and first bite: firmness and meltability. The rheological analogues for these attributes are the linear viscoelastic and (post-)yielding properties respectively. Small-strain shear rheometry provides insight in both creep response as a function of cheese composition and cheese microstructure: it is modeled as an attractive soft glassy protein matrix filled with an emulsion of fat. Large Amplitude Shear and compression measurements reveal a clear relation between composition, yield point, and strain softening and/or hardening. We use this information together with the assumed microstructure and a glassy polymer model as an input for Finite Element calculations. Once validated, these models are used in virtual and rapid testing of mechanical properties of yet non-existent microstructures / compositions.

Wednesday 15:40 Clubraum

BF12

### Rheology of chocolate-flavored, reduced-calories coating as a function of conching process

Luis Medina-Torres\*<sup>1</sup>, Guadalupe Sánchez-Olivares<sup>2</sup>, Leonardo Moreno<sup>3</sup>, Fausto Calderas<sup>3</sup>, Octavio Manero<sup>3</sup>

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The rheological response of a chocolate coating is determined by the composition of the sample as well as the various phases involved during processing. The thermo-mechanical properties of flow and linear viscoelasticity of chocolate coating are studied in this work using fat substitute gums (xanthan, GX) and proposing an alternative conching process using a Rotor-Estator (RE) type impeller. We sought to obtain coating improved with mechanical properties to flow based on the particle size distribution (PSD), thermal characteristics via differential scanning calorimetry (DSC) and proximal analysis. The results indicate that xanthan gum is a good substitute for cocoa butter as a function of the mechanical characteristics of flow as, aside from being more stable, it also had particle sizes with less polydispersity and therefore, greater homogeneity; fusion points were also generated at around  $20^\circ\text{C}$  assuming crystal type I ( $b'_2$ ) and II (a). Moreover, xanthan gum exhibited crossover points (structural changes) between the viscoelastic modulus  $G'$  and  $G''$ . The coating which generated the best rheological properties when compared to a commercial brand was the one prepared with xanthan gum under maturing conditions of 36 h and  $35^\circ\text{C}$ , showing crossover points around 76 Pa and a 0.505 particle dispersion, and having an average particle diameter of 364 nm, and a fusion point at  $20.04^\circ\text{C}$  with a  $\text{DH}_f$  of 1.40 (J/g).

- [1] Afoakwa E., Paterson A., Fowler M., "Factors influencing rheological and textural qualities in chocolate review", *Food Science and Technology* 18 (2007):290-298
- [2] Afoakwa E., Paterson A., Fowler M., Vieira J., "Characterization of melting properties in dark chocolates from varying particle size distribution and composition using differential scanning calorimetry", *Food Research International* 41 (2008): 751–757
- [3] Macosko, C. W., "Rheology: principles, measurements and applications". VCH; New York, (1997). Chapter 3, 109-121.

Wednesday 16:00 Clubraum

BF13

### **Rheological optimization of pasta dough mixing by large-deformation properties in uniaxial extension**

Noemi Baldino\*<sup>1</sup>, Domeni Gabriele<sup>2</sup>, Lucia Seta<sup>1</sup>, Francesca Romana Lupi<sup>1</sup>, Bruno de Cindio<sup>1</sup>

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Mixing is an important step in producing dough with desired strength as a good quality end-product. Processing factors during flour-water mixing include the mixing time, work input, mixer type and temperature. In order to obtain the optimal dough development, operating parameters like mixing time and water have to be optimized in order to produce high quality dough.

In this work the mixing of dough based on durum wheat semolina, for pasta production, was investigated with the aim of optimising the mixing time and temperature as a function of the semolina protein content by using a rheological criterion.

Rheological tests were carried out in linear viscoelastic conditions, with small amplitude shear oscillations, and in non-linear conditions, with uniaxial extensional measurements for durum wheat semolina having different protein content. Samples prepared at different temperatures were tested at different mixing time to evaluate the effects of both parameters on rheological properties.

Strain hardening phenomena, similar to those observed for wheat flour, were evidenced during extensional tests and it was found that they are significantly affected by investigated operating conditions (i.e. time and temperature of mixing) and by the gluten content. Obtained results confirm that the rheological "optimum" of dough network is mainly governed by the gluten fraction and that extensional tests seem to be an interesting tool to optimise operating conditions.

Wednesday 16:20 Clubraum

BF14

### **Food Oral Design**

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Swallowing is a complex process and we first disintegrate the food into smaller particles and mix them with saliva to form a viscoelastic bolus which we transport to the back of the mouth. As soon as the bolus touches the pharyngeal arches we automatically swallow. During the short time it takes to carry out these activities the receptors of various senses in the oral cavity and in the nose are stimulated and we perceive all impressions about what we eat regarding aroma, taste, texture and mouth feel. Ideally this stimulation gives rise to pleasurable food experiences. Normally we do not think about these intricate processes and much of them are even automatic, still they are the basis of how we perceive the food we eat. This means that with detailed knowledge of the eating and swallowing processes we are able to develop food by Food Oral Design.

Saliva is one important component in the oral processing where it is involved in taste and aroma transfer, lubrication and thus strongly contributes to the perception of the food. Other major functions of saliva are to protect hard and soft oral tissues from wear, dehydration, demineralisation, chemical insult and microbial imbalance. It is particular salivary glycoproteins such as mucins and proline-rich proteins that have structural features that correlate to the protective function of masticatory lubrication. The saliva from the different glands is shown to have very different viscoelastic properties.

The actual swallowing is another important component of the oral processing. As healthy individuals we seldom consider it whereas for others it may cause discomfort and even serious health problems. Already over 50 years of age 22% suffer from swallowing disorders, or dysphagia, and in the age group above 70 years, 40% suffer due to factors such as degenerative diseases, side effects of medication and trauma. These persons must eat texture

adjusted foods, and the oral processing is considerably affected.

Wednesday 16:40 Clubraum

BF15

### Rheokinetics of salivary alpha-amylase catalised hydrolysis of starch: effect of inhibitors

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Dysphagia, or abnormal swallowing of solid foods and/or liquids, is a consequence of neurological diseases, several forms of cancer, or stroke. It is usually related to a reduced oral intake that easily leads to malnutrition and dehydration. The main objective of dysphagia assessment is to avoid food aspiration, because this may lead to pneumonia. Aspiration depends on clinical status as well as food/liquid flow properties and bolus volume. Swallowing disorders can be managed by the use of prescribed ready-to-use oral nutritional supplements (ONS) specially designed for the nutritional support at different stages of dysphagia. On the other hand, thickener powders are also widely used to modify the consistency of drinks or meals. The rationale behind altering or modifying the consistency of foods and/or drinks is to change the rate at which food is transported through the pharynx/esophagus and, thus, to reduce the risk of aspiration. There are three commonly used consistency levels in dysphagia care: nectar (low consistency); honey (medium consistency); and pudding (high consistency), which are prescribed to a dysphagia patient based on the level of the disease. ONS and thickeners may contain starch. If this is the case, a big issue is the hydrolysis of starch by salivary alpha-amylase. Alpha-amylase is a very effective enzyme in breaking down the structure of starch and converting it into simple sugars, yielding a dramatic decrease in viscosity. This fact complicates the treatment of dysphagia. In this work, mixing rheometry has been used to quantify the rheokinetics of this process. It has been demonstrated that, when a starch-based thickened fluid is mixed with saliva, its viscosity may be reduced up to 99% of the initial viscosity, its kinetics being dependent on mixing intensity and saliva concentration. On the other hand, the influence of different alpha-amylase inhibitors on the above-mentioned rheokinetics has also been studied.

## Interfacial Phenomena, Surfactants, Emulsions, and Foams - SF

Organizers: Jan Vermant and Crispulo Gallegos

Wednesday 13:10 Forum I

SF6

### Interfacial Rheology of Model Particles at Liquid Interfaces

Job Thijssen\*<sup>1</sup>, Rob Van Hooghten<sup>2</sup>, Eline Hermans<sup>2</sup>, Anja Vananroye<sup>2</sup>, Jan Vermant<sup>2</sup>

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Particle-stabilized liquid-liquid composites, including Pickering-Ramsden (PR) emulsions and bijels, have received considerable attention in recent years. The reasons for this are twofold: (1) PR composites are model arrested systems and (2) they have significant potential for applications in foods, personal-care products and catalyst supports. It has been demonstrated that the role of interfacial particles in stabilizing liquid-liquid composites can be quantified using interfacial rheology [1]. However, the full impact of interfacial rheology on the stability of PR composites remains far from fully understood. For example, equivalent particle-laden interfaces in stable emulsions can appear solid-like under compression [2], but fluid-like under shear. This rich behaviour arises from a complex interplay between liquid-liquid tension and interfacial particles. What is currently lacking is a comprehensive investigation of the interfacial rheology of model colloids at liquid interfaces and how that relates to PR composite stability.

Here, we present our results on the interfacial rheology of model microspheres at liquid-air and liquid-liquid interfaces. We consider both sterically stabilized PMMA particles and charge-stabilized silica particles, varying the wetting properties of the latter by wet-chemical functionalization. We confirm that particle wettability has a strong effect on interfacial rheology [3]. Moreover, we find that liquid interfaces laden with sterically stabilized rather than charge-stabilized particles have a markedly different mechanical response under both compression and shear, which we attribute to the interfacial mobility of the individual particles.

[1] L. Imperiali et al, Langmuir 28, P7990 (2012)

- [2] L. Maurice et al, *Soft Matter* 9, P7757 (2013)  
[3] D.Y. Zang et al, *Molecular Physics* 109, P1057 (2011)

## Wednesday 13:30 Forum I

SF7

**Deformation, orientation and bursting of microcapsules in simple shear flow: Wrinkling processes, tumbling and swinging motions**

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Microcapsules with polymer membranes as wall materials are often synthesized for technical, cosmetic, medical and pharmaceutical applications on grounds of their well-defined controlled release properties. Due to their simple structure and viscoelastic properties these particles are also used as artificial model systems to mimic the mechanical properties of biological cells. The investigation of bursting processes, capsule deformation and orientation in linear shear flow is, therefore, of great interest for technical applications and basic scientific research.

In a series of experiments we investigated the rheological properties of polysiloxane and poly-acrylamide microcapsules in an optical flow cell (rheoscope). In additional experiments we measured the regime of linear viscoelastic response and the shear rheological properties of the flat membranes in an interfacial rheometer. In spinning drop experiments, we determined the surface Young moduli and bursting process of the artificial particles. Measurements of the bending rigidity of the membranes were obtained from pendant-drop-experiments. The combination of these four experiments allowed evaluating the mechanical properties and the surface Poisson ratios of the capsule membranes.

In experiments of simple shear flow we noticed that the capsule deformation was influenced by several parameters, such as the viscosity ratio between the inner and outer phase, the water concentration of the oil phase, the polymerization time and the membrane bending rigidity. Besides these phenomena we observed a large number of different rheological processes like shear induced membrane wrinkling, tumbling, swinging and other dynamic particle motions. In additional experiments we investigated the flow induced bursting process of the viscoelastic capsules. It turned out that most of the non-linear experimental results were in fairly good agreement with new theoretical approaches and recent simulations.

## Wednesday 13:50 Forum I

SF8

**Morphology and Flow Properties of Multilamellar Structures in Surfactant Solutions**Angelo Pommella<sup>1</sup>, Dario Donnarumma\*<sup>2</sup>, Sergio Caserta<sup>2</sup>, Stefano Guido<sup>2</sup>

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Surfactant systems morphology is a topic of high scientific interest that has various industrial applications. However, while many studies have been addressed to the phase behaviour of water-surfactants solutions, only limited information is available in literature on flow-induced morphology of such systems. The recent advances in rheo-optical techniques help now to elucidate the changes in microstructural conformation taking place in the lamellar phase during flow. The focus of this work is to develop a quantitative investigation of the flow behaviour of single surfactant multilamellar vesicles (SMLVs). The fluid investigated is a solution of HLAS in water, a surfactant widely used in the detergent industry. Depending on concentration, different phases can be observed, such as planar lamellae, unilamellar and multilamellar vesicles. We focused on a range of concentration where lamellar phase inclusions are surrounded by an isotropic matrix, and eventually form SMLVs. Vesicle shape has been quantified by image analysis techniques. Different setups allow the direct observation of the sample, either during the flow or in static conditions, by several microscopy imaging techniques including high speed, bright field, phase contrast and confocal. A simple shear flow cell, where the fluid is placed among two parallel transparent glass plates one of which is translating respect to the other, allow the sample observation both along the vorticity and velocity gradient directions, using two different setups, hence allowing the three-dimensional reconstruction of the system microstructure. A different flow cell can be used to investigate the Poiseuille flow using a cylindrical microcapillary. The main result is that SMLVs are deformed and oriented by the action of shear flow while keeping constant volume, and exhibit complex dynamic modes (i.e., tumbling, breathing and tank-treading). SMLV deformation shows some analogies with the behaviour of a single droplet immersed in an immiscible fluid, thus suggesting possible non-dimensional scaling parameters such as the Capillary number, that is the ratio between the shear and the interfacial stress. Furthermore, 3D shape

reconstruction of confocal images of SMLVs, was used to identify the presence of both superficial and internal defect, whose role in the deformation dynamics is discussed. A possible application of the physical insight provided by this work is in the rationale design of processing methods of surfactant-based systems.

[1] S. Caserta, S. Guido, *Langmuir* 28, 16254-16262 2012.

[2] A. Pommella, S. Caserta, V. Guida, S. Guido, *Physical Review Letters* 2012 108, 138301.

[3] A. Pommella, S. Caserta, S. Guido, *Soft Matter*, 2013,9, 7545-7552.

### Wednesday 14:10 Forum I

SF9

#### **A Droplet as a mini-rheometer to evaluate interfacial viscoelasticity of solid particles-laden liquid/liquid interfaces**

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Solide nanoparticules-laden droplet may jam in an anisotropic shape when get deformed, depending on the concentration  $C$  and the affinity of the solid particles with the two liquid phases. Therefore we investigated in this study the relaxation of an isolated droplet of diluted aqueous suspensions of modified silica nanoparticles. The deformation of the droplet was monitored using a homemade counter rotating shear device developed at PCI. We used a Newtonian polyisobutene as a continuous phase and we recorder the droplet retraction after a controlled step strain. At low strain, the droplet jammed into a non-spherical shape resembling an ellipsoid of revolution that became more anisotropic when  $C$  increases. Thus, by deducing an apparent jamming stress  $S_{aj}$  of the deformed droplet given by the gradient of Laplace pressure at its interface, we found that  $S_{aj}$  showed a power law dependence with  $C$ . In addition, we measured the interfacial viscoelastic moduli of a model planar water/PIB interfaces using a shear stress controlled rheometer equipped with an interfacial geometry (Double Wall Ring) using the same silica nanoparticles. By increasing  $C$ , the water/PIB interfaces showed a liquid-solid transition and a power law dependence of the elastic modulus  $G_i'$  with  $C$  in the solid like behavior. Remarkably, the interfaciale elastic moduli were correlated to the anisotropic shape of the droplet since we found that  $G_i'$  was quasi-proportional to  $S_{aj}$  in all the experimental conditions of this study. Interestingly, the droplet behavior undergoing shear deformation could be used as a mini-rheometer to evaluate the viscoelastic moduli of solide particles-laden liquide/liquide interfaces.

### Wednesday 14:30 Forum I

SF10

#### **Measuring the Surface Tension of Yield Stress Fluids**

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Various industrial process involve the formation of a layer of a yield stress fluid over a solid surface. So far the characteristics of yield stress fluid flows along solid surfaces have generally been considered under the assumption that interfacial effects were negligible and viscous effects were dominant. For fluids made of elements in suspension in a simple liquid, such as foams, emulsions, suspensions, colloids, it was suggested that surface tension is simply equal to that of the interstitial liquid, since all the elements are generally surrounded by liquid. Actually the above physical argument might fail for concentrated systems for which the liquid layer along the interface is very thin or when the components of the liquid layer along the air-fluid interface are unknown. Here we focus on the possibility of measuring the surface tension of a yield stress fluid with the help of a technique derived from the Wilhelmy technique, i.e. by withdrawing a film from a fluid bath. We show that before a progressive breakage of the film, the force amplitude goes through a maximum which is independent of the initial depth of penetration and the timing for blade lifting, but increases with the material yield stress and the blade thickness. This critical force is shown to reflect both capillary and viscous effects, even at vanishing blade velocity. We demonstrate that the ratio of this force to the blade perimeter provides the surface tension of the yield stress fluid in the limit of low ( $\ll 1$ ) Capillary number (ratio of yield stress times blade thickness to surface tension). Moreover we show that all our data for the force to perimeter ratio fall along a master curve which may be used to deduce the surface tension from measurements obtained at Capillary number up to 1, even if viscous effects are significant. Finally Carbopol gels appear to have almost the same value of surface tension whatever their yield stress, but this value is almost 10% smaller than that of pure water.

Wednesday 15:20 Forum I

SF11

**Dilatational rheometry using a circular trough**Jan Vermant<sup>†1,2</sup>, Tom Verwijlen<sup>1</sup>, Eline Hermans<sup>1</sup>, Joe Samaniuk<sup>1</sup>

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Dilatation or compression of complex fluid-fluid interfaces occurs frequently in processes involving multiphase systems such as foams and emulsions. Also biological systems can depend on the dilatational behavior of membranes, for example the breathing mechanism of lung alveoli. A proper quantification of the interfacial mechanical resistance against dilatational deformations can capture significant information regarding the stability of these systems and the selection of suitable stabilizers. Most current days designs of dilatational rheometry have mixed deformation modes. Here, a newly designed and constructed radial Langmuir trough is discussed, which applies a pure dilatio/compression to the interfaces. Experimentally obtained isotherms and small amplitude area oscillations on poly(tert-butyl methacrylate) (PtBMA and some other components) at the air-water interface are presented and compared, using the radial trough as well as a rectangular trough with different Wilhelmy plate orientations.

Wednesday 15:40 Forum I

SF12

**Rheotaxis: The Sensing and Migratory Response of Microvascular Endothelial Cells to Local Wall Shear Stress Profiles**

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Endothelial cells (ECs) line the inner diameter of our blood vessels and control the dilation of those vessels to ensure that wall shear stresses remain within desirable ranges. However, the manner in which these cells sense wall shear stress is not known. Existing observations have long been available, however, that establish that healthy ECs elongate and orient in the direction of wall shear stress for uniform fields. However, it has been observed that disruption in wall shear stress can misalign these cells. This lecture presents data where live cell imaging has been used to follow the migratory response of microvascular ECs exposed to well defined, stagnation point flows. These flows are generated by aiming jets of fluids at monolayers of ECs at modest Reynolds numbers. Impinging jet flows generate wall shear stress profiles that are zero at the stagnation point and that rise to a maximum in the vicinity of the jet diameter before dissipating to zero far from the jet. It is found that the ECs migrate upstream, against the wall shear stress and realign to an orthogonal orientation at the location of maximum stress. This distinctive migratory pattern is shown to be exquisitely sensitive to mechanotransduction pathways within the cells and this is confirmed by introducing chemical inhibitors that block proteins thought to be involved with signalling pathways.

Wednesday 16:00 Forum I

SF13

**Food emulsion interfaces to manipulate digestive behaviour**

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The digestive behaviour of food emulsion can be manipulated by the interfacial design of the emulsion as it is presented to the digestive tract. The ex-vivo interfacial behaviour of food emulsions is largely controlled by the chosen ingredients and the manufacture process. Upon ingestion interaction with saliva combined with the mechanical action of tongue and teeth may alter the interfacial composition which needs to be taken into account when investigating the digestive behaviour of food emulsions. In the case of fat continuous foods, these are emulsified during oral processing and the question arises whether the interfacial composition of this in-vivo processed emulsion is dominated by salivary proteins or by surface active components of the formulation or both. In our research we are interested in the process design as well as the in-vivo design of food emulsion interfaces for manipulation of digestive behaviour.

Process design: A molecular amphiphile demonstrated to delay lipolysis when co-adsorbed with phospholipids at oil-in-water emulsion interfaces is the glycolipid digalactosyldiacylglycerol (DGDG). Use of pure DGDG is commercially not viable and we have been able to demonstrate that a crude lipid extract rich in DGDG may be used instead

functionality using interfacial rheology as one of the experimental methods.

In-vivo design: Fat continuous foods often contain lecithin and we have seen that these products phase invert into an oil-in-water emulsion during oral processing. Examining the competitive adsorption between salivary protein and lecithin we have found that the presence of lecithin rendered the salivary protein less elastic confirming that a mixed protein-surfactant film is being presented to lipolysis.

Wednesday 16:20 Forum I

SF14

### Dynamic rheological response of entangled worm like micellar solutions

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Micelles are “living polymers”, which behave very similarly to standard polymer chains. Structure and morphology are strongly dependent on the concentration of the surfactants and on the main parameters of the systems (PH, temperature, etc). The polymers have a covalent bonded backbone, whereas the micelles are held together by weak physical attractions. As such, when deformed, the micelles could have access to different ways to relax. Depending on their morphology, micellar systems show different rheological responses both in the linear and non-linear regime [1], but a direct relation between rheology and morphology is still lacking.

Micellar systems of an anionic (linear alkylbenzene sulphonic acid, HLAS) and two non ionic surfactants (triethylene glycol dodecyl ether and heptaethylene glycol dodecyl ether) have been prepared. Their rheological properties have been studied with a strain controlled rheometer (ARES, TA instrument) both in linear and non linear regime. Creep tests in a linear regime have also been performed with a stress controlled rheometer (Bohlin CVO, Malvern) in a way to enlarge the frequency window. Large amplitude oscillatory shear experiments have been carried out and the results have been analyzed in the Fourier space [2].

The experimental results show that changes in the relative surfactant concentrations determine two completely different rheological responses. In one case, the classical Maxwell-like behavior typical of linear wormlike micelles is observed in the linear regime [3]. In the other, at least two characteristic times are measured, suggesting the formation of a branched micellar structure [4]. The qualitative difference in behavior is confirmed also in the non linear regime.

[1] Dreiss, *Soft Matter*, 2007, 3, 956-970.

[2] Wilhelm, *Macromol. Mater. Eng.* 2002, 287, No. 2.

[3] Cates and et al, *J. Phys*, 1990, 2, 6869-6892.

[4] Hassan et al., *Current Science*, vol. 80, No. 8, 2001.

Wednesday 16:40 Forum I

SF15

### Emulsion morphology evolution by phase inversion method

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Oil in water emulsions can revert into water in oil and vice versa by varying phases volume fraction, by changing temperature, by particular flow tipology (e.g, extensional rather than shear flow), pH changes. Surfactants behavior within emulsion is the key factor leading to the inversion of the phases. Emulsification via phase inversion is a process to obtain nanoemulsions and microemulsions, because emulsion phase inversion process is a route to obtain finely dispersed droplets in a continuous phase and for these reasons is widely used in fabrication of cosmetic products, pharmaceutical products, foodstuff, detergents, particles and vesicles. This work has been focused on emulsification of mixtures composed by water, mineral oil and two non-ionic surfactants. The “emulsion inversion point” preparation method, i.e., the dropwise addition of water to the oil-surfactant mixture in order to produce an oil in water nanoemulsion, allowed us to obtain long term stable nanoemulsions with significant energy saving, due to the low energy mixing requirement and the possibility to run the emulsification process at room temperature. Droplet size distribution has been detected by static light scattering. To better understand the inversion process, confocal microscopy and rheological measurements have been exploited to characterize emulsion morphology development. Here we probe by rheology measurements the increased viscoelastic behavior of the oil-surfactant solution induced by water addition till the point of the inversion of the phases, followed by a monotonic decrease of the viscoelastic

behavior induced by further water addition. Confocal microscopy reveals the formation of complex micrometric sized bicontinuous structure formation associated with the viscoelastic behavior.

## Polyelectrolytes, Associating Fluids, and Liquid Crystals - LC

Organizers: Christian Friedrich and Valery G. Kulichikin

Wednesday 13:10 Forum II

LC6

### Shear Banding in a Lyotropic Lamellar Phase Studied by Nuclear Magnetic Resonance Diffusometry and Velocimetry

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The lamellar phase of the system triethylene glycol mono n-decyl ether ( $C_{10}E_3$ )/water under shear in a cylindrical Couette cell was investigated by NMR velocimetry, diffusometry, and <sup>2</sup>H-NMR spectroscopy.  $C_{10}E_3$ /water is known to form multilamellar vesicles under shear flow in a certain range of temperature and shear rates [1]. The investigation of the flow field shows that the transformation from multilamellar vesicles (MLVs) to aligned planar lamellae is accompanied by a transient gradient shear banding [2]. A high-shear-rate band of aligned lamellae forms next to the moving inner wall of the shear cell while a low-shear-rate band of the initial MLV structure remains close to the outer stationary wall. The band of layers grows at the expense of the band of MLVs until the transformation is completed. This process scales with the applied strain. Wall slip is a characteristic of the MLV state, whereas aligned layers show no deviation from Newtonian flow. NMR diffusometry results confirm that an intermediate structure resembling undulated multilamellar cylinders occurs during the opposite transformation from aligned layers to MLVs [2,3].

[1] C. Oliviero, L. Coppola, R. Gianferri, I. Nicotera, and U. Olsson, Coll. Surf. A 228, 85 (2003).

[2] M. Medronho, U. Olsson, C. Schmidt, and P. Galvosas, Z. Phys. Chem. 226, 1293 (2012).

[3] M. Medronho, J. Brown, M. G. Miguel, C. Schmidt, U. Olsson, and P. Galvosas, Soft Matter 7, 4938 (2011).

Wednesday 13:30 Forum II

LC7

### 3-D reorientational motion in sheared nematic platelet dispersions

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Dispersions of platelets in the nematic phase are submitted to large amplitude oscillatory shear flow (LAOS) and probed by high temporal resolution small-angle X-ray scattering (SAXS) [1]. The rheo-SAXS set-up has the unique property that the X-ray beam is directed in the vertical direction. We exploit this feature by using cone-plate and couette geometries, so that the full 3-D reorientational motion can be followed. Moreover, we can scan the gap of the couette cell in order to check for heterogeneities in the structure. The response displays rich dynamic and structural behavior. Under small amplitude deformations we observe an elastic response, while structural symmetry is broken: a preferential direction of deformation is selected which induces off-plane orientation of the platelets. We associate the elastic responses with tilting of the director of the platelets towards the flow direction. This response is however limited to the region close to the wall. At large strain amplitudes there is a yielding transition between elastic and plastic deformation, accompanied by a 3-D flipping of the director. At intermediate strain amplitudes the director has a rich dynamic behavior, illustrating the complex motion of platelets in shear flow.

[1] M. P. Lettinga, P. Holmqvist, P. Ballesta, S. Rogers, D. Kleshchanok, and B. Struth. Nonlinear Behavior of Nematic Platelet Dispersions in Shear Flow. Phys. Rev. Lett. 109, 246001, (2012)

Wednesday 13:50 Forum II

LC8

**Stability of thin foams films stabilized with surfactants investigated by Lattice Boltzmann phase field method**

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We investigate the stability of thin films and Plateau borders of foam. Thin films are investigated using the configuration of the Sheludko cell. For foams the stability of thin films is of particular interest. To this end we use our phase field method for immiscible fluids with surfactants [1]. Previously, the model is applied to emulsion droplets stabilized by surfactants, and it is able to describe realistic Langmuir adsorption isotherm and Ward-Tordai adsorption kinetics for flowing emulsion droplets with soluble surfactants. It is a so-called phase field model, where the interface is represented by a continuous order parameter, with the interface represented by an approximation of the delta function, being the squared gradient of the order parameter. Here, we apply the model to the stability of foams. These simulations will be the first step towards a multiscale simulation framework for foams.

The phase field model is implemented using Lattice Boltzmann. For foams we have incorporated some improvements, like an alternative analytical representation of the delta-function, Frumkin adsorption isotherm, and differential solubility for the liquid and gas phase. Furthermore, we discuss how to extend the framework with ionic surfactants, via transforming the sharp-interface model of Diamant and Andelman, to a diffuse interface/phase field model [2]. Via the imposed boundary conditions we can extract fluid from the Sheludko cell – by which the two interfaces of the film will approach each other. Due to the flow and changing curvature of the film, the surfactants on the film will migrate, and generate Marangoni stresses retarding the flow. We will present the simulation results of this problem - and quantify the impact of the Marangoni stresses on the flow.

[1] R. G. M. van der Sman and S. van der Graaf. *Rheologica Acta* (2006).

[2] H. Diamant, G. Ariel, and D. Andelman. *Colloids and Surfaces A* (2001).

Wednesday 14:10 Forum II

LC9

**Time-dependent rheology and microstructure of fresh cement-based mortars**Nino Grizzuti<sup>1</sup>, Roberta Alfani<sup>2</sup>, Claudia Capone<sup>3</sup>, Gianluca Lezzi<sup>2</sup>, Giuseppe Manganeli<sup>2</sup>

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Cement-based mortars are innovative building materials for a variety of applications. In particular, they can be used to produce objects and structures of complex shape by using processing techniques such as vacuum molding and injection molding. Cement mortars are aqueous suspensions of cement and other solid particles. Small quantities of polymer additives are also included. They act as Rheology Modifiers (RM) and Super Fluidificants (SF), the latter reducing the particle agglomeration tendency during the processing stages. Additives are also crucial in determining the morphology and texture of the final, solid-state manufact. In view of the above, the study of the rheology and of the evolving microstructure of the mortar is particularly relevant. In this paper, we investigate the rheology of cement mortars of varying cement type and different additive composition during the early stages immediately following the mortar preparation. Experimental measurements are carried out on a Viskomat XL rotational rheometer, which is particularly suitable for measurements on large size, sedimenting suspensions. The experimental results clearly show that the flow has a crucial effect on the microstructure development related to particle agglomeration. In particular, it is shown that an increases in flow intensity (shear rate) delays the formation of the agglomerated structure. The time dependent phenomena are modelled in the framework of the Krieger-Dougherty theory for suspensions, by assuming that the volume fraction of agglomerates is described by a simple, shear rate-dependent kinetics. The predictions of the model show a satisfactory agreement with the experimental data and allow to build master curves for the microstructure evolution. It is also shown the this approach can be used to estimate the effect of SF concentration on the flow performance of the cement-based mortar formulations.

## Industrial Rheology and Processing - IR

Organizers: Dick J. Dijkstra and Bettina Wolf

Wednesday 14:30 Forum II

IR1

### High Melt Strength Polypropylene (HMS-PP) from the Borealis Daploy™ HMS process: Process optimisation, characterisation techniques and applications

Katja Klimke\*<sup>1</sup>, Hermann Braun<sup>1</sup>, Minna Aarnio<sup>2</sup>, Markus Gahleitner<sup>1</sup>

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Standard linear polypropylene (PP) has become the preferred material for many plastic conversion technologies. However, for conversion processes where stretching flows occur, both a higher melt strength as well as a higher melt extensibility are required. By increasing either the molecular weight or the molecular weight distribution of linear PP, a higher melt strength can be achieved, however, the melt extensibility cannot be improved by this approach. An increase of both parameters at the same time is usually only shown by PP with a long chain branched molecular structure, meaning that the branch length is above the critical molecular weight  $M_c$ . In order to generate such long chain branched PP (LCB-PP or HMS-PP), the patented Borealis Daploy™ HMS process, a reactive modification process, was developed [1]. This innovative technology combines grafting and recombination reactions in the intermediate between the solid state and the melt phase of PP via the use of special equipment. Continuous optimisation of the processing settings and the starting materials has led to excellent control of the process and its products. The qualitative and quantitative description of the molecular topology of the Daploy™ HMS PP materials was further improved by the use of specific non-linear rheological parameters from Large Amplitude Oscillatory Shear (LAOS) and uniaxial extensional flow [2]. This extensive, continuous research and development program has led to the development of a strong Daploy™ HMS PP portfolio. It contains specialised grades with a wide range of flowability (MFR) providing excellent properties for foaming, coating and blown film conversion technologies.

[1] M. Rätzsch et al., Prog. Polym. Sci. 27 (2002), 1195-1282

[2] K. Klimke et al., EPF European Polymer Congress (2011), Conference Proceedings

Wednesday 15:20 Forum II

IR2

### Elongational Flow Properties Of Long-Chain Branched Poly(Ethylene Terephthalate)

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It is well-known that long-chain branches (LCB) significantly influence the rheological properties of polymer melts in shear and elongation. In particular, the LCB structure leads to the so-called strain hardening effect in elongational flow. This yields an improved homogeneity of thickness e.g. for blown films of low-density polyethylene or thermoformed polypropylene beakers.<sup>1</sup> While there exist several investigations for the isothermal elongational behavior of polyolefins, practically no information can be found dealing with poly(ethylene terephthalate) (PET) melts. The main reasons for that are the inherently low melt viscosity and the linear molecule topography of PET, which hamper the measurements of the elongational properties. One successful way to increase the melt viscosity is reactive processing using low molar mass chemicals.<sup>2</sup>

In this contribution a commercial PET grade is reactively processed with different concentrations of a low molar mass modifier in order to create LCB structures and to enhance the melt viscosity. For the first time isothermal elongational properties of a branched PET melt are measured, which demonstrate a pronounced strain hardening behavior. The flow properties are discussed with respect to the molecular structure and the level of branching, which were analyzed by size exclusion chromatography with triple detection.

[1] Münstedt, H., Kurzbeck, S., Stange, Macromol. Symp. 2006, 245, 181.

[2] Incarnato, L., Scarfato, P., Di Maio, L., Acierno, D., Polymer, 2000, 41, 6825.

Wednesday 15:40 Forum II

IR3

**Extensional behavior of Poly (lactic acid)**Maria Josefina Carbone\*<sup>1</sup>, Bart Goderis<sup>2</sup>, Peter Van Puyvelde<sup>1</sup>

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During many decades, the behavior of fossil-based polymers has been intensively studied. However, in recent years, bio-based polymers have gained (commercial) interest. One of the currently most available bio-polymer is poly(lactic acid). Despite its valuable and attractive properties, there are still some key aspects that need to be optimized in order to provide an industrially viable alternative to fossil-based polymers. PLA's relatively low melt strength inhibits its widespread use, since this is crucial for current industrial processing techniques such as fiber spinning, film blowing and extrusion. This technical issue is widely solved by adding chemical chain extenders, being PLA not the exception. However, the additive concentration is a critical parameter to obtain the desired effect. Different research groups studied the change of PLA extensional properties when adding commercial chain extenders by using different techniques. Dean et al. (2012) performed rheotens measurements on PLA while Milhai (2010), Liu (2010) and Takamura (2012) chose a rotational rheometer (ARES) combined with the extensional viscosity fixture (EVF). Unfortunately, these techniques only can be used under certain circumstances since when trying to measure low viscosity PLA, they meet their limitations. In this case, rheotens measurements resulted on unreproducible data as the measured forces and the detection limit of the commercial unit were the same order of magnitude, being the outcome susceptible to the test conditions. Furthermore, EVF measurements were almost impracticable due to sagging. Besides, the extensional rates available with this technique are restricted up to  $10\text{s}^{-1}$ . This work presents a method to rank combinations of low molecular weight PLA and commercial melt chain extenders to detect strain hardening and gelling situations by using capillary rheometry data, in cases when traditional techniques cannot be used.

Wednesday 16:00 Forum II

IR4

**Extensional flow properties of lubricating grease and the effect of tackiness additives**Oliver Steinhof\*<sup>1</sup>, Arne Kull<sup>2</sup>

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A new method was developed to assess the tackiness of lubricating greases in an objective manner by means of extensional rheometry. The method is used for quality control as well as for product and process research. In the application, tackiness is considered to be an important aspect of the quality of lubricating grease, as it is believed to improve surface adhesion and water resistance. Experimentally, grease is placed between two sample plates, which are moved apart at defined speed using a CaBER1 instrument. A characteristic break point and strand diameter are reported, resulting from systematic variation of stretching speed. Greases of varying composition were analyzed to gauge the limits of the method. The influence of the treat rate of the tackiness additives as well the influence of base fluid viscosity were clearly identified and quantified. The method is described and discussed in detail. Results are shown to demonstrate the capability of the approach to discriminate grease formulations containing effective and ineffective tackiness additives. These results are also compared with data generated by rotational rheometry.

Wednesday 16:20 Forum II

IR5

**Influence of polymer structure on the rheological behaviour and the shear stress stability of lubricants**Damien Chaveroux<sup>1</sup>, Raphaële Iovine<sup>2</sup>, Jean-François Tassin\*<sup>1</sup>

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In order to reduce the decrease of lubricant viscosity with temperature, Viscosity Index Improver (VII) additives such as ethylene-propylene copolymers (OCP) or hydrogenated polyisoprene-styrene (PISH), can be added in a concentration range around the overlap concentration in lubricants formulation. The OCP series are basically linear chains whereas the PISH are either linear or star block copolymers. The objective of this study is to characterize and

correlate the efficiency of a VII with its chemical structure, its molecular weight and its concentration. A series of OCP and PISH were thoroughly characterized by NMR, Size Exclusion Chromatography and a dedicated protocol was used to determine the intrinsic viscosity in a given base oil over a large temperature range ( $-10 \leq T \leq 135$  °C). Furthermore the possible degradation of the polymers during engine running was also investigated by using a shear stress stability test.

For the OCP series, it was shown, that whatever the composition, the intrinsic viscosity does not depend strongly on temperature, except at low temperatures where an intra-chain crystallization occurs for a sufficient ethylene content. The degradation of the polymer chains depends on their molecular weight and their ethylene or propylene sequences content, with a direct relationship with the hydrodynamic volume. For the PISH the flexibility offered by changing either the structure (linear or star) or the styrene content allowed us to change the rheological behavior as well as the degradation under shear. For instance, star shaped polymers with a sufficient styrene content show an increase of the intrinsic viscosity above a critical temperature as well as a good stability under high shear. Finally, if linear chains containing the same number of main chain carbon atoms are compared between OCP and PISH series, it can be deduced that a slight aggregation or micellization processes are favorable to increase stability of the polymer chains under high shear.

### Wednesday 16:40 Forum II

IR6

#### **Bubble growth in a strain hardening polymeric fluid**

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This is a study of the growth of a bubble within a polymeric melt during a rubber foaming process. As the foaming proceeds, the extensional viscosity of the melt increases due to strain hardening. Further, in the case of a vulcanisation reaction taking place, the evolving branching of the chains accelerates strain hardening. The changes in the viscoelasticity of the polymer melt are estimated by utilising the theory of Tsenoglou et al. (2006)[1] that relates the degree of branching with the damping function in the flow. The goal of the project is to generate knowledge that can be applied in the manufacturing of rubber foam used for insulation.

Bubble growth is initiated by the explosive decomposition of a grain of the foaming agent. The vulcanisation reaction results in evolving changes in the relaxation spectrum of the polymer and the degree of branching. Both of these affect the elongational viscosity of the melt and, especially, its strain hardening behaviour. The changing viscoelasticity of the melt influences the growth rate of the bubbles, as well as their final size. When the maximum packing capacity of the spherical bubbles is approached, their shape has to change to accommodate further growth. At the end of the process, when crosslinking is complete, the growth of the bubbles stops and the final foam has been formed. Thus, the density of the produced foam depends on the foaming agent, the rate of the vulcanisation reaction, the foaming agent grain size, the initial relaxation spectrum of the polymer and the evolving form of the damping function of the melt.

Acknowledgement: This research has been co-financed by the European Union (ESF) and Greek national funds (OPELL-NSRF) program THALES, COVISO.

[1] C.J. Tsenoglou, E. Voyiatzis and A.D. Gotsis, J. Non Newt. Fl., 138:33-43 (2006)

# Wednesday Evening

## Poster Session - PO

Wednesday 17:00 Weinbrenner

The Poster abstracts can be found in the end of this book, see page 131.

## Public Committee Meeting of the European Society of Rheology

Wednesday 18:00 Clubraum

Public meeting of the committee of the European Society of Rheology. All participants of the AERC 2014 are allowed to participate as they have a free individual membership for the ESR for one year.

# Thursday Morning

## Plenary Lecture 2

Thursday 8:30 Hans-Thoma

PL2

### Rheology in Oro-Gastro-Intestinal Structure Engineering

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An important category of flows with rheologically complex fluids acts in the human body and concerns the intake, transport and digestion of food. The area of oro-gastro-intestinal processing investigated deals with the characterization of flows in the human mouth, esophagus, stomach and small intestine and the related rheological behaviour of food matter at its various degree of digestive disintegration by acting mechanical stresses and biochemical reaction conditions. Rheology and related oro-gastro-intestinal (OGI) flow characteristics determine the transport phenomena of functional food components to specific receptors. This is equally relevant e.g. for flavour perception in the mouth and micronutrient bioavailability in the human small intestine. Within the work presented we focus on emulsion/emulsion droplets as macroscopic and their interfaces as mesoscopic or macromolecular structural food entities and follow their track through the human digestive tract from the mouth to the intestine. Consequently it's the non-Newtonian rheology of emulsions in human OGI-flows being particularly addressed. In order to characterize local velocity fields in OGI-flows, least invasive methods like Magnetic Resonance Imaging (MRI), Ultrasound-Doppler Velocimetry (UDV) or High Resolution Computer Tomography ( $\mu$ CT) are preferred, which can not only be applied to our in vitro model geometries, but as well for comparative in vivo flow investigations. Rheological measurements were carried out using rheometers with bulk fluid and interfacial measuring setups applying relevant food emulsion systems. Exemplary experimental and numerical simulation results will be demonstrated for mixed shear/elongation flows of non-Newtonian fluid (emulsion) systems in mouth, esophagus, stomach and small intestine [1-2].

[1] Nahar S., Jeelani S., Windhab E. J. (2013), Chem. Eng. Com., Vol. 200, 820-835

[2] Rühls P. A., Affolter C., Windhab E. J., Fischer P. (2013) J. Rheol., Vol. 57, 1003.

## Polymer Melts, Blends, Copolymers, and Nanocomposites - PM

Organizers: Ulrich Handge, Manfred Wagner, Dimitris Vlassopoulos, and Alexei Likhtman

Thursday 9:40 Hans-Thoma

PM16

### Resolution of the local segmental mode in amorphous polymers

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The mechanisms responsible of the softening "glass to rubber" dispersion in amorphous polymers are the segmental, sub-Rouse, Rouse and terminal relaxation modes. These four mechanisms are additive and their contributions to the overall creep compliance can be described with a stretched exponential function. For polystyrene and polycarbonate the softening dispersion is too narrow and generally it is not possible to resolve the four different mechanisms simply looking at the retardation spectra. Dissolution of these polymers into a solvent diminishes the intermolecular coupling, makes the retardation spectra wider and helps for the identification of the contribution of each single mode to the overall retardation spectra.

Here the retardation spectra experimentally obtained for different polystyrene solutions have been fitted using stretched exponentials and assuming that the segmental relaxation follows the Andrade creep ( $1-n\alpha = 1/3$ ) and that

the Rouse mode is described by a simple exponential function ( $nR = 0$ ), in addition to the relaxation mechanisms addictiveness.

The main finding is that, differently to what is generally assumed in the literature, the segmental relaxation terminates slight before the shoulder of the overall retardation spectra. This happens because also the sub-Rouse and the Rouse modes contribution to the short time tail of the retardation spectrum are not negligible with respect to the segmental one. We, indeed, observe that in the time window, where the segmental retardation spectrum begins to decrease, even the small fraction of the Sub Rouse and Rouse relaxation mode cannot be neglected when compared to the segmental retardation strength. Finally, the comparison of the shear retardation spectra with the bulk retardation spectra suggests that the latter could be affected by either the segmental and chain modes.

Thursday 10:00 Hans-Thoma

PM17

### **Simultaneous measurements of rheology and crystallization of an isotactic polypropylene**

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In common polymer processing operations such as injection molding, film blowing, and fiber spinning, semicrystalline polymers are largely adopted. For this class of materials, the mechanical and rheological properties are strongly affected by the morphology. Therefore the study of the relationship between rheology and morphology is of high scientific and industrial interest.

In this work, by using a new generation rheometer, the Haake Mars II, rheological experiments during crystallization of an isotactic polypropylene are conducted. By adopting a parallel plates geometry, in which one of the plates is transparent, simultaneous measurements of rheology and observations of the morphology are performed. In this way, a better understanding of the relationship between rheology and morphology can be achieved compared to a test that match parallel measurements of rheology and evolution of morphology. During the isothermal crystallization of a polypropylene at 140 °C oscillatory tests are carried out to measure the rheological behaviour of the material. Images of the sample showing the evolution of the morphology along the entire thickness are simultaneously acquired. By analysing the images, the evolution of the density of crystal nuclei and the growth rate of the crystal structures (spherulites) are observed. Furthermore also the crystallinity evolution of the material during each rheological test is evaluated. The measured complex viscosity and the corresponding morphological parameters are correlated and discussed.

Thursday 10:20 Hans-Thoma

PM18

### **Nodular morphology of melt solidified iPP suggests crucial role of melt before solidification**

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iPP has been solidified under quiescent conditions from the melt by a Continuous Cooling Transformation, CCT, approach in a wide range of cooling rates. The morphology has been studied by true non contact AFM fictitiously enhancing the merit factor of the cantilever. At cooling rates of 600K/s the nodular morphology is observed consisting of isometric nodules so far related to the onset of the mesomorphic phase. Also at cooling rates of 10 and 1K/s, where the alfa-monoclinic phase develops, nodules are clearly observed eventually aligned recalling the supramolecular architecture typical of lamellae. After applying FFT to the scan on a sample solidified at cooling rates below 0.1K/s, fully monoclinic as the narrow WAXD peaks confirm and with an apparent cross hatched lamellar morphology, nodules are observed albeit contiguous and aligned to form lamellae.

Although generalizations might appear precipitous, modeling literature appears to drive further away from the traditional approach. More modestly, always from CCT experiments, the observation of speed up of crystallization at high cooling rates by oligomeric plasticizers in polyesters suggests local mobility to have a critical role on crystallization kinetics. A comparison of the knots distance in melts to the crystalline stem length confirms that the melt is significantly constrained as crystallinity develops and growth of crystalline domains driven by a marginal surface energy gain to give rise to lamellae is unreasonable. The secondary nucleation mechanism can vice versa dominate if massive segregation takes place, i.e. if time is long enough and/or molecular weight is small. Unfortunately, these are typical conditions adopted to study polymer crystallization kinetics.

Such view were correct had been a pity so much effort was made on studying solidification conditions so departed from those met in processing. This challenging subject certainly deserves also other disciplines to contribute to

clarify this debate.

Thursday 11:10 Hans-Thoma

PM19

### Dielectric Relaxation of Entangled Monodisperse Polyisoprene: Contribution of Constraint Release

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Cis-polyisoprene (PI) has the type-A dipole parallel along the chain backbone so that its slow dielectric relaxation detects the orientational memory (two-time correlation) of the end-to-end vector (for linear PI) and/or end-to-branching point vector (for star PI). In contrast, for both linear and star PI, slow viscoelastic relaxation detects decay of isochronal orientational anisotropy of the chain segments. Thus, comparison of dielectric and viscoelastic data can reveal some details of entanglement dynamics. Indeed, the comparison had demonstrated success of the molecular picture of constraint release (CR)-activated full dynamic tube dilation (DTD) for monodisperse linear PI, and success of partial-DTD picture for star PI [cf. Watanabe, *Polymer J.* 2009, 41, 929]. However, these pictures just specify a relationship(s) between the dielectric and viscoelastic relaxation functions, not the time scale of the terminal relaxation. For this problem, we have conducted dielectric and viscoelastic tests for blends of a dilute probe PI (either linear or star) in a matrix of much longer linear PI to detect the probe dynamics: Blending quenches the CR/DTD contribution to the probe dynamics in monodisperse bulk. The relaxation of linear probe was found to be moderately retarded on blending. However, this retardation became less significant with increasing probe molecular weight and was considerably weaker than that expected for reptation along fully dilated tube in monodisperse bulk. This result suggests that the linear probe in monodisperse bulk reptates along a partially dilated tube that wriggles in the fully dilated tube. In contrast, for star probe, the retardation on blending was found to be exponentially enhanced with increasing probe arm molecular weight. The magnitude of this retardation appeared to be consistent with that expected for the star arm retraction along the partially dilated tube assumed for monodisperse bulk.

Thursday 11:30 Hans-Thoma

PM20

### Rheo-Dielectric Responses of Entangled cis-Polyisoprene under Uniform Steady Shear and LAOS

Yumi Matsumiya<sup>1</sup>, Takashi Uneyama<sup>2</sup>, Kazushi Horio<sup>1</sup>, Yuichi Masubuchi<sup>1</sup>, Hiroshi Watanabe\*<sup>1</sup>

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Cis-polyisoprene (PI) has type-A dipoles parallel along the chain backbone so that its large-scale (global) motion over the end-to-end distance activates slow dielectric relaxation. This relaxation was examined for entangled solutions of linear and star-branched PI under steady shear and large-amplitude oscillatory strain (LAOS). For linear PI, the dielectric relaxation (detecting the end-to-end fluctuation in the shear gradient direction) was hardly affected by the steady shear in a range of Weissenberg number  $Wi = \kappa\tau G < 7$  (with  $\kappa$  and  $\tau G$  being the shear rate and the terminal relaxation time in the linear regime) whereas the viscosity  $\eta$  exhibited considerable thinning at those  $\kappa$ . In contrast, for star PI, the dielectric relaxation was moderately accelerated by the steady shear in a similar range of  $Wi$  but this acceleration was considerably less significant compared to the thinning of  $\eta$ . These rheo-dielectric features, noted also in a previous study, emerged under uniform shear without shear-banding and/or secondary flow, as confirmed in this study from particle tracking velocimetry. Thus, the rheo-dielectric difference between the linear and star PI suggests an essential difference of the entanglement dynamics of linear and star chains, which possibly reflects, at least partly, the constraint release effect at equilibrium being saturated for linear chains but not for star chains. The rheo-dielectric behavior of the linear and star PI chains was also examined under uniform LAOS field. The relaxational current  $I_{relax}$  under rectangular electric field exhibited oscillatory decay with the main oscillation period being close to  $\pi/\Omega$  ( $\Omega$  = LAOS angular frequency). This behavior lent support to the previous analysis based on the Green-Kubo theorem. The decay of the non-oscillating part of  $I_{relax}$  appeared to be rather insensitive to LAOS, which was in harmony with the behavior observed under steady shear.

Thursday 11:50 Hans-Thoma

PM21

**Highlighting the role of ionic liquids in the control of the morphology of immiscible polymer blends by interfacial tension assessment**

Mohamed Yousfi, Maxime Lebeau, Marie-France Lacrampe, Patricia Krawczak, Jérémie Soulestin\*

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During the last decade, number of studies has demonstrated the potential of organo-modified nanoparticles as compatibilizing agent of immiscible polymer blends. However, if the effect is known, its origin remains partially understood only and the control of this compatibilization way remains imperfect. This study aims at elucidating separately the effects of the ionic liquid (ILs, surfactant) and of the nanofiller in the stabilization of morphology of polymer blends. PP/PA-6 (80/20 w/w) systems were chosen as model of immiscible polymer blend and were compounded adding solely ionic liquids (similar to those used to modify the various organoclays).

Tetraalkylammonium salts containing the same chloride-based anion but differing by the polarity of their cations were introduced at various concentrations and the polymer blends were processed by twin-screw extrusion using a laboratory scale extruder. Then, a microcompounder equipped with a rheological slit capillary die was used to determine the relative melt viscosity from the pressure drop in the recirculation channel. The Rabinowitsch correction was implemented to calculate the non-Newtonian viscosity of each formulation. Scanning electron microscopy allowed investigating the influence of ILs on the different morphologies of the binary polymer blends. The Serpe equation was also used for this purpose to estimate the interfacial tension, which takes into account the effect of the ILs on the variation of the viscosity ratio in each formulation. The changes in the morphologies and polydispersity evolution of dispersed phase of the blends as a function of the surfactant amount show that this compatibilizing effect should be attributed mainly to the reduction of interfacial tension during the melt processing, the viscosity ratio reduction being less significant. In addition, the ionic liquid-compatibilized blends exhibit great improvement in the thermal properties compared to the uncompatibilized blends.

Thursday 12:10 Hans-Thoma

PM22

**Dynamics of linear polymer chains in a binary melt**Michael Langeloth<sup>\*1</sup>, Yuichi Masubuchi<sup>2</sup>, Michael C. Böhm<sup>1</sup>, Florian Müller-Plathe<sup>1</sup>

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Molecular Dynamic (MD) simulations of entangled polymer melts have been a challenge ever since. The extremely large timescales make it impossible to study chain lengths with much more than 10 entanglements when using coarse grained models that prevent chain crossing by excluded volume potentials.

Our newly developed Slip-Spring approach for dissipative particle dynamics (DPD)[1] mimics uncrossability constraints of polymer chains by temporary cross-links. According to our estimate, chains in the present DPD approach require 7 times fewer beads and the simulation is 500 times faster than in an equivalent molecular dynamics calculation. With the development of this model, simulations of strongly entangled polymer chains have become feasible and facilitate the study of more complicated systems. In our present study we discuss the influence of short chains in a binary melt on the dynamics of the longer chains and compare our results with experiments.

So far, binary melts have not been thoroughly addressed in computer simulations. However they are of particular interest not only because polydispersity is the rule rather than the exception in polymer processing but mostly because of to the underlying mechanisms that involve constraint release processes and lead to a interesting dynamic different from the monodisperse melt.

[1] J. Chem. Phys. 138, 104907 (2013)

## Non-Newtonian Fluid Mechanics and Flow Simulation - FM

Organizers: Pier L. Maffettone and Evan Mitsoulis

Thursday 9:40 Johann-Peter-Hebel

FM1

### Effect of RBC migration phenomena on the hemodynamics in stenotic microvessels under pulsating flow conditions

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The current study deals with the numerical simulation of the hemodynamics in stenotic microvessels under pulsating flow conditions. The flow of blood in microvessels differs significantly from that in large arteries and veins, because the Red Blood Cells (RBCs) are comparable in size with the radius of the microvessels and consequently local effects such as the interaction between cells, the development of aggregates, migration phenomena and the deformation of their membrane are more pronounced. In terms of complexity of the flow, viscoelasticity along with stress-gradient induced migration effect have a more dominant role which outmatches the viscous, inertial and transient effects. Recently, a non-homogeneous viscoelastic model has been proposed [1] (see also [2,3]), which can accurately predict the Fahraeus effects [4] and account for the contribution of the RBC to Cauchy stress tensor via their fragmentation and aggregation rates into rouleaux. We developed a numerical algorithm for the time-integration of the set of differential equations that arise from the coupling of momentum, mass, and population balances for RBCs & aggregates with the constitutive laws for both species. The algorithm is based on the mixed Finite Element method with second order backward finite differences for approaching the time-derivatives and the EVSS/SUPG technique for a stable discretization of the constitutive equations. The simulation shows that a cell-depleted layer develops along the vessel wall with an almost constant thickness. Along this layer, the shear stresses are almost Newtonian because of the plasma, but the normal stresses that are exerted on the wall are high due to the contribution of the individual RBCs & rouleaux.

[1] Moyers-Gonzalez M et al., J. Fluid Mech., 617:327-354, 2008.

[2] Owens R., J. Non-Newt. Fluid Mech., 140: 57-70, 2006.

[3] Iolov et al., Int. J. Numer. Meth Biomed Engrg, 27:1321-1349, 2011.

[4] Fahraeus R., Physiol. Rev., 9:241-274, 1929.

Thursday 10:00 Johann-Peter-Hebel

FM2

### 3D multiscale FENE dumbbell simulations on massively parallel multi-GPU clusters

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Numerical simulations of viscoelastic fluids often suffer from stability issues after reaching a critical Weissenberg number (cf. high Weissenberg number problem). One attempt to overcome this problem is multiscale modeling. This approach directly solves the kinetic equations of the polymeric system to compute the viscoelastic stress tensor in the momentum equations. We apply the multiscale FENE model to a 3D square-square contraction flow problem. For this purpose, we couple the stochastic Brownian configuration field method (BCF) with our fully parallelized three-dimensional Navier-Stokes solver NaSt3DGPF. The robustness of the BCF method enables the numerical simulation of high Weissenberg number flows [1]. In this talk, we compare the results of our simulations with that of experimental measurements from literature and obtain a very good agreement. In particular, we are able to reproduce effects such as a strong vortex enhancement, streamline divergence and a large extra pressure drop at the contraction for highly elastic flows. Due to their computational complexity, our simulations require massively parallel computations. We have accelerated our implementation by using Nvidia's CUDA architecture that enables computations on graphic processing units (GPUs). Using our GPU cluster, we achieve excellent speed-up results compared to classical CPU based computing.

[1] C. Mangoubi, M. A. Hulsen, R. Kupferman, J. Non-Newt. Fluid Mech., 157 (2009), 188-196

Thursday 10:20 Johann-Peter-Hebel

FM3

**PGD-based parametric solutions of double-scale Fokker-Planck equations: application to suspensions involving aggregates of rods**Francisco Chinesta\*<sup>1</sup>, Emmanuelle Abisset-Chavanne<sup>1</sup>, Amine Ammar<sup>2</sup>, Marta Perez<sup>1</sup>, Roland Keunings<sup>3</sup>

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When suspensions composed of rods become concentrated enough rods aggregate to create clusters. These clusters can interact when the clusters concentration is large enough, or not when it remains small enough. The kinetic theory modeling of such systems requires a double scale description; the fine scale related to the rods orientation distribution existing in each cluster, and the coarse one related to clusters distribution itself. In the coarse scale the distribution depends on the second and fourth order moments of the orientation distribution of rods composing the clusters. The resulting Fokker-Planck equation involves the physical coordinates, the time and a number of conformational coordinates. Moreover it involves some material parameters related to the configuration relaxation time and the cluster's softness, as well as other parameters related to the enforced flow: shear and elongation rates. In order to analyze the influence of each material or flow parameter on the distribution function the classical route consists of performing a sampling of the parametric space and then solving the resulting multidimensional Fokker-Planck equation for each choice of those parameters. Obviously the computational complexity becomes rapidly prohibitive and then only very (too) coarse samplings of the parametric space remain affordable. PGD was proposed by the authors some years ago for addressing efficiently the solution of multidimensional Fokker-Planck equations encountered in computational rheology. Then, it was extended for addressing the solution of standard models in which parameters were considered as model extra-coordinates resulting in a parametric multidimensional equations. In this work we combine both proposals for addressing the efficient solution of parametric Fokker-Planck equations, making special attention to the advective stabilizations issues.

Thursday 11:10 Johann-Peter-Hebel

FM4

**Influence of channel aspect ratio on the onset of elastic instabilities in three-dimensional cross-slots**Filipe A. Cruz\*<sup>1</sup>, Robert J. Poole<sup>2</sup>, Alexandre Afonso<sup>1</sup>, Fernando T. Pinho<sup>3</sup>, Paulo J. Oliveira<sup>4</sup>, Manuel A. Alves<sup>1</sup>

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In this work, we investigate by means of numerical simulations the existence of purely-elastic flow instabilities in three-dimensional cross-slot geometries. Specifically, we probe the effect of aspect ratio – defined as the ratio between the height and width of the rectangular cross-section of the channels – for both the upper-convected Maxwell and the Phan-Thien-Tanner constitutive models.

For both models, we observe the occurrence of a supercritical bifurcation, from a steady-state symmetric flow to an asymmetric but still steady pattern, above critical values of the Deborah number ( $De$ ) and also of the aspect ratio. Further increase in  $De$  triggers a transition to time-dependent flow, a situation akin to that previously reported for two-dimensional cross-slot devices [Poole et al., Phys Rev Lett 99(16):164503, 2007].

For sufficiently low aspect ratios (shallow channels), no intermediate steady asymmetric states are observed and a direct transition to time-dependent flow occurs. Interestingly, this transition occurs at progressively lower  $De$  values when the aspect ratio of the cross-slot channel is decreased. Stability maps of aspect ratio vs.  $De$  are presented, together with a discussion on possible mechanisms for the onset of elastic instabilities.

Thursday 11:30 Johann-Peter-Hebel

FM5

**Non-linear dynamics of an ellipsoid in a sheared viscoelastic fluid**Gaetano D'Avino\*<sup>1</sup>, Francesco Greco<sup>2</sup>, Martien A. Hulsen<sup>3</sup>, Pier Luca Maffettone<sup>1</sup>

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Non-spherical particles in non-Newtonian liquids are encountered in several industrial and biological applications such as fiber-reinforced polymer processing, spermatozoa swimming in viscoelastic cervical mucus, etc. Experiments have shown that fluid viscoelasticity strongly alters the ellipsoid dynamics as compared to a Newtonian liquid, even in the simple shear flow case. The experimental evidences are only partially predicted by the available theories that are limited to infinitely elongated particles and vanishing Deborah numbers.

In this work, the dynamics of an ellipsoidal particle in a sheared, unconfined viscoelastic fluid is addressed by numerical simulations. The Giesekus constitutive equation is used to model the suspending liquid. A wide range of Deborah numbers and aspect ratios is investigated. The simulation results reveal a complex dynamics with different regimes as the Deborah number is increased. For low Deborah numbers a drift through the Jeffery's orbits is found with the ellipsoid major axis following a spiraling motion towards the vorticity. As the Deborah number is increased, the equilibrium orientation gradually moves from the vorticity to the flow direction, and, beyond a critical Deborah number, such a solution coexists with alignment near the flow direction. The latter becomes the only stable solution for high Deborah number values. The present results favorably compare with experimental data available in the literature.

Thursday 11:50 Johann-Peter-Hebel

FM6

### **Simulations of the behavior of a spherical elastic particle in Newtonian and viscoelastic fluids under confined shear flow**

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In systems such as filled polymers or microgel suspensions, elastic particles are suspended in a fluid; moreover, elastic particles can be models for more complicated systems, e.g. cells.

The deformation and cross-streamline migration of an initially spherical neo-Hookean elastic particle suspended in confined shear flow of Newtonian and Giesekus viscoelastic fluids is studied through 3D arbitrary Lagrangian Eulerian finite element method numerical simulations. If the particle is initially closer to a wall of the channel than to the other, in addition to deformation, it migrates transversally to the flow direction towards the center plane of the channel. The influence of the geometrical and physical parameters on the phenomenon is studied. In a Giesekus viscoelastic fluid, transversal migration is again detected, the direction being influenced by the competition between the effects of the particle elastic deformation and the fluid elasticity.

Thursday 12:10 Johann-Peter-Hebel

FM7

### **On the abrupt increase of the rise velocity of a deformable bubble in viscoelastic solutions**

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A long-standing problem that is not well-understood is related to the motion of a deformable bubble in polymeric liquids. In particular, the steady rise velocity of the bubble exhibits an abrupt increase, when the bubble radius exceeds a critical value. In all reported experiments [1-3] the bubble shape forms a cusp in its back side and in some experiments [4, 5] the bubble shape loses its axial symmetry and forms a wedge in its back side. Some authors have related the velocity jump with the wedge formation. We have undertaken a computational study to explore the mechanisms causing this sudden velocity increase. To this end, we have used the ePTT model and determined its rheological parameters by fitting it to experiments [3]. Then we developed a finite element code (using elliptic grid generation to account for large bubble deformations and the SUPG and EVSS methods [6] to get the weak form of the constitutive equations) and calculated the bubble rise and deformation as its radius increases, which simultaneously affects all important parameters: Bond, Archimedes and Deborah numbers involving the material density, viscosity, elasticity and surface tension and the gravitational acceleration and the radius of a spherical bubble of the same volume. Our predictions reproduce very accurately the experimental results up to the velocity jump [3]. We followed the jump discontinuity region introducing arc-length continuation methods in our algorithms. Our results so far predict that changing the parameter affecting elongational thinning of the constitutive model leads to two different velocity fields that could explain the discontinuity in the rise velocity.

[1] Astarita & Apuzzo, AIChE J. 11 (1965) 815-820

[2] Herrera-Velarde, Zenit, Chehata, Mena, JNNFM 111 (2003) 199-209

- [3] Pilz & Brenn, JNNFM 145 (2007) 124-138  
 [4] Hassager, Nature 279 (1979) 402-403  
 [5] Liu, Liao, Joseph, JFM, 304 (1995) 321-342  
 [6] Brown, Szady, Northey and Armstrong, Theoretical Comp. Fluid Dynamics 5, (1993) 77-106.

## Colloids and Suspensions - CS

Organizers: Matthias Ballauff and Moshe Gottlieb

Thursday 9:40 Alfred-Mombert

CS16

### Alignment of spheres in confined geometries

Rossana Pasquino<sup>\*1</sup>, Roberta Aprea<sup>1</sup>, Gaetano D'Avino<sup>1</sup>, Pier Luca Maffettone<sup>1</sup>, Francesco Greco<sup>2</sup>, Nino Grizzuti<sup>1</sup>  
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Alignment of particles is known to occur in viscoelastic media due to the specific rheological properties of the suspending medium [1]. In particular, shear thinning and elasticity are necessary for particle string formation in the flow direction [2]. Alignment of spheres has been studied as function of shear rate, particles diameter, suspending fluid properties [3,4]. Alignment and migration were shown to happen on the same time scale. As such, the two phenomena are competitive and alignment in the bulk of the system appears only in specific cases [5,6]. This work is aimed to study and quantify alignment of spheres in a wormlike micellar solutions (100mM CPyCl, 60mM NaSal, 100mM NaCl). Dilute suspensions of polystyrene spheres with different diameters (Fluka: 15, 100, 200 micrometers) have been prepared. Alignment kinetics has been studied in a Linkam flow cell by varying the ratio between the gap size and the particle diameter, from very low (confined) to high values (not confined). The competition between migration and alignment has been carefully analyzed. We found that the alignment factor kinetics follows an exponential rise to max dependence on time. The long-time plateau value is significantly dependent on the confinement ratio. More specifically, confined geometries hinder string formation and no alignment is observed below a critical confinement ratio.

2D simulations with a standard viscoelastic constitutive equation (Giesekus fluid) have been performed. A lower limit of the confinement ratio for particle alignment is found, thus qualitatively reproducing the same experimental results.

[1] M. Grzelczak et al ACS Nano 4 (2010) 3591-3605

[2] J. Michele et al Rheol. Acta 16 (1977) 317-321

[3] R. Scirocco et al J. Non-Newtonian Fluid Mech. 117 (2004) 183-192

[4] D. Won et al J. Non-Newtonian Fluid Mech. 117 (2004) 141-146

[5] R. Pasquino et al Rheol. Acta 49 (2010) 993-1001

[6] R. Pasquino et al. J. Colloid Interface Sci. 394 (2013) 49-54

Thursday 10:00 Alfred-Mombert

CS17

### Effect of attractive nanoparticles on the gelation of bimodal suspension

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Some coating fluids such as cathode slurries used in manufacturing Li-ion batteries and Ni pastes in multi-layer ceramic capacitors include different types of particles to improve the performance of the product. In these liquids, the size of the particles is very different; one is micron and the other nano-meter scale, for example. It does not mean broad distribution, but distinctively two different sizes. Because of distinctively different size of the particles, these bi-modal dispersions show more complex flow behavior compared to colloids of a single size. There have been some studies to understand their kinetics, mechanics, and microstructure. However, most studies were limited to ideal particle surfaces such as hard spheres and opposite charged spheres. In this study, we set the surface of the particles to mimic the industrial slurries. The submicron PS latex particles were electrostatically stabilized and nanosized alumina-coated silica particles were not stabilized. With this model slurry, we investigated the effect of attractive nano-particles on the microstructure formation and flow behavior in the bi-modal suspensions. The

nano-particles tend to aggregate and form a network structure due to their high surface energy, which affects the stability of the dispersions with just a small amount even though large portions of big particles are well dispersed. As a result, stable particles form a bimodal gel by mixing with attractive nanosized particles. Scaling analysis of viscoelastic properties was performed to investigate the nature of structure formation between two different sized particles. We will show a unique scaling behavior of bimodal gels by comparing with common colloidal gels. Visualization of microstructure using microscopy and scattering will be also supplemented to understand the different scaling behavior of bimodal gelation.

Thursday 10:20 Alfred-Mombert

CS18

### Capillary Suspensions- A New Formulation Route for Printable Electronics

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In existing formulations for printed electronics, stabilizers are used to prevent settling and thickeners are used to control the flow properties. These additives can remain in the heat treated product and decline the electronic properties. To demonstrate a new formulation route, a smart solid-solvent combination, a so-called capillary suspension, is employed to improve processing and product properties. Adding small amounts of a second immiscible fluid changes the rheological properties of a suspension dramatically due to the formation of a sample-spanning and stable network between particles and secondary fluid and leads to a controlled, remarkable increase in viscosity and yield stress. In such a so-called capillary suspension settlement of particles is avoided and flow behavior can be adjusted just by a liquid combination, which can be totally evaporated in subsequent processing steps. Several model systems including TiO<sub>2</sub>, metal particles and more complex systems, as they are for example necessary in the Li-Ion battery production, are presented to discuss the tunable rheological behavior depending on the choice and amount of secondary fluid. Low and high shear response, relevant for printing applications, was examined with rotational and capillary rheometry. Resulting benefits for the printing process (e.g. shape accuracy) were investigated using various printing methods. The applicability of capillary suspensions is proven for process relevant materials with high density and also for multi-component systems, comprising several different solid phases. Besides the rheological aspects, formulations based on the capillary suspension concept also beneficially influence the drying behavior and crack formation of particulate thin films can be suppressed.

Thursday 11:10 Alfred-Mombert

CS19

### Rheology, structure and dynamics of concentrated colloidal suspensions and glasses during start-up shear and cessation

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The evolution of the microscopic structure and dynamics during start-up shear and shear cessation tests and their relation with the mechanical properties is studied in model hard sphere systems using experiments and computer simulations [1,2]. We investigate how concentrated suspensions exhibiting slow dynamics and liquid like response as well as glasses with solid like and yield stress behavior flow when subjected to steady start-up shear and how such systems relax upon shear switch-off. We probe the interplay of Brownian motion and shear-induced rearrangements at different shear rates. The stress, structure and dynamics are followed by experimental rheology and Brownian Dynamics simulations. We find that Brownian motion assisted cage escape dominates at low shear rates while escape through shear-induced collisions is dominant at high ones. We probe a shear-induced structural anisotropy which builds up during a start-up shear and is related with a stress overshoot and follow how such structure relaxes during a stress relaxation. For start-up tests we relate the dependence of the magnitude of the overshoot on the shear rate and volume fraction with structural changes [1], while during switch off we link residual stresses [2], with partial relaxation of the structure build under shear. The above phenomena are also compared with Mode Coupling Theory predictions for colloidal suspensions under transient shear.

This work has been performed in collaboration with: J. F. Brady, M. Ballauff, J. M. Brader, M. Fuchs, S. U. Egelhaaf, J. Horbach, M. Kruger, M. Laurati, K. Mutch, M. Siebenburger, Th. Voigtmann, and J. Zausch.

[1] N. Koumakis, M. Laurati, S.U. Egelhaaf, J. F. Brady and G. Petekidis, Phys Rev. Lett. 108, 098303 (2012)

[2] M. Ballauff, J. M. Brader, M. Fuchs, S. U. Egelhaaf, J. Horbach, M. Kruger, N. Koumakis, M. Laurati, K. Mutch, G. Petekidis, M. Siebenburger, Th. Voigtmann, and J. Zausch Phys. Rev. Lett. 110, 215701, (2013)

Thursday 11:30 Alfred-Mombert

CS20

**Combining coherent X-ray scattering with Rheology**Fabian Westermeier\*<sup>1</sup>, David Pennicard<sup>1</sup>, Pavlik Lettinga<sup>2</sup>, Peter Schall<sup>3</sup>, Bernd Struth<sup>1</sup>, Heinz Graafsma<sup>1</sup>

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We report on the possibilities of coherent scattering experiments using an unique rheology setup at PETRA III that combines rheology with simultaneous X-ray scattering experiments. We expanded this combination to include scattering experiments with coherent X-rays, namely X-ray Photon Correlation Spectroscopy (XPCS), exploiting the features of the novel LAMBDA pixel detector. XPCS measures the intensity fluctuations of coherently scattered X-rays. By calculating the corresponding normalized intensity time auto-correlations, we obtain information about the dynamics of the sample at different length scales, which are in the range of mesoscopic colloidal systems in small angle X-ray scattering geometry.

In itself, XPCS requires a detector with a high frame rate, sufficiently small pixel size and high signal-to-noise ratio. To probe anisotropic sample dynamics, as in rheology experiments under applied shear, the use of a 2D area detector is crucial. DESY has developed a new photon-counting pixel detector, LAMBDA (Large Area Medipix3-Based Detector Array), which offers both fast readout and a small pixel size and is thus ideally suited for XPCS experiments.

As a model system, we investigated the effect of shear on a colloidal system in the liquid phase. Due to direct electrostatic particle interactions, the system exhibits short range order. We extracted both the dynamics and the structure of the system in equilibrium. By shearing the system, we obtained the velocity distribution of the moving colloidal particles, while in addition the applied strain was monitored with high precision. This provides simultaneously information about the dynamics of the sample on different length scales and its overall viscoelastic properties.

Thursday 11:50 Alfred-Mombert

CS21

**Coupled measurements for local rheogram construction**Florence Gibouin\*<sup>1</sup>, Sébastien Jarny<sup>1</sup>, Philippe Monnet<sup>1</sup>, Jean-Christophe Dupré<sup>2</sup>, Valéry Valle<sup>2</sup>

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Many materials have a complex rheological behavior such as concentrated suspensions which are thixotropic yield stress fluids. In order to well characterize them, a local analysis is needed. In this aim a specific local measurement method is developed. Local shear rates are obtained from local velocity fields using a particle image velocimetry (PIV) technique. In the other hand shear stresses are obtained by measuring the fringe density of birefringent fluids after the determination of the rheo-optic law. In this study a simple birefringent fluid is chosen to validate the method: a milling yellow suspension which behaves as a shear thinning fluid following a Cross law and possesses high birefringent properties. After a thixotropic yield stress laponite suspension is characterized using the same method. First a modified rheometer with a transparent Couette cell is used to link the fringes density to the local shear stress. Indeed local shear stress field is known with this flow configuration whatever the gap width. For low birefringent material a specific phase shifting method is proposed to enhance accuracy of the measurements. Secondly the same material is sheared in a large size geometry composed of two parallel coaxial discs. A rotation is imposed to the upper disc whereas the lower disc is maintained fixed. Velocity fields and fringes densities are measured for different parallel plans within the gap of the shear cell. Cartography of the shear rate and the shear stress can then be plotted. The combination of these two measures enables us to trace the evolution of local shear stress as a function of local shear rate. A comparison between those measurements can then be made with a rheogram given by classical methods.

Thursday 12:10 Alfred-Mombert

CS22

**Rheology and microstructure of concentrated, near hard-sphere colloidal dispersions under steady shear and LAOS**A. Kate Gurnon<sup>1</sup>, Lionel Porcar<sup>2</sup>, Norman J. Wagner\*<sup>1</sup>

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The intriguing rheology of concentrated colloidal suspensions (i.e., shear thickening fluids or “STFs”) that exhibit increases in viscosity under high shear rates of deformation motivates this work as such suspensions have been demonstrated to respond to an impact stress. Therefore, these novel materials have the potential to be implemented in any number of impact protection applications. STFs have been critically studied for their steady shear properties [N.J. Wagner and J. F. Brady, *Physics Today*. 27-32: (2009)]. However, little is understood about the nonlinear dynamic properties of STFs. To address this, we utilize large amplitude oscillatory shear (LAOS) to investigate the dynamic rheological properties of a model STF suspension and use small angle neutron scattering (SANS) methods to measure the dynamic microstructure. Here, the first experimental measurement of the complete 3-D microstructure of a sheared, near hard-sphere colloidal dispersion [Kalman, D.P. and N.J. Wagner, *Rheol. Acta*. (2009)]. These unique measurements are made possible by the development of a new flow-SANS sample environment for time and spatially resolved measurements in the plane of flow and combine this with rheo-SANS in the radial direction and tangential direction and implemented on the SANS beamlines at the ILL and the NIST Center for Neutron Research. We elucidate the connection between the microstructure and the measured shear rheology using stress-SANS rules. The flow-induced microstructure and stress-SANS rules successfully separate the thermodynamic and hydrodynamic components of the stress that drive shear thinning, shear thickening, and first normal stress differences. A new non-equilibrium microstructure symmetry is discovered during LAOS that proves to be important for understanding the rheology of concentrated colloidal suspensions.

**Biopolymers, Active Fluids, and Food Rheology - BF**

Organizers: Hans Wyss and Mats Stading

Thursday 9:40 Clubraum

BF16

**Rheological Examination of Chicken Meat Restructuring**

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The texture of meat products plays significant role in consumer acceptance; therefore the rheological and textural measurements are very important.

Three Methods were applied to improve the structure of the poultry meat; 1) fermentation; 2) Addition of calcium-alginate and 3) Addition of enzyme transglutaminase.

This study explains the structuring mechanisms of minced meat taken from poultry wings. Within the framework of model experiments, study the effect of lactic acid fermentation, calcium-alginate and transglutaminase by different technological application on the structuring processes. The aim is to analyse the structure formation of reconstituted meat. The pH-Values were during the structuring processes determined.

By the use of Timesweep-test the complex structuring mechanisms of these three technologies are detected depended on their pH-gradient, temperature and the time.

According to loss factor  $\tan \delta$  and storage module  $G'$  different phases of the structuring process were detected and assigned. The fermentation process begins with an adaption phase, in which pH-Value is about 6 and follow to the acidification phase and pH-Value decrease continually to 5, but there was no significant pH changes by addition of alginate or transglutaminase.

By Addition of calcium-alginate starts the ion reaction high dynamically and decreases sigmoidally. The spans and temperatures of the fermentations differ significantly, as well as the formed texture.

Thursday 10:00 Clubraum

BF17

**Rheological properties of Costa Rican guava (*Psidium friedrichsthalianum* (O. Berg) Niedenzu) pulp**Daniel A. Mendez\*<sup>1</sup>, Lina M. García<sup>1</sup>, Alfredo A. Ayala<sup>2</sup>, José A. Muñoz<sup>1</sup>, Henry A. Váquiro<sup>1</sup>, José F. Solanilla<sup>1</sup>

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Costa Rican guava is a tropical fruit more aromatic and sour than the common guava, native from the seasonally flooded forest from south Mexico to northern South America. The interest for better understanding of processing and properties of this and other exotic fruits has been increasing due to their nutraceutical benefits [1]. An important tool for unit operations design and process optimization is the rheological characterization, which has not been studied yet for this exotic fruit. In the present work the dynamic shear rheological properties of Costa Rican guava (*Psidium friedrichsthalianum* (O. Berg) Niedenzu) pulp has been evaluated. Pulp samples were reconstituted with distilled water to 10 °Brix, from lyophilized and milled pulp. Flow behavior of the samples was measured at temperatures between 0-80 °C and evaluated using the Casson (C), Herschel-Bulkley's (HB), Mizrahi-Berk (MB), Bingham (B) and power law (P) models. The yield stress was calculated by extrapolation from experimental data for the C, HB and MB models. The models best described the flow behavior were the P and the HB models ( $R^2 > 0.95$ ). The consistency coefficient (CC) and flow behavior index (F) of these models were described as function of temperature by Arrhenius ( $R^2 > 0.95$ ) and linear ( $R^2 > 0.89$ ) equations respectively. The results showed that CC decreased when temperature increased, with a significant change between 40 and 60 °C (16.99-7.96 Pa sn). The F was in the range of 0.27-0.32 and 0.31-0.41 for P and HB models, respectively. The temperature effect on yield stress was not significant for both models. The parameters of HB and P models of guava pulp were influenced by temperature; however yield stress of pulp could be affected by milling process. The obtained data are useful for future studies on food properties.

[1] Flores, G.; Dastmalchi, K.; Wu, S.-B.; Whalen, K.; Dabo, A. J.; Reynertson, K. A.; Foronjy, R. F.; D'Armiento, J. M.; Kennelly, E. J. *Food Chem.* 2013, 141, 889-895.

Thursday 10:20 Clubraum

BF18

**Structuration and Rheological Properties of Gels made from Gluten Proteins**Mohsen Dahesh<sup>1</sup>, Amélie Banc\*<sup>1</sup>, Agnès Duri<sup>2</sup>, Marie-Hélène Morel<sup>2</sup>, Laurence Ramos<sup>1</sup>

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Wheat gluten proteins are among the most complex protein networks in nature, due in particular to their poor solubility in water and to their viscoelastic behavior. Gluten networks are often considered as transient networks comprising extensible biopolymer segments of flexible or semiflexible chains between junction points. However, the exact structure of the network, the nature of the junction points, its mechanical properties and the way it gets structured under shear remain to be clarified.

Here we report the visco-elastic behavior of model systems composed of gluten proteins near gelation. We build model systems by dispersing in ethanol-water mixtures two major protein groups, gliadins and glutenins that we have purified from gluten. Rheological properties show a slow evolution over time scales of the order of days of the linear frequency dependence complex modulus of the samples, with a concentration-dependent liquid to solid transition. Interestingly, we find that all data acquired at different protein concentrations and different times after sample preparation (different sample ages) can be scaled onto a master curve, showing a cross-over from a soft solid behavior at low frequency to a visco-elastic fluid at higher frequency, and revealing the self-similarity of the gels. Rheological data are completed by scattering experiments in order to elucidate the complex structure of the materials. For gel samples, the scattering profiles display at small length scales features typical of semi-dilute polymer solutions. At larger length scale a fractal structure is measured, that we interpret as being due to the highly disordered spatial organization of the junction points, at the origin of the solid behavior.

Thursday 11:10 Clubraum

BF19

**Rheology of hagfish slime – a marine biopolymer**

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Hagfish are able to gel immense quantities of water in seconds when provoked or stressed by predators through the release of exudate. This remarkable defense mechanism results in the formation of an elastic gel with high water content and fiber-like protein structures coated with mucins [1]. Whereas the chemical and physical composition of the hagfish slime are well known, little is known about the gelling and structuring potential of hagfish exudate. To address this shortcoming, both bulk and extensional rheology of hagfish slime in comparison with other marine based and gelling hydrocolloids was studied. By separating the different gel components, we were able to understand the rheological contributions and their synergistic effects. Microscopy combined with electrophoretic mobility measurements allowed us to understand the colloidal interactions between the different components. Additionally, through optimization of pH value, temperature, salt and solvent conditions, the gel forming ability and thus the water entrapment was studied.

[1] Fudge D.S., Levy N., Chiu S., Gosline M. J: The Journal of Experimental Biology 208 (2005), 4613-4625.

Thursday 11:30 Clubraum

BF20

**Concentration effects on the sol-gel transition of HPC aqueous solutions**Salvatore Costanzo\*<sup>1</sup>, Rossana Pasquino<sup>2</sup>, Nino Grizzuti<sup>2</sup>

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Inverse thermogelation is a growing area in polymer science, encompassing many different systems, from synthetic polymers to biopolymers [Jeong et al., *Advanced Drug Delivery Reviews* 54 (2002) 37–51]. Its understanding will allow tailoring the properties of soft materials at molecular scale. Cellulose derivatives (which, in contrast to pure, raw cellulose are water-soluble) are known to undergo inverse thermogelation in aqueous solutions upon heating. An in-depth understanding of the phenomenon relies on systematic studies of the effects of concentration and temperature on the gel transition of common cellulose derivatives, which are currently missing.

In the present work, the inverse thermogelation of hydroxypropylcellulose (HPC) aqueous solutions is studied by rheology. In particular, a stress-controlled rheometer is used to perform dynamic rheological tests in the linear regime with HPC aqueous solutions at different weight concentrations. More specifically, the effect of temperature is investigated and the results demonstrate that a two-step phase transition occurs during the heating process. A precipitation of the polymer, followed by the formation of a gel phase, is observed while increasing the temperature of the system from room value to higher values [Carotenuto et al., *Rheol. Acta* (2006) 45: 468–473]. Frequency sweep tests demonstrate the transition from a viscous behaviour of the HPC solution at room temperature to a gel-like behaviour at higher temperatures. If the loss and storage moduli are plotted as a function of the frequency, they are found to be parallel at the gelation temperature [Chambon and Winter, *Journal of Rheol.* 31 (8) 683-697 (1987)]. The gelation temperature and the gel strength are evaluated for the different solutions and the effect of concentration and heating rate properly analysed and discussed.

Thursday 11:50 Clubraum

BF21

**Rheological Properties of highly refined Cellulose: Carboxymethylcellulose Mixtures compared to other commercially available Fibres**

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This work aims to investigate the rheological properties of highly refined cellulose (HRC): carboxymethylcellulose (CMC) suspensions and comparison with commercially available fibres. Highly refined cellulose is a network of cellulose fibres and fibrils produced by subjecting pure cellulose pulp to either chemical or mechanical processes [1]. In order to stabilize the network after drying, carboxymethylcellulose was added to avoid the hornification

phenomena. Oscillatory measurements showed that from concentrations 0.5 % to 3.5 % w/w suspensions showed gel-like behaviour where storage modulus ( $G'$ ) is almost ten times greater than loss modulus ( $G''$ ). Whereas all HRC suspensions showed little dependency on frequency, i.e. there is slight increase in both moduli ( $G'$  &  $G''$ ) with increase in frequency. All HRC: CMC suspensions showed shear thinning behaviour (decrease in viscosity with increase in shear rate) with no sign of thixotropy [2] nor phase separation, independent of concentration (upto 0.5%w/w concentration). Comparison has been made with commercially available fibres (citrus fibres, microcrystalline cellulose and Bacterial Cellulose), measuring the effect of concentration on phase volume (water occupancy) and resultant rheological properties. Underlying principles for rheological control are investigated.

Acknowledgement: Sincere thanks Oslojordfond, Norway for funding this study.

[1] Henriksson, M., Henriksson, G., Berglund, L. A., & Lindstrom, T. (2007). An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. *European Polymer Journal*, 43, pp. 3434–3441.

[2] Lotti M., Gregersen Ø. W., Moe S., Lenes M. (2011). Rheological studies of Microfibrillar cellulose water dispersions. *J Polym Environ*, 19, pp. 137-145.

Thursday 12:10 Clubraum

BF22

### Unravelling the dynamics of Semi-dilute Polymer Solutions using DNA Rheology

Sharadwata Pan<sup>\*1,2,3</sup>, Duc At Nguyen<sup>3</sup>, P. Sunthar<sup>1,2</sup>, Tam Sridhar<sup>1,3</sup>, J. Ravi Prakash<sup>1,3</sup>

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Extensive theoretical and experimental studies have been carried out so far to investigate the rheological properties of dilute polymer solutions and polymer melts in shear flow. However, a systematic experimental study to understand the rheological properties of polymer solutions in the semi-dilute regime is currently lacking in terms of understanding the influence of concentration, temperature and molecular weight. Knowledge of the rheological behaviour of semi-dilute polymer solutions, which is characterized by significant intermolecular interactions, is of crucial importance in a number of industrial and biological contexts. In this work, the shear rheology of linear DNA molecules in a wide range of molecular weights (25-165.6 kilobasepairs), temperatures and concentrations, has been investigated. DNA solutions have the advantage of being nearly perfectly monodisperse. Steady state shear viscosities in semi-dilute regime have been determined. The dependence of the zero shear rate viscosity on concentration is observed to display universal behaviour that can be understood in the framework of scaling theories for polymer solutions. Further, the shear rate dependence of viscosity, at various temperatures and concentrations, can be collapsed onto master curves when interpreted in terms of a concentration dependent Weissenberg number. The material functions obtained in this work will provide benchmark data that are useful for the characterization of these industrially important systems, and for the validation of theoretical studies.

## Interfacial Phenomena, Surfactants, Emulsions, and Foams - SF

Organizers: Jan Vermant and Crispulo Gallegos

Thursday 9:40 Forum I

SF16

### Application of FT-rheology to the Characterization of Beer Foam

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In this presentation, we demonstrate that it is possible to use FT-rheology to characterize the nonlinear rheological properties of beer foam. One of the challenges that needed to be overcome is the detection of low torques, which were on the order of  $\mu\text{Nm}$ . These measurements were made on a state of the art ARES G2 rheometer from TA Instruments because it had the highest sensitivity of available strain controlled rheometers and is able to measure torques down to 50 nNm. For this study, different brands of dark and light beer foam were measured and it was discovered that the nonlinear rheological properties between dark and light beer foam differed by a factor of 10. These results serve as an indication of the potential of this technique for the characterization of foams in the food industry.

Thursday 10:00 Forum I

SF17

**The new interfacial rheometer: study of spreading phenomena on water surface**

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The new interfacial rheometer for testing surface layer between liquid and air has been designed, based on Lengmuir bath. Deformation of the surface was induced by slow oscillation of the plate movable along surface with large amplitudes. Under action of this deformation the surface layer flows through flat capillary. The force is measured by transducer located behind capillary. The electronic scheme is very sensitive to registration of very weak signals. The first series of experiments was carried out on testing of spreading kinetics of different liquids including surfactants, polymer solutions, silica-soles, emulsions, etc. The main results allowed us to estimate storage and loss moduli during spreading process, as well as their equilibrium values.

**Advances in Rheometry - AR**

Organizers: Maik Nowak and Thomas Schweizer

Thursday 10:20 Forum I

AR1

**Transition from ductile to cohesive fracture of photo-oxidated LDPE**

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The transition from ductile failure to cohesive rupture and the aspects of the cohesive rupture in polymer melts and gels are studied. It has been found recently that low-density polyethylene (LDPE) samples with different degrees of photo-oxidation represent an interesting system to study the transition from ductile to cohesive failure in elongational flow. Characterisation methods include Fourier transform infrared spectroscopy, gel fraction determination by solvent extraction method, and rheology in shear and uniaxial extensional flows. Linear viscoelasticity is increasingly affected by increasing photo-oxidation due to crosslinking of LDPE, as corroborated by the carbonyl index, acid and aldehydes groups and gel fraction. This has a crucial influence on the modeling. Instead of the generalized Maxwell approach for describing the linear viscoelasticity of polymer melts, the relaxation modulus with only three parameters for polymer gels is implemented in the MSF model for those samples with high gel content. Highly non-linear results can be modeled by use of only one non-linear material parameter, which is correlated to network properties such as the gel content. True strain and true stress at cohesive fracture as well as energy density used during the experiments were analyzed. At low gel content, rupture occurs mainly in the melt fraction, while at high gel content, rupture occurs predominantly in the gel structure. The equilibrium modulus of the gel structures was correlated with the true strain at rupture. The stiffer the gel structure, the lower is the deformation tolerated before the sample breaks. Strain at break was found to be independent of strain rate, in contrary to stress at break and the energy density. Thus, it seems to be the true strain and not the stress at break or the energy density, which is the relevant variable to describe the cohesive fracture behavior of photo-oxidated LDPE.

Thursday 11:10 Forum I

AR2

**Direct Measurement of Rheological Properties of Viscoplastic Fluid in Laminar Hagen Poiseuille Flow Using Different Measurement Techniques**Juha Salmela<sup>1</sup>, Sanna Haavisto<sup>1</sup>, Antti Koponen\*<sup>1</sup>, Markku Kataja<sup>2</sup>, Maria Cardona<sup>3</sup>, Mike McCarthy<sup>3</sup>, Robert Powell<sup>3</sup>, Emilio Tozzi<sup>3</sup>

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Rheological properties of complex fluids are mostly characterized using viscometers or rotational rheometers with very small measurement gaps. By definition rheology is a study of flow and deformation of material and therefore the flow geometry should not restrict the material free deformation with applied force. Many complex fluids like particle

and fibre suspensions are prone to flocculation and wall depletion. Often in small flow geometries the walls restrict the flocculation and wall depletion leads to effects like apparent slip velocity. Changes in floc size vary the bulk properties of the suspension and slip velocity often dictates the suspension flow behaviour.

Therefore this has complicated the interpretation of rheological measurements both in microscopic and macroscopic scales. A new experimental method based on velocity profile measurements in fully developed pipe (18.5 mm diameter) flow is presented for direct measurement of the rheological behaviour of any opaque fluid. In our work Magnetic Resonance Imaging (MRI) or the Ultrasound Doppler Velocimetry (UDV) technique is utilized for measuring the velocity profile in the interior parts of the pipe and Optical Coherence Tomography (OCT) is applied for high-resolution measurements of the boundary layer flow and structure near the pipe wall. While MRI and UDV are well established techniques OCT has only recently been utilized for rheological characterizations. As MRI and UDV, OCT is a non-invasive technique that allows simultaneous real time imaging of the structure and velocity of opaque media with very high spatial and temporal resolution. Suspension rheological properties are also measured using state of the art rotational rheometer and results are compared. The results obtained for a moderately dense micro-fibrillated cellulose suspension show typical shear thinning behaviour with yield stress in the interior part of the tube while near the wall there is a slip layer approximately 200  $\mu\text{m}$  thick.

Thursday 11:30 Forum I

AR3

### Extensional rheometry of magnetic dispersions

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The complete rheological characterization of fluids, and in particular of magnetic colloids (ferrofluids –FF- and/or magnetorheological fluids -MRF-), should also include their assessment in extensional flows. For shearing rheometric flows many rotational rheometers have been conveniently modified with fixtures to apply external magnetic fields to the sample undergoing deformation, either using magnetic circuits or solenoids. However, to our best knowledge, measurements of rheological material functions in uniaxial extension of FF and MRF have not been carried out, at least for low viscosity solutions.

In this talk we present some new results of measurements of commercial ferrofluids (FF40, FF200 and FF500) obtained on a Capillary-breakup extensional rheometer (Haake CaBER 1, Thermo Scientific) adapted with a new fixture to allow the application of uniform external magnetic fields aligned and normal to the direction of strain deformation. The experimental results show that all these fluids exhibit a Newtonian-like behaviour in extension when no magnetic field is applied. However, a yield-stress filament thinning is observed under the influence of the magnetic field, especially when the magnetic field is aligned with the flow kinematics.

The invention here reported (patent pending) is precisely that of the unique fixtures adaptable to CaBER-type rheometers, which allow the application of an external magnetic field parallel (or perpendicular) to the flow kinematics undergone by the fluid sample while the filament thinning is being recorded. The same principle can be also adapted to FiSER-type rheometers with relative ease. Thus, the use of the present apparatus extends the range of application of extensional rheometers to characterize magnetic dispersions (MRF and FF) while subjected to an external magnetic field.

Thursday 11:50 Forum I

AR4

### Pressure distribution evolution during squeeze-flow of cement-based mortars

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The squeeze-flow is a rheological test based on the compression of a cylindrical sample between two parallel plates and has been used as an alternative/complementary method for characterizing fresh mortars. Its geometry change during gap reduction makes the technique particularly interesting, as it creates flow conditions similar to those involved in processing and application of mortars, e.g. pumping and spraying; spreading and finishing; squeezing between bricks; extrusion [1,2]. As a result, a testing method for rendering and masonry mortars was recently standardized in Brazil (ABNT NBR 15839:2010). During squeezing-flow of mortars, phase separation is

likely to occur due to the multiphase nature of the material and should be considered for an adequate analysis of its rheological behavior [1,2]. Up to date, methods assume that the stress (load/plate area) under the plate evolves uniformly; however, stress distribution may not take place as expected, either because of the occurrence of segregation or by the presence of macroscopic particles. In this research, a thin-flexible pressure sensor was placed under the samples in order to assess the pressure distribution evolution throughout the squeezing-flow of different mortars. The squeezed samples were then subjected to microwave drying for the quantification of fluid-solid segregation induced by the test [2]. The methodology associating these 3 experimental techniques allowed for the identification of load fluctuations and flow instabilities caused by stress concentrations due to localized increase of solids content, depending mainly on the plate's displacement rate and mortar features.

[1] F.A. Cardoso, V.M. John, R.G. Pileggi. Rheological behavior of mortars under different squeezing rates, *Cem. Concr. Res.*, 39, 748-753, 2009.

[2] F.A. Cardoso, Mix design method for rendering mortars based on particle size distribution and rheological behaviour, Doctoral thesis, University of São Paulo, 2009 (in Portuguese).

#### Thursday 12:10 Forum I

AR5

### Applying a High Sensitive Force Measurement to a Commercially Available CaBER for Measuring Elongational and Tack Properties

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The Capillary Breakup Extensional Rheometer (CaBER) is the only commercially available rheometer to measure the elongation properties of liquids [1-2]. Up to now the CaBER experiment can only measure the time-dependent diameter of a low viscous sample under stretch. Thus, the analysis of the data measured with this device is limited to models which are based on the time-dependent diameter of the filaments,  $D(t)$ . Some samples show a more complex behaviour of the capillary flow which cannot be covered by the applied models. For those samples the measurement of the force, which the filament exerts on the plates during the initial stretching and during the subsequent filament break up, could give new insights into the material properties.

In this work, we use the upgrade for the HAAKE CaBER 1 that was developed by us for measuring different extensional properties, i.e. the extensional viscosity and the separation energy. [3] The normal force acting on the lower plate is measured as a function of time. To measure these small forces (down to 0.05 mN) with a very high time resolution (i.e. dwell-times down to 0.2 ms) a piezoelectric transducer is used in combination with modern data oversampling. This advanced setup allows a simultaneous measurement of the force and the diameter in the CaBER. With this new setup the separation energy  $W_{sep}$  of a sample can be determined. This new quantity is related to the tack value. [4] As an example for the capability of the upgraded CaBER, the curing behaviour of two different PVAc based glues is studied. [5]

[1] P. Tripathi, S. H. Spiegelberg, and G. H. McKinley, *J. Rheol.*, 44 (2000) 653–670.

[2] S. Gaudet, G. H. McKinley and H. A. Stone, *Phys. Fluids* 8 (1996) 2568–2579.

[3] C. O. Klein, I. F. C. Naue, J. Nijman and M. Wilhelm, *Soft Materials*, 7 (2009), 242-257.

[4] A. Zosel, *Colloid & Polymer Sci.*, 263 (1985), 541-553.

[5] I.F.C. Naue. PhD thesis, Karlsruhe, 2013.

## Industrial Rheology and Processing - IR

Organizers: Dick J. Dijkstra and Bettina Wolf

#### Thursday 9:40 Forum II

IR7

### Rheological behaviour of thin PVOH films for industrial applications

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Water soluble films like PVOH are becoming more and more important in many applications (i.e packing of agrochemicals, laundry bags for sanitary purposes or household cleaning products). One of the challenges of PVOH films is

the big impact that moisture and temperature have on its mechanical behaviour and the implications in equipment design. Film mechanical properties were characterized by means of Dynamic Mechanical Analysis (DMA) in tension mode across the temperature and relative humidity ranges involved in film later industrial conversion process. Oscillation time temperature superposition (TTS) was then used in order to characterize mechanical properties of films across the wider range of strain deformation rates involved on film transformation during manufacturing. In analogy to TTS methodology, a relative humidity superposition (TRHS) approach was used in order to quantify the impact of humidity on mechanical properties of films. This mechanical properties characterisation of commercial films was also compared to standard methodology ASTM D882, correlated to T<sub>g</sub> values found using Differential Scanning Calorimetry (DSC) as well microscopy characterisation. Additionally, the film relaxation properties and its impact on industrial usage of the material will be discussed.

Thursday 10:00 Forum II

IR8

### Unprecedented high-modulus high-strength tapes and films of Ultra High Molecular Weight Polyethylene via solvent-free route

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Ultra High Molecular Weight Polyethylene (UHMWPE) having average molar mass greater than a million g/mol is an engineering polymer. Due to its light-weight, high abrasion resistance and biocompatibility it is used for demanding applications such as body armour, prostheses etc. At present, because of its high melt viscosity to achieve the uniaxial/biaxial properties in the form of fibers/films the polymer is processed via solution route where solvent is used to process 5-10 wt% of the polymer. In past several attempts have been made to process the polymer without using any solvent. However, compared to the solvent processing route the achieved mechanical properties were rather poor. Here we show that by controlled synthesis it is feasible to obtain UHMWPE that could be processed free of solvent to make uniaxial tapes and biaxial films having unprecedented mechanical properties, exceeding that of the solution spun fibers. We address some of the fundamental aspects of chemistry, physics, rheology and processing for the development of desired morphological features to achieve the ultimate mechanical properties in tapes and films in the polymer processed via solid-state, free of solvent.

[1] Nature Material 2005, 4, 635

[2] Phys. Rev. Lett. 2006, 96, 218303

[3] Macromolecules 2008, 41, 2514

[4] Macromolecules 2011, 44 (14), 5558–5568

[5] Macromolecules 2011, 44 (20), 8042-8055

[6] Macromolecules 2011, 44 (12), 4952-4960

[7] Patent US2006142521(A1), 2006 [8] Patent EP2014445(A1), 2009

Thursday 10:20 Forum II

IR9

### Process Rheology Of Extruded Wood-PVC-Composites

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The market of Wood Polymer Composites (WPC) has been growing very fast in the last couple of years [1]. For the production of WPC articles, extrusion process is often used for WPC with 50-70 wt % wood whilst injection moulding can be applied for compounds with 20-50 wt % wood content. The characterisation of melt rheology of WPC with more than 50 wt % wood fibre loading is very complicated and still remains a big challenge. It could also not be found often in the scientific literature [2]. In order to characterise the rheological behaviour of WPC formulations in a practical and application related way, we have developed a by-pass rheometer which is adapted to a conical twin screw extruder dedicated to the production of fibre composites [3]. The composite materials are mixed and plasticized in the extruder and rheological measurements are carried out during processing. Process variables such as throughput, thermal history and mixing quality can be adjusted similar to the big scale production. This allows an application relevant material flow behaviour characterisation.

In this study, investigation of the process rheology of PVC-based WPC-melt was carried out. The effect of colour masterbatch as additive and its viscosity on the process rheology of PVC-WPC melt and the processing parameters

during extrusion is investigated and discussed. Furthermore, the influence of melt temperature on the process rheology was characterised. A comparison of process rheology between PVC-based WPC and PP-based WPC was also discussed.

[1] A. Eder: Market Information on Wood-Plastic Composite, Decking and Siding in Europe, Wood K plus Study (2009)

[2] H. Hansmann, S. Kühn, N. Laufer: WPC-Schmelze unter Beobachtung; Kunststoffe 9, 111-115 (2011)

[3] H.L. Nguyen, R. Putz: Rheology and Mechanical Properties of Wood Fibre-Polypropylene-Composites using By-Pass Extrusion Rheometer; PPS (Polymer Processing Society) Americas Conference 2012; Niagara Falls, Ontario, Canada, (2012)

#### Thursday 11:10 Forum II

IR10

##### **Viscoelastic behaviour of Polymer modified Bitumen at low temperatures**

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High voltage submarine cables are armoured by galvanized steel wires. These wires are corrosion protected by polymer modified bitumen (PMB). During spooling of the cable between turntables and for example laying-vessel sometimes "bird-cageing" (bulging) in the armouring occur when the temperature is low. This bulging is related to the shear forces between the armouring and the bitumen. The viscosity of the polymer modified bitumen varies during start and stop in the armouring process in the manufacturing. It is therefore of interest to investigate the relationship of the viscoelastic properties of PMB vs. softening point and temperature. Material testing has included characterization of bitumen by a controlled stress rheometer from -20 to 30 °C. The different parallels were analyzed due to the variance/precision in the data. The complex shear modulus,  $G^*$  is plotted against frequency at different strains and temperatures. The results indicate that the lowest variance is at high strain at high temperatures and at low strain at low temperatures. The average of the parallels was used for the making of a mastercurve and cole-cole plot.

#### Thursday 11:30 Forum II

IR11

##### **Controlled shear history in rheological characterization of cement- and gypsum-based construction materials**

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Rheological properties are important aspects in the formulation of cement- and gypsum-based construction materials. However, reproducibility of measurements of such materials are frequently plagued by artefacts such as wall slip, while small changes in the shear history can have a large effect on the rheological response. These effects make it difficult to differentiate among formulations, accordingly it is not possible to optimize a formulation.

We have applied a commercially available geometry that was designed to counteract wall slip to study rheological properties of cement- and gypsum-based construction materials. For this purpose we have developed a measuring protocol that imposes a fixed shear history to the sample material. The protocol consists of a series of segments in which the material is subjected to a pre-shear followed by measurement of the rheological response using 'snapshot' flowcurves. The shear rate associated with the pre-shear is increased for subsequent segments. For the actual evaluations Bingham parameters were retrieved, and these form an evolution curve.

It turns out that evolution curves show a good reproducibility overall, although datapoints from individual segments do not. By means of the evolution curves it is easy to differentiate among formulations containing different additives, thereby making it possible to optimize these formulations.

Thursday 11:50 Forum II

IR12

**Paste Rheology as Key to a Successful Development of an Industrial Dispensing Process for Solar Cell Metallization**Maximilian Pospischil\*<sup>1</sup>, Markus Klawitter<sup>1</sup>, Martin Kuchler<sup>1</sup>, Markus König<sup>2</sup>, Oliver Doll<sup>3</sup>, Monica Schneider<sup>4</sup>, Norbert Willenbacher<sup>4</sup>, Roland Zengerle<sup>5</sup>, Florian Clement<sup>1</sup>, Daniel Biro<sup>1</sup>

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Industrial silicon solar cell metallization is still dominated by screen printing technology. On the front surface, high yield stress silver pastes are printed, dried and sintered subsequently forming a robust grid structure of reliable contacts with proven long term stability. Dispensing technology uses similar pastes, but offers the possibility to obtain more homogeneous contact fingers at significantly higher aspect ratios (= height : width) ensuring higher finger conductivity and lower shading losses. Furthermore, an adaption of paste elasticity including yield stress and elastic shear modulus  $G'$  allows for a precise adjustment of contact finger geometry in a wide range [1]. Initially, various silver pastes were characterized using capillary and rotational rheometry in order to receive input parameters for a CFD-model based on the description of Herschel and Bulkley [2]. In the following, this CFD model was applied to develop a central fed, parallel ten nozzle dispensing unit including a parallel shutter valve and specially designed dispensing nozzles.

Subsequently, the influence of various rheological parameters on this high throughput dispensing process including required system pressure and transient behavior during start and stop is discussed and compared with theory. Furthermore, important aspects of surface interaction between paste and nozzle on the one hand and during contact formation on the wafer on the other hand were investigated. Finally, various aspects of particulate dispersion rheology applied on silver pastes were used to develop an industrial dispensing process that allows for homogeneous contact finger widths of less than 30  $\mu\text{m}$  on industrial solar cells and thus for increased cell efficiencies.

[1] M. Pospischil et al., IEEE JPV 2, 2156 (2013), DOI: 10.1109/jphotov.2013.2278657, to be published

[2] M. Pospischil et al., Energy Procedia (2013), accepted for publication

Thursday 12:10 Forum II

IR13

**Continuous Pharmaceutical Melt Granulation: Rheology as a predictive Tool to determine processability of the Formulation**Tinne Monteyne\*<sup>1</sup>, Klaus Oldörp<sup>2</sup>, Thomas De Beer<sup>1</sup>

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Within the scope of increased pharmaceutical process efficiency, there is a growing interest in continuous processes. Twin-screw hot melt granulation (HMG) is a valuable, still unexplored alternative to granulate temperature and moisture sensitive drugs. The understanding of the material behavior during processing is necessary to reduce the amount of preliminary experiments and to optimize the process. The aim of this study is to evaluate rheology combined with microscopy as predictive tool for the elucidation of the agglomeration mechanism, and examine how rheological information can be used to optimize the process.

Soluplus® was used as a binder to agglomerate the model drug caffeine. The Soluplus®/drug ratio was varied from 5/95 to 70/30 (w/w %). Continuous HMG was performed using a co-rotating twin screw granulator. Rheological measurements were executed in parallel using two rheometers: 1. the Haake Mars III, and 2. the Haake Mars III Rheoscope.  $\tan(\delta)$  is used as an index for mixture deformability. Rheoscope measurements revealed that samples with a binder concentration  $\geq 25\%$  (w/w) showed phase separation at high temperatures (T). Furthermore, these mixtures are not suitable for granulation since big lumps are formed. These observations show that the deformation of these mixtures was too high (i.e.  $> 0,1$ ). Hence, it can be hypothesized that the  $\tan(\delta)$  value of the mixture cannot be  $> 0,1$  to be suitable for continuous HMG. Furthermore, during granulation experiments it is seen that the T resulting in the maximum  $\tan(\delta)$  value, correlates with the T leading to the maximum mean granule size.

The combination of rheological parameters and microscopic images seem a useful tool to reach an in-depth

understanding of the material behavior during HMG processing and a promising predictive tool to optimize the binder concentration and the process T. Furthermore, it gives a view on granule particle size in function of T, which makes it possible to optimize the yield fraction.

# Thursday Afternoon

## Polymer Melts, Blends, Copolymers, and Nanocomposites - PM

Organizers: Ulrich Handge, Manfred Wagner, Dimitris Vlassopoulos, and Alexei Likhtman

Thursday 13:40 Hans-Thoma

PM23

### Coarse grained models for polyurethanes

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We present a molecular dynamics simulation study in comparison to experiments of two polyurethanes. The hierarchical modeling includes an atomistic model and a structure based coarse graining (CG) model. Atomistic melt simulations are used as a reference to develop coarse grained models for two polyurethanes following the iterative Boltzmann inversion method. The coarse grained model explicitly represents hydrogen bonds and allows to study their influence on structural and dynamical properties in coarse grained simulations, especially by switching off their attractive interaction. Static properties of atomistic systems are well reproduced by CG simulations. Hydrogen bond lifetimes and diffusive processes show a consistent speed-up in CG simulations and allow to study dynamical properties in CG simulations. The coarse grained models are used to calculate stress autocorrelation functions (SAF) of entangled polymer melts. A primitive path analysis of the systems predicts the entanglement length of the polymers, which compares well with the SAF data and experiment.

Thursday 14:00 Hans-Thoma

PM24

### Rheological Investigations of the Gelation of Polyvinylbutyral Solutions by Tetrabutyl-Orthotitanate

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Polyvinylbutyral (PVB) solutions are frequently used for the manufacture of ceramic particle-filled green tapes. Recently it was observed that the viscosity of an alcoholic PVB solution increases by the addition of tetrabutyl-orthotitanate (TBOT) due to the cross-linking of PVB. It is presented how powerful rheological experiments are to elucidate this process.

Frequency sweeps were used to investigate the dependence of cross-linking on reaction time and TBOT concentration. The storage modulus  $G'$  rises during one week for a solution with 0.10 vol. % TBOT without reaching a plateau value after that time, i.e. the cross-linking reaction is rather slow. The amount of TBOT has a strong effect on  $G'$ . By changing the TBOT content from 0.06 vol. % to 0.30 vol. % the storage modulus of the solutions with 12 wt. % PVB increases by about four decades after one day at room temperature.

The frequency dependence of  $\tan\delta$  was used to determine the gel point of the solutions. For the solution with 0.10 vol.%,  $\tan\delta$  becomes independent of frequency after 24 h, i.e. the gel point is reached after that time. It is further demonstrated in which way the gel point depends on the concentration of TBOT.

Moreover, it is shown how the cross-linking process can be controlled by adding water to the dissolved TBOT. Water reduces the gelation. For example, the addition of 1 vol.% water to a solution with 0.30 vol.% TBOT suppresses the gelation completely.

Amplitude sweeps were performed to characterize the strength of the network of a TBOT/PVB solution with 0.30 vol.% TBOT. At deformations of around 100 % the storage modulus  $G'$  drops sharply. The loss modulus increases first at this amplitude, but goes down then, too. For the TBOT/PVB solution with 0.30 vol.% TBOT stored over one day a total reversibility of  $G'$  was observed.

Based on the results of the rheological investigations a model for the cross-linking reaction in the PVB/TBOT solutions is discussed.

Thursday 14:20 Hans-Thoma

PM25

**Coarse Grained Computer Simulations of Star Polymer Melts**Barry W. Fitzgerald\*<sup>1</sup>, Helen Lentzakis<sup>2</sup>, Dimitris Vlassopoulos<sup>2</sup>, Wim Briels<sup>1</sup>

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Star polymers are macromolecules composed of a number of linear polymers (otherwise referred to as arms)  $f$  covalently bonded to a common centre whose behaviours are intermediate between linear polymers ( $f = 1,2$ ) and hard colloids ( $f \rightarrow \infty$ ). The number of arms and molecular weight of each arm control their interpenetrability and as a result these hybrid particles demonstrate their own unique rheological properties. Recently a coarse-grained algorithm, responsive particle dynamics (RaPiD) algorithm [1] has been developed which allows for the simulation of large amounts of polymer solution or melt over relatively long times. RaPiD is a mesoscopic model based upon Brownian dynamics where each polymer is viewed as a point particle. The eliminated degrees of freedom are used in the description of an effective inter-particle potential in addition to frictional forces between polymers. In addition the thermodynamic state of these eliminated degrees of freedom can be monitored with a small set of dynamic variables. In this presentation we use the RaPiD algorithm to simulate the linear rheology and non-equilibrium response of two polystyrene (PS) star polymer melts where the stars are of low to moderate functionality and low molecular weight [2]. Firstly we use linear rheology experimental measurements to adjust the RaPiD dynamic variables. Subsequently we simulate the non-equilibrium response of these melts when subject to a number of shear protocols. We confirm the presence of a stress overshoot during start-up shear for approximately the same shear rate as observed in experiments.

[1] A. van den Noort, W. K. den Otter, and W. J. Briels, *Europhys. Lett.* 80, 28003 (2007).

[2] B.W. Fitzgerald, H. Lentzakis, D. Vlassopoulos and W.J. Briels, in preparation, (2014).

Thursday 14:40 Hans-Thoma

PM26

**Primitive path dynamics, Constraint Release and Contour Length Fluctuations in a model Polyethylene melt: A first principles, atomistic simulation study**Stefanos D. Anogiannakis<sup>1,2</sup>, Christos Tzoumanekas\*<sup>1,2</sup>, Doros N. Theodorou<sup>1,2</sup>

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We will present a study of Primitive Path (PP) dynamics, Constraint Release (CR) and Contour Length Fluctuations (CLF) in a model Polyethylene melt. By using the CReTA algorithm, a long atomistic molecular dynamics trajectory of a C500 PE melt is reduced to the corresponding trajectory of PPs. We then introduce suitable correlation functions which track PP dynamics, CR and CLF, and enable us to extract the entanglement time,  $\tau_e$ , the Rouse time,  $\tau_R$ , and the reptation time,  $\tau_d$ , from the PP trajectory. The identified times are compared with the characteristic times that can be extracted from the mean square displacement of the real chain monomers, and it is shown that they are in very good agreement to each other. We will also discuss about the difficulty of tracking CR processes, how our CLF results are affected by CR, and we will compare our CLF predictions to those of the classical Doi-Edwards model.

Thursday 15:00 Hans-Thoma

PM27

**Equilibration and rheological properties of high molecular-weight polymer melts**Livia Moreira<sup>1</sup>, Guojie Zhang<sup>1</sup>, Torsten Stuehn<sup>1</sup>, Kostas Daoulas<sup>1,2</sup>, Kurt Kremer\*<sup>1</sup>

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A modeling strategy is proposed for studying rheological properties of high molecular-weight polymer melts described with microscopic detail. The microscopic model is generic but retains features including hard excluded volume interactions and realistic melt densities, which hamper the equilibration of chemistry specific models. Equilibrated microscopic configurations are created by a backmapping strategy based on a coarse-grained (CG) model representing polymer chains as strings of fluctuating blobs [1-3]. Each blob represents one subchain of  $N_b$  microscopic beads. By varying  $N_b$ , a hierarchy of CG models with varying resolutions is obtained. Within this hierarchy, CG configurations equilibrated at low-resolution are sequentially fine-grained into CG melts of higher resolution. Subse-

quently, microscopic details are slowly introduced into the latter via a modified version [4] of the scheme of Auhl et al. [5]. All backmapping steps involve only local polymer relaxation, thus the computational efficiency of the method is independent of chain length, being only proportional to system size [3]. This strategy is implemented to equilibrate melts with different persistence lengths and polymerization degrees up to 55 entanglement lengths,  $N_e$ . The  $N_e$  is measured from topological structure of entanglements and dynamical properties of equilibrated melts using primitive path analysis and mean-square displacement of monomers, respectively. The effects of finite system-size and chain length upon  $N_e$  are discussed. A master curve for the estimating  $N_e$  for polymer melts with different chain lengths and persistence lengths is provided [4]. We comment on alternative estimations of  $N_e$ , e.g., from plateau modulus of polymer melts.

- [1] Vettorel et al., *Soft Matter* 6, 2282 (2010)  
 [2] Zhang et al., *Macromol. Chem. Phys.* 214, 214 (2013)  
 [3] Zhang et al., submitted  
 [4] Moreira et al., in preparation  
 [5] Auhl et al., *J. Chem. Phys.* 119, 12718 (2003)

Thursday 15:50 Hans-Thoma

PM28

### **A new approach for pressure drop calculations in flow of viscoelastic fluids through short channels**

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There are two standard methods for treating flow through short capillaries. The first one consists in using the formal concept of end corrections and calculating pressure drops basing on the Bagley difference method. The second one is based on computer solution of field equations in application to different rheological models of flowing fluids.

We proposed a new approach to calculating pressure drops in flow of polymeric viscoelastic liquids through short capillaries. This approach is based on the supposition that the domination part of energy consumption is related to elastic deformation of an elastic liquid. Then we introduced the average time of deformation for a flowing medium as a measure of these deformations. The dimensionless measure of this factor is the Deborah Number,  $De$ . The point for discussion is the determination of the characteristic relaxation time which should enter  $De$ . We suppose that no standard methods for calculating a discrete relaxation spectrum can be used for this aim because of uncertainty in the choice of the approximation method. Instead of it, we propose to use the continuous spectrum with limitation from the long-term side. We used a power type function with the upper boundary for characterization of relaxation properties of viscoelastic liquids. This upper boundary was treated as the maximal relaxation time determining  $De$ . This new approach was applied for several polymer systems. Experiments on flow were carried out using four capillaries of different length. Viscoelastic properties were measured on the base of the usual modulus vs. frequency dependencies and the soft-ware was used for finding constants of continuous spectra. It was proven that this method works quite well and allows us to construct a universal dependence of the pressure drop on  $De$  in the 4-5 decimal order range of the latter at  $De$  not less than  $\approx 0.3$ . Dependence of the "Newtonian" shear stress on  $De$  is expressed by the scaling law with a power equal to 0.425.

Thursday 16:10 Hans-Thoma

PM29

### **Chain Conformation and Thermal Annealing of Electrospun Polystyrene Fibers: A Small Angle Neutron Scattering Study**

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Stability of electrospun fibers can be considered by studying the polymer chain conformation and relaxation dynamics after thermal annealing. Electrospun scaffolds of aligned fibers were made of amorphous polystyrene, PS, having narrow polydispersity index and analyzed by small angle neutron scattering technique (SANS). Previous SANS studies of micron-sized PS electrospun fibers were dealing with the polymer chain conformation in as-spun state [1]. The radius of gyration, broadly equivalent to that of the bulk, reveals a slight anisotropy of the polymer chains.

Herein, we report a different approach for studying the anisotropy of polymer chains within electrospun fibers. Unlike classical approaches for studying the chain conformation and radius of gyration that involve complex SANS data modeling, we obtained the characteristic size of macromolecular chains through investigation of the chain elongation

ratio from experimental SANS data and iso-intensity curves. SANS experiment on polystyrene fibers in as-spun state showed a notable anisotropy of polymer chains in the direction of the fiber alignment axis. The elongation ratio in the axial direction of as-spun fibers was found to be 1.22 while the corresponding ratio of the radius of gyration parallel and perpendicular to the fiber alignment axis was 1.34. Furthermore, the chain relaxation dynamics after thermal annealing at different temperatures and time intervals were reported. Fast relaxation of the surface of electrospun fibers and rather slow chain relaxation within the fiber bulk were observed. The thermal annealing experiments enabled us to estimate the characteristic relaxation time of the polymeric chains within the electrospun fibers.

[1] S.D. Mohan; G.R. Mitchell; F.J. Davis. "Chain extension in electrospun polystyrene fibres: a SANS study", *Soft Matter*, 7, 4397, 2011.

Thursday 16:30 Hans-Thoma

PM30

### **PHA obtained from mixed microbial cultures fed with food industry by-products: thermorheological characteristics and benchmarking with commercial PHA**

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Polyhydroxyalkanoates (PHA) have two major assets which make them promising polymers for future packaging application to reduce the ecological footprint of plastics: they are fully biodegradable and bio-based. However, PHA are not yet used in plastic bags, pouches or flat thin films because they are still 10 times more expensive than conventional plastics used for such application, and most of all, because they show a very narrow processing window. PHA are very difficult to transform in films or extruded sheets, and thus the film blowing of commercial PHA has only been recently successfully achieved by our group. We report on the thermorheological characterization of new PHA obtained from mixed microbial cultures (MMC) fed with food industry by-products, namely cheese whey and olive mills wastewaters produced at lab scale and also from the up-scaling of the bioengineering process. These MMC PHA possess a high degree of HV copolymerization (HV molar fraction between 8 and 20 % with respect to HB). The melting temperatures measured from DSC and temperature sweeps in SAOS are consistent with data reported in the literature for PHA obtained from pure culture, and are nearly 20 °C below the melting point of commercial PHA possessing few amounts of HV. The thermal degradation of the MMC PHA assessed rheologically and with TGA analysis occurs at lower temperatures than those reported in the literature. This is related to the large content of impurity remaining after the recovery of the PHA from the MMC, as shown by data obtained after a purification process. The effects of such impurities on the crystalline structure obtained from WAXD and on the crystallization kinetics measured with SAOS will be discussed. Mechanical spectra and flow curves of the melts will be benchmarked with the ones measured with commercial products in order to assess the processability of these new bioplastics. Finally, the use of MMC PHA as processing aids for commercial PHA will be discussed.

Thursday 16:50 Hans-Thoma

PM31

### **The Rheological Behaviors of Polyethylene oxide in Ionic Liquids**

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Ionic liquids (ILs) have attracted considerable attention and are widely used in the field of polymer science because of their negligible volatility, thermal stability, non-flammability, and high ionic conductivity. However, the polymer conformations in ILs are not clear because of the different structures of ILs and the complex interactions between anion and cation of ILs. The properties of polymer/ILs solutions were investigated by rheological measurements and other methods.

First, the solubility, crystallization and melting of semicrystalline polyethylene oxide (PEO) in different kinds of imidazolium ILs were studied. The melting temperatures of PEO crystals in ILs are much lower than that of the neat PEO. The depression of melting points is mainly related to the interaction between polymer and ILs, which is consistent with the order of the contact angle of ILs on PEO crystal surface.

The rheological behaviors of PEO in ILs with different anions with distinct interaction were investigated covering the PEO concentrations from 0.0004 to 0.06 g/ml. For the scaling exponents of the specific viscosity against the polymer

concentration are similar in dilute regime, semidilute unentangled regime and entangled regime. Further, the scaling exponents are consistent with theoretical predictions of neutral polymer solutions in theta conditions. However, the Mark-Houwink exponent describing  $M_w$  dependence of intrinsic viscosity increases with the anion size, which implies the effect of Coulombic interaction between cation and anion in ILs.

Thursday 17:10 Hans-Thoma

PM32

### **Brownian dynamics of self-assembly and rheology of stiff pi-stacking polymers**

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We introduce a novel model aimed to study the self assembly process of long slender laths, that interact perpendicular to their areas. The potential energy depends both on the angle between orientation vectors, along the long axis of the laths as well as the normal vectors pointing out of the plane. The model depends on only one energetic parameter. We find how the self assembly process generates long ordered aggregates of laths, called whiskers, and show the way the stress auto-correlation in the system develops with their formation. This model shows the same quantitative characteristics that are seen on the aggregation of P3HT molecules due to the aromatic interaction, as has been reported in the literature. This system being the most widely used in the production of organic solar cells.

## **Non-Newtonian Fluid Mechanics and Flow Simulation - FM**

Organizers: Pier L. Maffettone and Evan Mitsoulis

Thursday 13:40 Johann-Peter-Hebel

FM8

### **Simulations of deformable systems in fluids under shear flow using an arbitrary Lagrangian Eulerian technique**

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An arbitrary Lagrangian Eulerian finite element method based numerical code for viscoelastic fluids using well known stabilization techniques (SUPG, DEVSS, log-conformation) is adapted to perform a 3D study of soft systems (drops, elastic particles) suspended in Newtonian and viscoelastic fluids under unbounded shear flow. Since the interface between the suspended objects and the matrix needs to be tracked, a finite element method with SUPG stabilization and second-order time discretization is defined on the interface, with the normal velocity of the interface equal to the normal component of the fluid velocity and a tangential velocity such that the elements on the interface are evenly distributed. This allows the mesh to get rid of the tank-treading motion of the particle. The code is validated for drops and elastic particles in a Newtonian fluid through comparison with data from literature. New results on the deformation of an elastic particle in a viscoelastic fluid are presented.

Thursday 14:00 Johann-Peter-Hebel

FM9

### **High-Weissenberg number predictions for contraction-expansion flow and micellar fluids**

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This study is concerned with the modelling of thixotropic and non-thixotropic materials in contraction-expansion flows at high Weissenberg number ( $We$ ). Thixotropy is represented via a new micellar time-dependent constitutive model for worm-like micellar systems and contrasted against a network-based time-independent EPTT model. The work focuses on steady-state solutions in axisymmetric rounded-corner 4:1:4 contraction-expansion flows for the benchmark solvent-fraction of  $\beta=1/9$  and moderate hardening characteristics. Simulations are performed to high  $We$  with a novel hybrid algorithm, in which a finite volume scheme is utilized to solve the constitutive equation, whilst finite elements deal with the continuity and momentum equations, in an incremental pressure-correction

time-stepping structure. Enhanced pressure drop, stress fields and vortex dynamics are analysed, where evidence of new upstream vortices and its relationship with  $N_2$  is obtained. These flows have importance in industrial oil-reservoir recovery and the plastics industry, biological and food flow applications, typically provoking thixotropy, yield stress and shear banding. To obtain high-We solutions, both micellar and EPTT constitutive equation f-functionals have been amended by (a) adopting their absolute values, and (b) through a change of stress variable,  $\Pi = \tau_p + (\eta_{p0}/\lambda_1)I$ , that prevents loss of evolution in the underlying initial value problem. A boundary condition is imposed at the centreline, for which the shear gradients vanish identically. As a consequence, highly non-linear solutions are now attainable, given at impressively high We. For example and with micellar fluids, the numerical breakdown is shifted from critical states of  $We_{lim}=4.9$  without correction, to  $We_{lim}=\mathcal{O}10^3$  with correction. Furthermore, such constitutive correction has been found to have general applicability.

Thursday 14:20 Johann-Peter-Hebel

FM10

### Symmetry-breaking bifurcations in T-channel flows: effects of fluid viscoelasticity

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It is well known that, beyond a critical aspect-ratio-dependent Reynolds number, the flow in a three-dimensional T-channel junction, i.e. two-opposing planar channel streams joining and turning through 90 degrees, can break symmetry [1-2]. For the case of two square cross-section inlets and an outlet arm of equal area (i.e. aspect ratio of two) this bifurcation is to a steady asymmetric flow. This flow bifurcation has been proposed as a method of enhancing mixing in microfluidic channels where significant increases in mixing quality are observed beyond the bifurcation. In the current work we investigate numerically the effects of viscoelasticity on this supercritical pitchfork bifurcation. The three-dimensional numerical simulations make use of a finite-volume technique based on the log-conformation formulation [3], together with the high-resolution "CUBISTA" scheme for the convective terms in the momentum and constitutive equations. Results from both the upper-convected Maxwell and Oldroyd-B models, using three consistently refined meshes, show that the instability occurs at lower Reynolds numbers for viscoelastic fluids in comparison to the Newtonian base case. The influence of the Deborah number and solvent-viscosity ratio are analysed. At higher Deborah numbers the transition leads directly to an unsteady flow. A map of flow patterns produced shows demarcation zones for the different flow regimes, i.e. symmetric steady, asymmetric steady and unsteady flow. Knowledge of such zones may prove useful in the design of micro-fluidic chips for enhanced mixing, for example.

[1] Kockmann, N., Föll, C. and Woias, P., 2003. In the International Society for Optical Engineering. San Jose, CA, 2003. SPIE

[2] Poole, R.J. Alfateh, M. and Gauntlett, A.P., 2013. Chem. Eng. Sci. 104 pp 839–848

[3] Fattal, R. and Kupferman, R., 2004. J. Non-Newt. Fluid Mech. 123 pp 281–285

Thursday 14:40 Johann-Peter-Hebel

FM11

### Time-dependent secondary flows of FENE-CR fluids in a curved duct of square cross-section

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Great efforts have been devoted to study time-dependent flows in curved ducts, especially in relation to blood flow in vessels, in order to better understand blood circulation and vascular diseases. Such flows exhibit complex flow patterns, oscillating between one-pair to multiple-pairs of vortices, from symmetric to asymmetric pairs of vortices, and also from stable to unstable flow patterns. Despite all this interest, most studies of unsteady flows in curved ducts have been carried out for viscous incompressible fluids obeying the Navier-Stokes equations, and relatively less attention has been paid to the flow of viscoelastic fluids.

In the present numerical study, we present results of simulations for three-dimensional unsteady laminar flows of viscous and viscoelastic incompressible fluids through a curved rigid duct, in order to better understand the time-dependent developing flows and Dean instabilities. The time development of such a flow along a square cross-section curved duct at 180 degrees will be described in detail, based on numerical solutions with a finite volume method on a collocated mesh arrangement. A fully developed velocity profile is assumed at the entrance

duct to the curve and, due to the possibility having flow asymmetries, the whole geometry is considered in the simulations. The problem is solved for Newtonian viscous fluids and the viscoelastic FENE-CR fluid model, which describes the behaviour of dilute polymer solutions. Numerical simulations were carried out for different Dean and Weissenberg numbers, in the case of the viscoelastic fluid. Velocity and stress profiles are analysed in both space, across the duct square cross-section, and time. Our results reveal stationary and time-dependent instabilities when inertia and elasticity are increased, and show significant variations in the distribution of stress and velocity together with complex secondary flow patterns.

Thursday 15:00 Johann-Peter-Hebel

FM12

### **Fiber spinning under filament pull-out conditions: a stability analysis**

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In wet-spinning, a polymeric fluid is pushed through a spinneret die. Subsequently, the extruded filament is taken up downstream at a higher velocity than the average extrusion velocity and cooled (e.g. in a water bath) to form a solidified fiber. As the take up velocity increases, a periodic variation of the filament diameter can occur beyond a critical draw ratio which is generally referred to as the draw resonance instability. Also, if the fluid strength is sufficiently high, upon increasing the take up velocity or, with an increase of the stretching force, the filament may be pulled out from the extrusion die. At a high Trouton ratio, filament pull-out is the phenomenon where the upstream fluid detaches from the die wall which is known to occur in isothermal solution spinning of silk by spiders as well as solution spinning high performance polymers. This pull-out condition complicates the dynamic stability analysis in the sense that the upstream boundary conditions are no longer constant but depend on the deformation history of the polymeric fluid in the spinning die. Moreover, the upstream boundary conditions depend on the position of the detachment point as the filament length can vary in time.

In this work we determine, and obtain an understanding of, the stability limits in fiber spinning under pull-out conditions. This includes the stability analysis depending on the upstream conditions in the die, i.e. the dynamic contact point when pull-out of the filament occurs. The approach incorporates the full viscoelastic computational analysis of the fiber spinning dynamics where also possible slip phenomena of the melt/solution with the extrusion die wall are taken into account. In addition, we perform experimental validation of our analysis using a well-defined IUPAC-A polymer melt.

Thursday 15:50 Johann-Peter-Hebel

FM13

### **Finite element simulations of the displacement of a thin blade in an elasto-viscoplastic medium**

Giovanni M. Furtado<sup>1</sup>, Fernanda B. Link<sup>1</sup>, Lober Hermany<sup>1</sup>, Sérgio Frey<sup>1</sup>, Mônica F. Naccache<sup>\*2</sup>, Paulo R. de Souza Mendes<sup>2</sup>

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This work investigates the flow around a flat thin blade of finite length as it travels at constant speed in an incompressible elasto-viscoplastic medium. The mechanical model is composed of the usual mass and momentum balance equations, coupled with a modified Oldroyd-B equation that accommodates the dependence of the relaxation and retardation times as well as of the viscosity on the structuring level of the microstructure, represented by the structure parameter field.

The model is approximated by a 2-D stabilized four-field Galerkin least-squares finite-element method in terms of the fields of the structure parameter, the extra-stress tensor, the pressure, and the velocity vector. The influence of the elastic modulus, yield stress and blade velocity on the fields of velocity and pressure, as well as on the fields of the intensities of stress and strain rate is investigated for relevant ranges of these parameters. The field of elastic strain in both the yielded and unyielded regions is also given. Finally, the dependence of the thickness of the yielded region near the blade as a function of the governing parameters is determined.

Thursday 16:10 Johann-Peter-Hebel

FM14

**A numerical investigation of the flow of thixotropic elasto-viscoplastic materials through a planar sudden expansion**Fernanda B. Link<sup>1</sup>, Sérgio Frey\*<sup>1</sup>, Mônica F. Naccache<sup>2</sup>, Paulo R. de Souza Mendes<sup>2</sup>

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Finite element solutions were obtained for the flow of incompressible thixotropic elasto-viscoplastic materials through a one-to-four sudden expansion. The mechanical behavior of the material is described by a recent constitutive model the extra-stress equation of which is a modified Oldroyd-B model possessing structuring-level dependent viscosity, relaxation time and retardation time. The local structuring level is given by the structure parameter, a scalar-valued field that is governed by a kinetics-type evolution equation. The differential equations of the constitutive model are integrated numerically in conjunction with the mass and momentum balance equations using a multi-field Galerkin least-squares (GLS) method that employs as primal variables the structure parameter  $\lambda$ , the extra-stress  $\tau$  and the fluid velocity  $u$  and the isotropic pressure  $p$ . Since the GLS method is immune to the Babuska-Brezzi stability condition, the computational domain is partitioned into equal-order (bi-linear) Lagrangian finite elements, a very attractive feature from the computational point of view. The influence of the thixotropic equilibrium time, elastic modulus, yield stress and flow intensity on the fields of velocity and pressure, as well as on the fields of the intensities of stress and strain rate is investigated for relevant ranges of these parameters. The field of elastic strain in both the yielded and unyielded regions is also given, as well as the topology of the yielded surfaces. The results show that thixotropy postpones the buildup of the microstructure to further downstream locations. Elasticity causes a time delay of the microstructure breakup of the unyielded material that leaves the plug-flow region of the upstream channel, crosses the expansion plane (where high extensional stresses occur) and enters the downstream channel.

Thursday 16:30 Johann-Peter-Hebel

FM15

**Theoretical and numerical analysis of shear banding instabilities in thixotropic fluids**

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The stability of simple shear flows of the class of thixotropic fluids modelled by Coussot et al. [1] is studied both theoretically using a linear stability analysis and by direct numerical simulation using a finite element method.

Asymptotic stability gives analytical criteria on the flow and rheological parameters allowing to predict the onset of shear banding instabilities.

The finite element simulation uses a variational multiscale method for the stabilization of transport and mixed problems and an original anisotropic mesh adaptation method that uses an edged based error with gradient recovery [2]. This method captures accurately the shear banding instability at its onset and is then used to study the nonlinear features of the problem. Extensions to more complex flow geometries will then be presented, showing unexpected flow patterns induced by local shear bands around geometrical singularities of the flow domain.

[1] P. Coussot et al., "Viscosity bifurcation in thixotropic, yielding fluids", J. Rheol., 46 (2002)

[2] T. Coupez, "Metric construction by length distribution tensor and edge based error for anisotropic adaptive meshing", J. Comput. Physics, 230 (2011)

Thursday 16:50 Johann-Peter-Hebel

FM16

**Rheology of Poly lactides: Experiments and Simulations**Evan Mitsoulis\*<sup>1</sup>, Thanasis Zisis<sup>1</sup>, Norhayani Othman<sup>2</sup>, Savvas G. Hatzikiriakos<sup>2</sup>

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Polymers from renewable resources such as polylactides (PLAs) have attracted an increasing amount of attention over the last decades, predominantly due to environmental concerns. In the present work, several commercial PLAs have been rheologically characterized using both a parallel-plate and capillary rheometers. The data has been used

to formulate a K-BKZ constitutive equation to describe their rheology. It has been found that PLAs with  $M_w$  greater than a certain value, exhibit severe slip at the wall during capillary flow. The slip velocity was found to increase with decrease of  $M_w$ . The entrance pressure drop was also measured using capillaries of various diameters and lengths. Numerical simulations based on the K-BKZ constitutive model with slip at the wall gave a good representation of the experimental data and therefore can be used for design purposes in the processing of PLAs.

Thursday 17:10 Johann-Peter-Hebel

FM17

### Active control of convective heat transfer using electrorheological fluids

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Electrorheological fluids (ERF) are suspensions of particles in a nonconducting fluid with a particle-fluid dielectric mismatch. Under the application of an electric field, these suspensions show reversible viscoplastic characteristics. We propose a novel application of ERF in designing a heat transfer switch where by controlling the applied electric field one tunes the heat transfer between the fully convective Newtonian and the purely conductive viscoplastic limit. When the electric field is applied, we use the Bingham model to study convection of viscoplastic fluids in a rectangular cavity with differentially heated sidewalls. When there is no electric field, the Newtonian constitutive law is used. We use computational and analytical techniques to report proof-of-concept results demonstrating the applicability and performance range of the proposed design.

We investigate variation of the flow pattern as yield stress changes and determine the minimum yield stress necessary to maintain a stationary field in a rectangular domain of arbitrary aspect ratio. Transition between the convective Newtonian field and the stationary viscoplastic field, and vice versa, are examined at different values of the dimensionless groups. Using the energy equations, we examine the stability of the stagnant field and show that if the (ER-activated) yield stress is sufficiently large, the kinetic energy decays to zero in a controllable finite time, hence effectively switching to conductive mode.

## Colloids and Suspensions - CS

Organizers: Matthias Ballauff and Moshe Gottlieb

Thursday 13:40 Alfred-Mombert

CS23

### Optical coherence tomography combined with rheological characterization of microfibrillated cellulose suspensions

Anni Sorvari<sup>1</sup>, Sanna Haavisto<sup>2</sup>, Tapio Saarinen<sup>1</sup>, Juha Salmela<sup>2</sup>, Jukka Seppälä<sup>1</sup>, Antti Koponen\*<sup>2</sup>

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Rheology of microfibrillated cellulose (MFC) water suspensions was characterized with a rotational rheometer, augmented with optical coherence tomography (OCT). OCT is a non-invasive technique facilitating fast real-time imaging of the internal structure and velocity of an opaque medium with high temporal and spatial resolution. OCT allows imaging in radial direction from the outer geometry boundary to the inner geometry boundary making both the shear profile and the structure of the suspension visible through the rheometer gap. Thereby an assumed velocity profile can be replaced with an actual, measured one. The aim of this work was to follow the structure of the suspensions in a rotational rheometer during the measurements and observe wall depletion and other factors that can interfere with the rheological results. The measurements were performed using a transparent cylindrical measuring system and combining the optical information to rheological parameters.

MFC suspensions have generally been reported to show strong shear thinning behaviour and flow curves often include a plateau between the low and high shear rate regions. With OCT, it was however evident, that MFC exhibited non-ideal behaviour in the whole shear rate region 0.1-500 1/s used in this study. With low and moderate apparent shear rates (0.1-70 1/s) only a very thin slip layer was being sheared on one or both walls. Outside the slip layer the bulk of the suspension moved as a plug. With higher shear rates (> 70 1/s) the velocity profiles still differed from the ideal one, but in this region the bulk of the suspension exhibited true shear flow. The shear

profile could be divided into three regions starting from the outer wall: 1) A thin wall slip layer where the viscosity of the suspension is close to water. 2) Wall boundary layer where the slope of the velocity profile is higher than in the middle of the gap. 3) The linear region, where the shear rates are 55-70 % smaller than the apparent shear rate.

Thursday 14:00 Alfred-Mombert

CS24

### Shear-induced irreversible breakdown of shear thickening fluids

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Amorphous fumed silica/polypropylene glycol (PPG) suspensions were subjected to multiple steady shear and oscillatory shears above the critical strain rate and critical strain amplitude. After each strain sweep, the steady shear viscosity and oscillatory shear moduli decreased over the entire measured range, and the on-set of shear thickening occurred at increasingly higher critical strain rates or strain amplitudes. Analysis of the oscillatory intra-cycle stress-strain (Lissajous-Bowditch) curves indicated a single-cycle shear thickening occurred at strain amplitudes below the traditionally defined critical strain and only during the first pass. The changes in the material properties appear to be irreversible and are attributed to breakdown of fumed silica-PPG agglomerates. Simultaneous rheology and small angle neutron scattering (RheoSANS) was also used to test this hypothesis. Finally intra-cycle and non-linear responses for fumed silica-PPG on parallel plate and cone and plate were analyzed via the MITlaos package. Although qualitatively similar, differences between the geometries will be discussed.

Thursday 14:20 Alfred-Mombert

CS25

### Evaluation of consolidation of different cement paste by Vicat, oscillatory rheometry and isothermal calorimetry

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In the science of cement and concrete, hydration, setting time and hardening are keywords related to the main properties of the hydraulic binder. Hydration is the chemical process in which hydrates are formed from the contact of the anhydrous cement with water. The setting time is the time corresponding to the transition of the fluid state of the slurry to a more rigid state and hardening involves increasing the strength of the material and depends on the physico-chemical parameters with degree of hydration, water-cement ratio, curing condition, etc. Thus, correlating between techniques for the measures is very important for understanding the phenomena involved in hardening, this being the main goal.

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[2] Romano, R. C. O., Liberato, C. C., Montini, M., Gallo, J. B., Cinotto, M. A., Pileggi, R. G. Evaluation of transition from fluid to elastic solid of cementitious pastes with bauxite residue using oscillation rheometry and isothermal calorimetry. *Applied Rheology*, 23:2 (2013) 23830

Thursday 14:40 Alfred-Mombert

CS26

### Monitoring of transition from fluid to solid state of cementitious suspensions with bauxite residue

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The cement hardening is resulting of chemical and physical changes after mix the binder in water. While the chemical reaction may be monitored by isothermal calorimetry, the physical changes may be continuously accompanied by oscillatory rheometry. Thus, the relationship between the results may help to understand the main phenomenon that is responsible to the hardening. In this work were evaluated the changes during the transition from behavior of viscous fluid to elastic solid of compositions formulated with Portland cement and bauxite residue - BR - used in partial substitution of cement. The results show that there were different interactions between the kind of binder and the residue resulting in microstructural changes: BR accelerates the cement hydration reaction, but in pastes with

pure cement, consolidation was faster, showing a distinct effect on the fluid-solid transition.

[1] Banfill P, Frias M: Rheology and conduction calorimetry of cement modified with calcined paper sludge. *Cement Concrete Res.* 37 (2007) 184 – 190

[2] Romano, R. C. O., Liberato, C. C., Montini, M. Gallo, J. B., Cincotto, M. A. Pileggi, R. G. Evaluation of transition from fluid to elastic solid of cementitious pastes with bauxite residue using oscillation rheometry and isothermal calorimetry. *Appl. Rheol.* 23 (2013) 23830

Thursday 15:00 Alfred-Mombert

CS27

### Negative first normal stress differences and microstructure in flocculated kaolin suspensions

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Aqueous suspensions of kaolin show negative first normal stress differences  $N_1$  as nonlinear response to steady shear. The magnitude of  $N_1$  depends on shear rate, kaolin volume fraction, pH and ionic strength. Thereby, the zeta potential and thus the interparticle interactions are adjusted. For flocculated suspensions with a volume fraction of 0.2, the shear rate dependence of  $N_1$  is characterized by a minimum of -200 Pa at intermediate shear rates. This unusual viscoelastic behavior is caused by shear induced changes of the microstructure of the suspension.

In order to gain insight into the suspension microstructure after steady shear, an experimental cryotechnique was developed. The method comprises shear load, sample freezing and ex-situ X-ray diffraction of frozen suspensions. Using the intensity ratios of the characteristic 001 and 060 X-ray reflections of kaolin, the average orientational order is described as a function of previously applied shear rate. Plotting  $N_1$  versus shear rate, a minimum of  $N_1$  corresponds to a minimum of the intensity ratio. In this case, the microstructure with lowest order causes the maximum of  $|N_1|$ . Increasing the kaolin volume fraction by 2 % approximately doubles the intensity ratio at a given shear rate. The intensity ratios are discussed in terms of volume fraction (ranging from 0.2 to 0.5) and pH (3.7 to 13.5).

Thursday 15:50 Alfred-Mombert

CS28

### Shear-induced migration in noncolloidal suspensions

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Suspensions of noncolloidal particles in Newtonian fluids develop normal stress differences[1], which come from the anisotropic microstructure due to direct contact interactions between the particles. A related phenomenon is the development of volume fraction inhomogeneities under shear. Indeed, a diphasic description of the suspensions attributes shear-induced migration to the gradients of the normal stresses exerted on the particle phase alone[2]. This problem has been partially investigated in the literature[3,4], but almost no information is found on its kinetics. Moreover, the behaviour of materials previously studied is not well-known due to problems recently highlighted: the viscosity divergence is not well characterized unless local methods are used[5]; different divergence properties are found in systems that look similar[1,3,5,6]; accurate measurements of normal stresses have emerged only recently[1,6]. We perform a complete study on a fully characterized unique system (same as[1]), and we develop methods to investigate the kinetics of migration. Suspensions of volume fraction ranging from 6 to 56%, initially homogeneous, are sheared in a wide gap Couette geometry at constant cylinder rotation velocity. Velocity and concentration profiles are measured as a function of time with MRI techniques, while inhomogeneities develop. We show that the amplitude of the inhomogeneities is always smaller, and that the migration kinetics is always faster, than expected from the model of migration based on the suspension normal stresses (as usually assumed [4]). We propose an expression of the particle normal stresses as a function of the particle volume fraction that allows accounting for our observations.

[1] Boyer et al., *J. Fluid Mech.* (2011) ; *Phys. Rev. Lett.* (2011).

[2] Nott et al., *Phys. Fluids* (2011).

[3] Phillips et al., *Phys. Fluids* (1992).

[4] Morris & Boulay, *J. Rheol.* (1999).

[5] Ovarlez et al., *J. Rheol.* (2006).

[6] Dbouk et al., *J. Fluid Mech.* (2013).

Thursday 16:10 Alfred-Mombert

**Non-colloidal Suspensions: The Relation Between Theory and Experiment in Shearing Flows**

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This paper considers the relation between theory, computation and new experiments in noncolloidal suspensions with Newtonian and viscoelastic matrices in shearing flow.

There are puzzles posed by the normal stresses in sheared suspensions. For a suspension with a Newtonian matrix in a simple shear flow various workers have found experimentally that the stress field is no longer a shear stress plus an isotropic pressure, and that both first and second normal stress differences ( $N_1$  and  $N_2$ ) occur and are negative. Our own experiments using an open semi-circular trough to find  $N_2$  agree reasonably well with the Zarraga et al. paper (2000) and the Brady-Morris theory of 1997. However, this theory predicts that  $N_1$  is zero, whereas it is measured to be negative and smaller in magnitude than  $N_2$ . The viscosity  $\eta$  and the normal stress functions ( $N_1$ ,  $N_2$ ) for non-colloidal suspensions of spheres in a Boger fluid matrix were also measured. Volume fractions ( $\Phi$ ) of 5, 10 and 20% were investigated. The relative viscosity ( $\eta_R = \eta/\eta_0$ ) and the (positive) first normal stress difference  $N_1$  showed increases with  $\Phi$  which were larger than the dilute suspension theory predictions of  $(1+2.5\Phi)$ , indicating semi-dilute suspension behaviour, even down to 5% concentration. The main interest centres on the second normal stress difference  $N_2$ . The matrix fluid showed a zero second normal stress difference, and the measurements showed that  $N_2$  was always negative for the suspensions. This agrees with the dilute suspension theoretical prediction found using the Landau-Lifschitz averaging procedure, but not with the ensemble averaging method, which predicts a positive  $N_2$ . The reason for this predictive failure is not known.

For larger concentrations (up to 0.4) the second normal stress difference was always negative. However, we saw a switch from a positive  $N_1$  to a negative value when the volume fraction exceeded 0.3, similar to the results of Aral and Kalyon (1997).

Thursday 16:30 Alfred-Mombert

**Autolubricated Flow and Transient Flow Phenomena**

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The theory of autolubricated flow for concentrated suspensions and pastes is based on the idea that a layer of suspension liquid, between the bulk and wall, thickens with increasing wall shear stress (Gleissle, AERC 2005). The growing slip layer thickness lessens the increase of the flow resistance with increasing slip velocity. The autolubricated flow theory predicts apparent transient flow properties because of a new arrangement of the slip layer if the flow conditions change. A stepwise increase in the speed of a rotational rheometer generates a sudden increase of the torque. Afterwards, the torque decreases over time as a consequence of the growing slip layer thickness. Thereby, the wall shear stress is reduced. If there is no information about the material's slip behaviour, such shear stress - time functions are often misinterpreted as thixotropy. Therefore, we called this phenomenon "pseudothixotropy", which is caused by a change of the slip layer thickness and not by the change of the internal structure of the material.

Wall slipping materials show pseudothixotropic effects even in capillary flow experiments. A volume rate step in a capillary rheometer shows a pressure maximum and then fading pressure over time until stationary value; the stationary slip layer thickness along the whole capillary is reached.

The pressure drop distribution has been measured for a paste in the region of pure bulk flow with a series of pressure transducers mounted along the axis of a slit capillary. This experiment shows that the local pressure drop decreases from the capillary entrance to the exit. The decrease of the pressure drop is caused by an increasing slip layer thickness from the entrance to the exit as the extrusion velocity is constant along the capillary.

Thursday 16:50 Alfred-Mombert

CS31

**Interplay Between Discontinuous Shear Thickening and Migration in Concentrated Cornstarch Suspensions**Abdoulaye Fall\*<sup>1</sup>, François Bertrand<sup>1</sup>, Daniel Bonn<sup>2</sup>, Anaël Lemaitre<sup>1</sup>, Guillaume Ovarlez<sup>1</sup>

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The mechanisms controlling the rheology of concentrated cornstarch suspensions in their discontinuous shear thickening regime are investigated experimentally. We use a Magnetic Resonance Imager (MRI) to measure the local velocity and particle volume fraction profiles in a Couette flow. We show that, when the imposed rotation rate is below a critical value, i.e. before the shear thickening regime, the system flows homogeneously and the particle volume fraction remains constant in the gap. However, as soon as we go slightly beyond the critical rotation rate, the velocity profiles are strongly localized. Upon increasing the rotational velocity in the shear-thickening regime, the thickness of the sheared region then grows until it reaches a final size (smaller than the gap). We also show that this happens because a strong and fast gradient in particle volume fraction develops in the gap. The volume fraction in the jammed region (near the outer cylinder) is then found to be close to the maximum packing fraction of the assembly of cornstarch particles. By contrast, the volume fraction in the flowing region (near the inner cylinder) is found to be close to its loose packing, for which the suspension's local behavior is close to that of a Newtonian material. This finally yields a state diagram for the flow behavior of cornstarch suspensions as a function of the particle volume fraction: at the local state, the material is always either in a fluid state or in a jammed state. This is reminiscent of recent numerical results of Seto et al. [Phys. Rev. Lett. 111, 218301 (2013)]

Thursday 17:10 Alfred-Mombert

CS32

**Study of maximum volume fraction of particles of inert suspensions**

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The variation of solids promotes changes in the rheological properties of suspensions which are modeled applying different theories. In this work, the main hypothesis considers that, in the system, only hydrodynamic forces and Brownian motion act on the particles, in other words, powders are treated as inerts. In many models, the relative viscosity ( $\eta_r$ , ratio of the viscosity of a solution to the viscosity of the solvent) are related to volume fraction of particles ( $\phi$ ). The concept of maximum volume fraction of particles ( $\phi_{max}$ ) is introduced. However, it is difficult to measure this parameter and for several times not given due attention, adopting a common value for all suspensions. Therefore, this study aims to evaluate the rheological properties of suspensions varying volume fraction of particles and the properties of the liquid medium to achieve optimize suspension with high solids content using the concepts of dispersants and packing of particles.

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**Viscoplasticity and Granular Media - VP**

Organizers: Philippe Coussot and Igor Emri

Thursday 13:40 Clubraum

VP1

**Buoyancy effects on micro-annulus formation in primary cementing of oil and gas wells**Marjan Zare<sup>1</sup>, Ian A. Frigaard\*<sup>1,2</sup>, Ali Roustaei<sup>1</sup>, Sarah Hormozi<sup>3</sup>

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In primary cementing of oil and gas wells, to provide complete and permanent isolation of the formations behind the casing, drilling mud must be fully removed from the long narrow annulus, and the annular space must be completely filled with the cement slurry. Due to the rheology of the displaced drilling mud it is relatively common that a thin

layer of this fluid is left attached to the walls – a so called micro-annulus. On setting, the cement dehydrates the micro-annulus leaving a porous dried mud channel that can allow gas to migrate. The objective of this study is to understand the formation of micro-annuli, by studying the displacement flow along a longitudinal section of the annulus, i.e. a plane channel. We study the thickness of residual wall layers in the density-stable miscible displacement of a Bingham fluid by a Newtonian fluid along a plane channel, i.e. the denser fluid displaces the lighter fluid in the upward direction. The flow is non-dimensionalized and described in terms of four dimensionless parameters: the Bingham number ( $B$ ), viscosity ratio ( $m$ ), Reynolds number ( $Re$ ), and Froude number ( $Fr$ ). Our results indicate that a more effective displacement is achieved when the displacing fluid is more viscous than the displaced fluid ( $m < 1$ ). At larger  $Re$ , the residual layer thins and consequently the efficiency of the displacement improves. We observe interesting dispersive flows in a cap region ahead of the propagating front, sometimes forming into spikes that advance ahead of the main front. Interfacial instability occurs at large values of  $Re/Fr$ , i.e. when the ratio of buoyancy forces to viscous forces is high, and provided  $m=1$ . These instabilities result in improved displacement efficiency, sometimes completely removing the Bingham fluid from the channel walls. By keeping  $Re/Fr$  large and constant, while decreasing  $Re$ , the instabilities grow faster, while by increasing  $Re$ , inertia appears to slow the growth of instability. In addition, at larger  $B$ , the displacement front tends to become increasingly uniform (plug-like). This tends to decrease the cap region in some instances and flattens the displacement front profile in other instances.

Thursday 14:00 Clubraum

VP2

### Challenges on measuring the yield-stress of waxy crude oils

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Production in reservoirs located in deep and ultra-deep water that contain waxy crude oils faces a huge obstacle imposed by the low temperatures of the environment. When the waxy crude oil is subjected to a temperature below the gelation temperature, as in the case investigated in the present work, it exhibits a variety of non-Newtonian features: elasticity, plasticity, viscous effects, and time-dependency, which renders to this material a highly complex behavior. A crucial feature that is frequently ignored when the determination of the yield stress is being carried out is the time-dependency nature of these materials. We demonstrate that this character has a significant impact on the measurement of the yield stress and, therefore, values obtained from a protocol that neglects time-dependency can be substantially different. Other distinct aspects of the measurement procedure that need a special attention are slippery, sample evaporation and shear banding.

Thursday 14:20 Clubraum

VP3

### Flow Behavior of Waxy Oils: from Local Rheology to Pipelines

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Transporting waxy crude oils through long pipelines at low temperatures may be challenging due to specific rheological properties created by its paraffinic components. This type of fluid has not only the classical yield stress, shear thinning and thixotropic characteristics but its rheological behavior also depends on the flow and thermal history. In order to evaluate those characteristics and better understand the pipeline flow with those oils, MRI velocimetry tests were performed with an equivalent model fluid with macroscopic behavior analogous to waxy crude oils, but at higher temperatures closer to the ambient one. This local flow data associated with stress measurement give information on the effective fluid properties unaffected by flow heterogeneities.

The model waxy crude oil flow in a 2 cm gap Couette geometry was measured for cooling under different shear conditions and then for various transient flow scenarios at constant temperature. It allowed mapping classical reversible thixotropic behavior towards the steady state behavior but also an effective flow curve evolution, associated with irreversible fluid structure changes depending on the shear history.

Flow heterogeneities were also measured in transient processes as flow restart or other velocity changes. Those heterogeneities are effects which likely play a significant role in pipeline flows and these specific features should be taken into account in mathematical models that intend to represent those transient flow conditions.

Thursday 14:40 Clubraum

VP4

**General aspects of yield stress fluids – Terminology and definition of viscosity**

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A lot of materials behave viscoplastic. A subset of viscoplastic materials is the class of viscoplastic liquids, called yield stress fluids. Here, general aspects of yield stress fluids with significance for practical phenomenological material modelling are discussed theoretically [1].

In this sense, a terminology is introduced so that the material class "yield stress fluid" is defined and can be distinguished from the terms "solid" and "liquid". This material classification is based on two criteria, the equilibrium relation and the flow function. In line with this terminology, an experimental procedure for classifying the material behaviour is presented. The equilibrium relation is introduced in terms of Haupt [2] and is based on an additive split of the total stress into an equilibrium stress and overstress. The working principle of the classification is illustrated by rheological elements of each class. A classification into the class of liquids is shown by the Maxwell element. The handling for solids is explained by a parallel connection of a kinematic hardening model and a Maxwell element. The class of yield stress fluids is represented by a parallel connection of the Prandtl element and the Maxwell element. [1]

The second key aspect of this contribution is a discussion on the proper definition of the term viscosity. The benefit of the differential viscosity over the dynamic viscosity in case of non-Newtonian fluids in general is worked out. This is shown by the most elementary yield stress fluid, the friction element, because it is the basis of the yield stress concept. Its constitutive equations are prepared for positive as well as negative strain rates and are also able to represent the preyield behaviour. [1]

[1] M. Boisly, M. Kästner, J. Brummund, V. Ulbricht; General aspects of yield stress fluids – Terminology and definition of viscosity, Applied Rheology 24 (2014) 14578

[2] P. Haupt; Continuum Mechanics and Theory of Materials (2002), Springer

Thursday 15:00 Clubraum

VP5

**Numerical modeling of thixotropic and viscoelastoplastic materials in complex flows**Michael F. Webster\*<sup>1</sup>, J. Esteban Lopez-Aguilar<sup>1</sup>, Alaa H. Al-Muslimawi<sup>1</sup>, Hamid R. Tamaddon-Jahromi<sup>1</sup>, Octavio Manero<sup>2</sup>

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This study is concerned with the modelling of thixotropic and viscoelastoplastic material systems using: (i) a new micellar viscoelastic-thixotropic model (solute viscoplastic-viscosity); and (ii) coupling this to a Papanastasiou–Bingham model (solvent viscoplastic-viscosity). The thixotropic model introduces a network-structure construction/destruction kinetic equation that dynamically links to fluidity evolution. Two steady-state complex flow problems are studied, axisymmetric rounded-corner 4:1:4 contraction-expansion flow and extrusion flow. In the former case, enhanced pressure drop, stress fields and vortex dynamics are analysed; whilst under extrusion, attention is paid to the swelling ratio, exit pressure loss and flow response. These flows have importance in industrial oil-reservoir recovery and the plastics industry, biological and food flow applications, typically provoking thixotropy, yield stress and shear banding. To obtain low solvent-fraction solutions, both micellar and EPTT constitutive equations have been amended by (a) taking absolute values of the driving f-functional (physical and thermodynamical consistency argument ( $f \geq 1$ ); dissipation function-micellar, related explicitly and inversely with the viscosity;  $\text{trace}(\tau)$ -PTT), and (b) with a change of stress variable,  $\Pi = \tau_p + (\eta_{p0}/\lambda_1)I$ , that prevents loss of evolution in the underlying initial value problem. A boundary condition is imposed at the centreline, for which the shear gradients vanish identically. As a consequence, highly non-linear solutions are now attainable, given at impressively high We and low solvent-fractions. Here, simulations are performed with a novel hybrid algorithm, in which a finite volume scheme is utilized to solve the constitutive equation, whilst finite elements deal with the continuity and momentum equations, in an incremental pressure-correction time-stepping structure.

Thursday 15:50 Clubraum

VP6

**Simulations of yield stress fluid flows : a novel optimization technique**

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In this work, the numerical simulation of steady yield stress fluid flows is considered. Existing techniques for treating the non-smoothness of the yield term can fall into two categories: regularizing methods (e.g. Papanastasiou model) and non-regularizing methods. Non regularizing methods rely on a variational formulation so that the velocity field is found as the minimum point of a convex non-smooth functional under linear constraints. Due to the combined presence of non-smoothness and derivatives, such problems are challenging to solve efficiently and have led to the development of specific numerical techniques such as the augmented Lagrangian approach.

The present work proposes to use a different numerical tool, namely second-order cone programming (SOCP) solvers, to solve the minimization problems arising in the variational formulation of non-regularizing methods. In particular, the variational problem is discretized using the finite element method and formulated as a conic optimization problem. Extremely efficient solvers (like the Mosek software package) are dedicated to this specific class of problems and can solve large-scale models in extremely reasonable computing times on a standard computer. Hence, contrary to the augmented Lagrangian approach, the constraints are not relaxed in the objective function and it is, therefore, unnecessary to discretize explicitly stresses and other Lagrange multipliers fields. The proposed formulation has, thus, the advantage of preserving the true visco-plastic nature of the fluid and offering a very interesting numerical performance to tackle complex problems compared to standard techniques. The method will be validated on classical benchmark examples (capillary flow, lid-driven cavity) and confronted to some experimental results as well including flows in model pores and flows induced by the displacement of a plate in a yield stress fluid bath.

Thursday 16:10 Clubraum

VP7

**Why do some simple flows of Carbopol gels remain elusive?**

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Carbopol gels are often referred to as 'ideal' or 'model' viscoplastic materials which exhibit a well-defined solid-fluid transition, are non-thixotropic and whose deformation states can be accurately described by the Herschel-Bulkley model. Several recent and rather simple hydrodynamic experiments unequivocally indicate that this picture is not universally valid. As a first example, I will refer to the slow and uniform motion of a solid object within a Carbopol gel and emphasize two flow features that are incompatible with the Herschel-Bulkley formalism: breakdown of the fore-aft symmetry, negative wake. As a second example, I will focus on a laminar unsteady pipe flow of a Carbopol gel and emphasize that the flow states are generally irreversible upon increasing / decreasing forcing and the degree of this irreversibility is directly related to the degree of the flow steadiness. As a third example I will illustrate the slow flow of a plate uniformly withdrawn from a bath filled with a Carbopol gel with a particular focus on the role of elasticity and the emergence of the negative wake phenomenon. As none of these three rather elementary flow problems can be sought within the classical Herschel-Bulkley framework, a simple model accounting for both the elasticity and the coexistence between solid and fluid behaviours near the yield point will be proposed and tested. In closing (and if time permits) a Gibbs field microscopic yielding picture inspired from the 2d Ising model for magnetization which reinforces in a thermodynamically validated manner the macroscopic model will be presented.

Thursday 16:30 Clubraum

VP8

**Suitability of the Ree-Eyring approach to describe yielding of polymer glasses**

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This paper focuses on the dynamic yielding of glassy polymers. Particularly, the dependence of the yielding behavior on the applied deformation rate and on the temperature is of interest. Different approaches have been used to describe these dependencies, e.g. the models of Argon [1], Richeton et al. [2], Eyring [3, 4] and its extension to

multiple processes by Ree and Eyring [5, 6], and the theory of Schweizer et al. [7, 8]. Earlier, these models were tested versus experiments by studying the deformation rate- and temperature-dependence of the yield stress [9-11], where in several cases the suitability of the Ree-Eyring approach was demonstrated. Recently, the Eyring theory [3, 4] has been criticized as to not represent characteristic features of experimental yield stress data appropriately [7, 8]. In this paper, the major points of criticism are addressed, most of them being resolved with the help of the Ree-Eyring approach [5, 6]. Particularly, the following points are discussed: the apparent dependence of the activation volume on stress, strain rate, and temperature, and the change in strain-rate dependence of yield stress upon cooling. In line with literature, PMMA is used as a prototype example.

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[3] H. Eyring, *J. Chem. Phys.*, 4, 283-291 (1936).

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Thursday 16:50 Clubraum

VP9

### Viscoelasticity of vibrated granular suspensions

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The mechanical properties of suspensions of non-Brownian particles with dimensions above a few microns control numerous natural phenomena such as landslides or debris flows and are of prime importance in a wide range of industrial applications. These materials are jammed at rest and a finite small perturbation induced by external shear or vibrations for example can cause the system to flow. In that context, we propose a model able to predict the rheological response of saturated dense gravitational suspensions subjected to vibrations and shear to stationary and non stationary mechanical solicitations. This model is based on the same phenomenological two state approach related to the bimodal character of chain forces used to predict the rheological response of a vibrated dry granular system [Marchal et al 2013]. In the dry case, the total shear stress is proportional to the frictional stress. In the case of granular suspensions, a supplementary viscous stress is added to the frictional stress to take into account the influence of the interstitial fluid viscosity. The resulting differential constitutive equation, relating stress to strain, is then able to predict the rheological response to stationary and non stationary solicitations, in linear and non linear regimes, with and without vibrations, for both granular suspensions and dry granular materials. The "dry" case may be regarded as the limit of the "saturated" case when the interstitial fluid viscosity tends to zero. The consistency of the model was tested by comparing experimental rheological measurements with the predictions derived from the differential equation. Despite its simplicity, since it involves only four independent parameters, the model is in very close agreement with experiments. Moreover, within experimental errors, the values of these parameters are independent of the type of test used to determine them, evidencing the self-consistency of the model.

Thursday 17:10 Clubraum

VP10

### Breaking Size-Segregation Waves in Granular Avalanches

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We experimentally prove the existence of the theoretically predicted breaking size-segregation wave within a binary granular avalanche. This complex structure involves the recirculation of particles through a pattern of shocks and rarefaction waves, and causes large particles to accumulate at the avalanche front and small particles in the tail.

Using the non-intrusive imaging technique of refractive-index matching we study particle-size segregation inside the flow (but) far from the sidewall on an inclined moving-bed channel. In this configuration the bottom layers of the flow are dragged upslope while upper layers are avalanching downslope due to gravity; effectively, the flow remains stationary in the reference frame of the observer. This allows us to time-average discrete particle positions in the steady-state flow and arrive at a continuous particle concentration. The measured particle concentration and particle trajectories match qualitatively with the theoretical predictions.

## Advances in Rheometry - AR

Organizers: Maik Nowak and Thomas Schweizer

Thursday 13:40 Forum I

AR6

### Orthogonal superposition (OSP) of small strain oscillation shear on steady or oscillation shear in a rotational rheometer

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Many simultaneous techniques are being used to follow structural changes in materials as a result of an imposed shear deformation. Orthogonal superposition, first mentioned by Philippoff in 1934 is a mechanical technique and uses a small amplitude oscillation shear applied orthogonal to a shear flow. In contrast to parallel superposition, the flow fields are not coupled and the orthogonal storage and loss moduli only measure the effect of shear on the microstructure. OSP has been implemented in the ARES-G2 by modifying the transducer to apply a small oscillatory displacement in normal direction, while the actuator of the rheometer performs the transient or oscillatory rotational shear deformation. The normal force transducer in this case applies the orthogonal deformation and records the force. The dynamic moduli, complex viscosity and phase are determined using the embedded instrument correlation technique. The flow cell used to apply the rotational and linear axial shear simultaneously is a modified double wall cylinder with an opening at the bottom to avoid annular pumping and windows at the top to eliminate surface tension effects.

An additional benefit of the OSP option is the capability to perform tension on thin films and fibers as well as compression and bending on bulky test specimen. With the OSP option the rheometer is capable to perform the following additional test modes: 1. Small linear strain orthogonal oscillation superposed on rotational steady shear; 2. Small strain orthogonal oscillation superposed on rotational oscillation at the same frequency with varying amplitude ratio between axial and rotational oscillation shear; 3. Standalone small axial displacement oscillations. Test results will be presented showing the changes in the orthogonal viscoelastic properties as a function of the applied rotational shear and how to perform quantitative measurements of shear induced anisotropy in gels using 2D oscillation experiments.

Thursday 14:00 Forum I

AR7

### An enhanced rotational rheometer system with two motors

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Recently, a new rheometer concept based on two air bearing supported electronically commutated (EC) synchronous motors was introduced, which represents a large step in rheometer development and extends the capabilities of a rotational rheometer dramatically. The combination of two motors into one rheometer system offers increased sensitivity and many new testing capabilities not possible before. Three completely different testing modes such as combined motor transducer (CMT), separate motor transducer (SMT) and counter rotation are available in one single rheometer system. It combines two EC motor units in a modular setup: The upper motor is integrated in the rheometer head as in a standard rheometer motor, whereas the lower motor can be extracted for the CMT mode and integrated for SMT and counter rotation modes, respectively. The lower motor can be exchanged much like an accessory system of a standard rheometer.

In the counter-rotation test mode the motors are set to rotate in opposite directions. The pre-set speed is divided and shared by the two motors, whereas the torque and normal force are measured at the upper motor unit. This

mode is an invaluable option for microscopy applications by creating a stagnation plane allowing the observation of the structure elements of the sample during shear. Further typical applications of the counter rotation mode are extensional rheology and the investigation of flow instabilities under different shearing conditions.

In the SMT mode the upper motor is kept at a fixed position and operated solely as a torque transducer, while the lower exclusively functions as a drive unit. In this way the new device is turned into an enhanced separate-motor-transducer rheometer for rotational and oscillatory tests at a wide measuring range down to extremely low torques and normal forces.

The aim of the paper is to present a variety of examples of the new measurement capabilities.

Thursday 14:20 Forum I

AR8

### **Advances in the Rheological Characterization of ER Fluids**

Carlos Gracia Fernández<sup>\*1</sup>, Aly Franck<sup>2</sup>, Aadil Elmoumni<sup>2</sup>

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Electrorheological fluids are suspensions of extremely fine non-conducting particles in an electrically insulating fluid, which show dramatic and reversible rheological changes when the electric field is applied. These changes in apparent viscosity can be up to five decades in magnitude and the suspensions can go from the consistency of a liquid to that of a solid, and back, with response times on the order of milliseconds. Both DHR and ARESG2 Instruments (TA Instruments), allows the capability of applying an electrical field coupled with the rheological measurements. The flexibility in applying a wide range of voltage profiles on ER suspension allows for characterizing the dynamics occurring during the formation and destruction of the structure. One-dimensional percolation induced by an external electrical field was conveniently identified by means of a multi-frequency rheological test performed with simultaneous application of an increasing electrical field. The use of multi-wave setup allowed applying simultaneously several frequencies and, thus, accurately determining the threshold voltage as the crossover point of  $\tan \delta$  traces at different frequencies. It was visually confirmed that the percolated structures are aligned in the rotation axis of the testing plate. The effect of voltage on the rheological properties was related to that of temperature, allowing constructing a master curve by assuming a time-voltage superposition (TVS) relation. The usefulness of the axial force to track the effect of the voltage on the percolation process is demonstrated. It is also confirmed that the axial force increases when decreasing the gap following a logarithmic trend.

Thursday 14:40 Forum I

AR9

### **Advanced Dynamic Mechanical Thermal Analysis (DMTA) an interdisciplinary tool in industry and research**

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The modern DMTA controls many environmental and load parameters experimentally, acquires and analyses data precisely and presents the results comprehensively. Increased dynamical loads (several thousand Newton) abolish sample size restrictions and the dual load constructions allow very large strains. The test temperatures (-150 °C to +1500 °C) and heating methods (UV or conventional) fit to most needs, the chamber atmosphere and humidity may be controlled exactly. Environmental influences on real parts are realized in-situ in the DMTA test chamber e.g. as immersion systems. Large working spaces facilitate the use of standard (e.g. bending, shear compression, tensile) but also user defined sample holders. Standard test routines like time, temperature, frequency and humidity sweeps fulfill common application needs, but more specialized applications are possible, too. The determination of non-linear material behavior requires sufficient load and the harmonic analysis of the material response function (Fourier Analysis). In this case the hysteresis representation is an option to visualize the non-linear material behavior very clearly. Vice versa the harmonic synthesis of exciting signals can be applied to generate material responses of well-defined shape even for non-linear materials. This leads to the pulsed DMTA (P-DMTA) and the method of predictive testing which gained importance in industry. One of the recent DMTA advances is the simultaneous dynamical mechanical and dielectric analysis (DEA/DMTA) within the same material state (DiPLEXOR). The influence of well-controlled physical parameters (e.g. time, temperature, humidity, load, ...) on the dielectric behavior of test samples can be monitored simultaneously with the associated mechanical properties. References subjected to polymers, rubbers, foams, resins, food etc. shed light on the interdisciplinary applicability and experimental flexibility of the modern Dynamic Mechanical Thermal Analysis methods.

## Microfluidic and Microrheology - MR

Organizers: Moncia Oliveira and Anke Lindner

Thursday 15:00 Forum I

MR1

### High frequency dynamics of a liquid crystalline, cyanobacterial, sulfated polysaccharide studied by DLS/DWS microrheology

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Recently we have extracted a novel polysaccharide “sacran” from a freshwater unicellular cyanobacterium, *Aphanothece sacrum*. This polysaccharide, containing carboxylate and sulfonate groups, has an extremely high molecular weight (more than  $10^7$  g/mol). Sacran has gelation properties binding efficiently with various heavy metal ions. Aqueous solutions of sacran form huge domains of liquid crystals at very low concentrations ( $\leq 0.5$  %), suggesting high rigidity of this polysaccharide which self-orientates. Sacran can be regarded as a good model of micro-scale rigid molecules but its rheological analyses by conventional techniques are limited due to the accessible frequency range. Here we studied microrheological properties of aqueous sacran solutions by dynamic light scattering (DLS) and diffusing-wave spectroscopy (DWS).

Polystyrene particles of 2 microns were used as probes. The mean square displacement of the particles was calculated from DLS and DWS autocorrelation functions. The complex modulus was calculated by using the generalized Stokes-Einstein relation with the inertial effect correction. The dynamic shear moduli measured by microrheology show good agreement with those measured by classical mechanical rheometry.

High frequency rheological properties accessible only by these microrheological techniques were characterized as a function of the frequency and the sacran concentration. We found Zimm-Rouse mode showing  $G^* \approx C^1 \omega^{5/9}$  as well as bending mode of the rigid polymer chain showing  $G^* \approx C^1 \omega^{3/4}$ . The persistence length,  $l_p$ , was determined from the transition frequency of the two modes. The value of  $l_p$ , showing slight concentration dependence, can be explained by Odijk-Skolnick-Fixman theory, giving the intrinsic persistence length of 50 nm. The interchain distance was measured from high frequency dielectric relaxation of counterion. We found that at higher concentration the entanglement length was shorter than  $l_p$ , showing  $G^* \approx C^{1.4}$ .

Thursday 15:50 Forum I

MR2

### Recent trends in diffusing wave spectroscopy based microrheology

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Diffusing Wave Spectroscopy (DWS) is an optical microrheology technique and has been applied successfully to several colloidal model systems like micellar polymer solutions and micro-gel systems. It is a fast and contact-free technique where the sample dynamics can be probed down to sub-nanometer resolution. These advantages allow time dependent measurements at high temporal resolution on highly viscous systems. As a result this technique is ideally suited to study aggregation and stability behavior of complex and concentrated systems. We present here some studies on Xanthan stabilized emulsions that illustrate the good quantitative agreement between DWS microrheology and bulk rheology. Finally, I will show that DWS microrheology can be applied in a qualitative manner to monitor complex industrial processes such as drying of films or emulsion preparation.

## Thursday 16:10 Forum I

MR3

**Measuring the solutions' relative viscosity with optical tweezers without Fourier transform**Manlio Tassieri\*

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Since their first appearance in the 1970s, optical tweezers (OT) have been extensively developed and have proved to be an invaluable tool for a variety of applications throughout the biophysical sciences. In the field of microrheology, OT are considered as exceptionally sensitive transducers able to resolve pN forces and nm displacements, with high temporal resolution. It has been shown [1] that they can be adopted to evaluate the linear viscoelastic properties (LVE) of rare or precious materials, such as those employed in biomedical studies [2, 3]. The materials' LVE properties can be calculated by means of the Fourier transform of time-averaged quantities (e.g. mean-squared displacement) derived from the analysis of the trajectory of an optically trapped bead suspended into the fluid of interest. Nevertheless, I wish to demonstrate that an important rheological parameter like the solutions' relative viscosity can be evaluated graphically via a direct/visual analysis of the particle normalised position autocorrelation function graph; without the need of Fourier transform. The advantage of the proposed method becomes evident when it is adopted for determining the materials' molecular weight by means of their intrinsic viscosity. The method has been validated by a direct comparison with conventional bulk rheology methods and it has been applied to study both synthetic and biological samples.

[1] Tassieri M. et al. *New J. Phys.* 14, 115032 (2012)[2] Robertson E.J. et al. *J Infect Dis.* (2013)[3] Watts F. et al. *J. Opt.* 16, 015301 (2014)

## Thursday 16:30 Forum I

MR4

**Using optical microrheology and microfluidic flows to extend the rheological characterization of complex fluids into high frequency and high shear rate regimes**John Duffy\*<sup>1</sup>, Steve Carrington<sup>1</sup>, Samiul Amin<sup>2</sup>

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Complex fluids are ubiquitous across a range of industrial and consumer sectors, with common examples being inks, paints, drilling fluids, cosmetics, personal care products and foodstuffs. The processing and product functionality attributes of such materials are often dependent on their rheological response and are inherently linked to the underlying microstructure, specifically in relation to the relevant process time or rate. Since microstructural rearrangement can occur on different length scales and over a wide range of timescales, multiple rheometric techniques are often required to fully characterise the material response. For example to evaluate the properties of an inkjet formulation in relation to its jetting performance, the behaviour at high frequency (short timescales) and high shear rate is most critical. For evaluating product stability attributes and resistance to sedimentation of the same ink formulation, its behaviour at low frequencies (long timescales) and shear rates (or stresses) is most relevant.

In relation to the above, the use of polymer solutions as model complex fluids has been studied using a combination of rotational rheometry, DLS microrheology and microfluidic flows in order to establish material behaviour over multiple decades of shear rate and timescale. The complementary benefits of these techniques are discussed with specific focus on the unique insights that each can offer in enabling the characterization of the dynamics of the material response (flow and viscoelasticity) under process-relevant conditions.

## Thursday 16:50 Forum I

MR5

**Deformation-dependent viscoelastic properties and inhomogeneity in physically cross-linked hydrogels by combining micro- and macro-rheology**Zahra Fahimi<sup>1,3</sup>, Gajanan M. Pawar<sup>2,3</sup>, Rint P. Sijbesma<sup>2,3</sup>, Hans M. Wyss<sup>\*1,3</sup>

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Quantifying and measuring deformation-dependent viscoelastic properties is still a challenge for many nonlinear

materials such as biopolymers, hydrogels, and other polymer networks that can exhibit significantly nonlinear viscoelastic behavior with increasing strain amplitude. Outside the linear viscoelastic regime, a meaningful interpretation of rheological data is not straightforward.

Here we approach this problem by combining microrheology, which inherently probes the linear viscoelastic response of the material, with standard macroscopic rheology. We combine a rheometer with a confocal microscope (rheo-confocal) to track the mean square displacement of embedded fluorescent particles while the material is deformed macroscopically in the rheometer.

We study a physically cross-linked hydrogel, based on segmented hydrophobic bisurea hard blocks and hydrophilic Poly (ethylene glycol) soft blocks. We are able to track particle positions applying different types of deformation, for example while the material is sheared at a fixed shear rate. The acquired images allow us to monitor the microscopic motion of particles inside the network and consequently we can gain information about the local dynamics and the viscoelastic properties of the material, based on the microrheology approach. In addition, we can study mechanical heterogeneities and non-affine deformations of these networks. We find that the local network changes are dependent on filament rigidity, bond strength, as well as the structure and density of the physically cross-linked gel. Results obtained by this combination of micro- and macro-rheology are compared to those from other methods, based solely on macroscopic rheological data. Combining micro- and macro-rheology to access the nonlinear behavior of our materials enables us to gain insight into the physical mechanisms that govern their mechanical behavior. The approach should be directly applicable to a wide range of other soft and biological materials.

Thursday 17:10 Forum I

MR6

### Thin Film shear Rheology of P(NIPAM-co-AA) Microgels

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Microgels form a class of soft deformable particles which are responsive to external stimuli. N-isopropylacrylamide (NIPAM) microgels functionalized with AA monomers [1] give “smart” polymeric particles of few micrometers with pH and thermosensitive elasticity, size and deformability. The fully swollen microgels are soft, elastic and deformable and behave at higher concentrations like weak elastic solid pastes that flow above a yield stress [2, 3]. In the current paper we show that when slip artifacts are avoided this critical stress level becomes a function of the level of confinement, in particular in confinements that reach the length scale of a single particle. Rheological shear measurements under such confined conditions are performed using a Flexture-based Microgap Rheometer (N-FMR) [4] at gaps ranging from 120  $\mu\text{m}$  down to 5  $\mu\text{m}$ . At rest and at sufficiently low stresses, particles are trapped in cages formed by neighboring particles. The particles require a sufficiently large stress to escape from their cage and commence a macroscopic flow evidenced by a successive increase of the yield stress with confinement. In a flowing state, the particles rearrange based on the balance between the hydrodynamic viscous drag force and the elastic force of the particles during rearrangement. It could be shown that the cage configuration and the duration of rearrangement of the particles are dependent on the level of confinement. The shear stress data measured for different confinement levels collapses into a single universal curve when scaled by the corresponding yield stress and when the shear rate is scaled by a confinement dependent characteristic time set by an effective viscosity of the matrix and the elasticity of the particles.

[1] Meng, Z., Smith, M. H., & Lyon, L. A. (2009). *Colloid and Polymer Science*, 287(3), 277-285.

[2] Cloitre, M., Borrega, R., Monti, F., & Leibler, L. (2003). *Physical Review Letters*, 90, 068303.

[3] Seth, J. R., Mohan, L., Locatelli-Champagne, C., Cloitre, M., & Bonnecaze, R. T. (2011), *Nature materials*.

[4] Baik, S. J., Moldenaers, P., & Clasen, C. (2011). *The Review of scientific instruments*, 82(3), 035121.

## Industrial Rheology and Processing - IR

Organizers: Dick J. Dijkstra and Bettina Wolf

Thursday 13:40 Forum II

IR14

### Influence of polymer extrusion on linear-viscoelastic properties of poly(ethylene terephthalate)

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The extrusion of poly(ethylene terephthalate) (PET) causes degradation processes which are mainly due to mechanical, thermal or chemical chain scission, but also coupling reactions occur which lead to longer polymer chains. To identify possible reactions during processing of three different PET homopolymers, thermal stability and frequency measurements in air and nitrogen were conducted at a temperature of 280 °C in a rheometer with plate-and-plate geometry. The thermal stability tests reveal that the storage modulus decreases drastically in air but increases in nitrogen atmosphere. The intensity of both effects depends on the initial molecular weight. Due to the rapid change of the molecular structure already during loading of the sample, the modulus is significantly shifted at the beginning of the measurement. An extrapolation to the zero loading time was carried out in order to quantify the initial state of the polymer. Frequency sweeps were conducted bidirectionally, i.e. by first increasing the angular frequency from 0.05rad/s to 500rad/s, which was then followed by a decrease from 500rad/s to 0.05rad/s, or vice versa. These tests were significantly affected by the rapid changes of the molecular structure and reveal that besides the dominating process, i.e. scission or chain enhancement, the opposite effect also occurs.

Relating these findings to the extrusion of PET, the air atmosphere corresponds to the conditions at the feeding zone and the die outlet, while the condition in the barrel of the extruder corresponds to inert nitrogen case. Different settings of extrusion (die geometry, vacuum, additional air) for a co-rotating twin screw extruder were conducted to prepare samples affected by different degradation processes. By use of frequency tests and capillary rheometer measurements we monitored the molecular changes caused by extrusion.

Thursday 14:00 Forum II

IR15

### Interrelationship between rheological behavior of continuous phase and phase separation of dispersed nano- und micro-particles

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Physical stability of dispersions - in the sense of sedimentation or creaming of their dispersed particles – is a necessarily prerequisite (sin qua non) for an adequate shelf life of liquid or semi-liquid products. Basic physics predicts that particle migration velocity under earth gravity or in centrifugal fields depends beside particle mass and concentration; on density difference between the particles and the fluid (DD) and the fluid dynamic viscosity (DV). On the other hand, product performance is also greatly influenced by rheological behaviour of continuous phase (CP). Therefore formulators attempt to tailor the rheological properties of CP and of dispersion products by means of different rheological additives or network forming polymers. In this paper we are going to describe the interrelationship between rheological behaviour of CP and phase separation under earth gravity or in centrifugal fields by simulation and sedimentation experiments. Particle velocity in a given CP was changed by centrifugal acceleration (CA:  $RCA = CA/g$ ). We present results for different particles dispersed in CPs exhibiting Newtonian and non-Newtonian behaviour. Sedimentation velocity in different Newtonian fluids may be easily scaled by DD and DV, both under gravity or centrifugal conditions. For a given non-Newtonian fluid (PAA-solutions, 0.01 – 0.1 % m/m), particle velocity is in addition clearly influenced by shear thinning of CP and using the Stokes law apparent viscosities were calculated. We obtained viscosities between about 700 mPas (0.1 %,  $RCA=33$ ) and 6 mPas (0.01 %,  $RCA=1900$ ). Based on estimated maximum shear rate generated by particle movement apparent viscosity-shear rate relationship was obtained, which was found to be very similar to data measured by a conventional rheometer (LS 40). In addition, evidence will be provided whether a yield point prevents phase separation depends on the interaction between dispersed particles and structured CP.

Thursday 14:20 Forum II

IR16

**Numerical Investigation of Film Blowing Process**

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The majority of polymer films are manufactured by film blowing. A single screw extruder is used to melt the polymer and pump it into a tubular die. Air is blown into the center of the extruded tube and causes it to expand in the radial direction. The extension of the melt in both the radial and down-stream directions stops at the freeze line. The nip rolls collect the film, and seal the top of the bubble to maintain the air pressure inside. This process is used extensively with polyethylene and polypropylene. Previous studies in the literature that modelled the film blowing process neglected the change of field parameters along the thickness. They also neglected the die swell effect at the die exit and they examined the polymer film only after the die exit. In this study the problem is modelled without any simplification and/or assumptions other than the axis symmetry around the z axis (machine direction) which is a consequence of the geometry of the process. The flow field starts with the die, after the extruder, up until the nip rolls. In the simulations the non-isothermal XPP model is used as a constitutive relation under the realistic process conditions. Using two space dimensions (radial and machine direction), the change of field parameters along the thickness, the die swell effect are considered where the flow is modeled both before and after die exit. Unlike the previous studies, this study introduces two free surfaces in the blown film region which is handled by two distinct height functions. The Finite Element Method is used to solve the unsteady momentum and energy balance equations accompanied with constitutive relations and kinematic relations for crystallinity. The crystallinity equations that are employed can handle both quiescent and flow induced crystallization conditions. The results are presented in terms of velocities, stress and thermal fields over the computational domain for both transient and steady state calculations.

Thursday 14:40 Forum II

IR17

**Semi-empirical equations for the description of Rheotens experiments**

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The Rheotens test is a well-established method to evaluate the extensional properties of polymer melts under processing conditions. During the test an extruded polymer melt strand is taken up by the counter-rotating wheels of the Rheotens device. The force along the strand is measured as a function of the take-up velocity or the draw ratio, respectively. The study presented proposes semi-empirical expressions for the description of the force versus draw ratio curve of Rheotens measurements. The tests are performed in the acceleration mode at which the take-up velocity is increased linearly in time. As a fact of its relevance for spinning processes, a commercial polypropylene grade was used. A fit function is revealed considering not only the steady-state curve of the experiment but also the force oscillations commonly known as draw resonance. The critical draw ratio at the onset of the instability in turn is the crucial limiting parameter for polymer processing (e.g. fibre spinning or film casting). Using the fit function one has access to the melt strength and the critical draw ratio which are both characteristic material parameters. The influence of the extrusion temperature and the acceleration rate on the parameters gained from the analysis are discussed.

Thursday 15:00 Forum II

IR18

**Dispersity and spinnability: Why highly polydisperse polymer solutions are desirable for electrospinning**Naveen Reddy<sup>1</sup>, Siddarth Srinivasan<sup>3</sup>, Ljiljana Palangetic<sup>1</sup>, Robert E. Cohen<sup>3</sup>, Gareth H. McKinley<sup>2</sup>, Christian Clasen\*<sup>1</sup>

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In this paper we present investigations on the minimum polymer concentration - molecular weight scaling relation for the electro-spinnability of solutions of narrowly distributed, polydisperse and blended polymer samples. For polymer samples with low molecular weights the necessary condition for fiber formation follows the known scaling law

obtained from the overlap concentration,  $c^* \sim M^{(3\nu-1)}$ , with  $\nu$  as the excluded volume exponent. For high molecular weight polymer samples we suggest a new power law scaling  $c_{spin} \sim M^{-(\nu+1)}$ . This new power law scaling is based on the assumption that the minimum required viscoelastic stress for fibre formation in the filament is proportional to the steady state extensional viscosity of the solution at high strain rates and thus to the finite extensibility of the polymer chains during electrospinning. Furthermore we show that for polydisperse polymers the correct measure of the average molecular weight to be used in new power law scaling is an extensibility-averaged molecular weight  $M_L$ . In particular for bidisperse blends or samples with a broad molecular weight distribution the choice of the right average molecular weight is crucial for understanding and predictions of the minimum required concentration  $c_{spin}$  for fiber formation during electrospinning.

Thursday 15:50 Forum II

IR19

### In-Situ Characterization of Model Thermoplastic Polyurethane Systems using Rheo-FTIR

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Coupling rheological measurements with fourier transform infrared spectroscopy (FTIR) results in a powerful technique for characterization of reactive systems. This study focused specifically on the in situ study of thermoplastic polyurethanes (TPU) to probe the nature of the reaction's progression. The work was enabled by using a parallel plate rheometer which simultaneously collected FTIR spectra using attenuated total reflectance (ATR) sampling mode. This method permitted the investigation of mechanical property development of the TPU while tracking the behavior of the reaction chemically in real time. Using this technique, model TPU systems were investigated using varying hard and soft segment ratios. Such an insightful technique is of interest for these systems to assist in optimizing the reactive extrusion process from which the TPU is polymerized. Consideration of the effect of the different segment ratios on the polymerization of the TPU will aid in building a link between the material's composition and corresponding processing conditions. Understanding the connection between bulk polymerization behavior and the reactive extrusion process potentially enables optimization of process parameters based on the specific system in use. Ultimately, this information may lead to significant enhancement of reactive extrusion efficiency.

## Flow-Induces Phase Transitions and Flow Instabilities - FI

Organizers: Christian Wagner and Sandra Lerouge

Thursday 16:10 Forum II

FI1

### Flow-induced crystallisation kinetics of polylactid-acids from large amplitude shear rheology compared to optical and thermal analysis

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Like many biopolymers polylactid-acids (PLA) are relatively poorly crystallising compared to other materials while also having a possible post-crystallisation afterwards, and therefore they are difficult to manufacture. In addition to the molar-mass distribution, PLA grades may vary also in terms of D,L-enantiomer distribution, which can result in different stereocomplex forms and largely influence the properties and performance, since chain folding and local mobility govern the morphology in lamellar crystals [1]. Therefore, various routes have been employed to improve the formation of crystal domains, e.g. by chain modifications, addition of nucleating agents (NA), and variation of flow conditions [1-3].

In this study the crystallisation behaviour of PLA with different molecular structures has been investigated both under quiescent and various large amplitude flow conditions in order to obtain better insights and control for the crystallisation kinetics in comparison to NA effects. Using mainly different shear rheology protocols thermo-mechanical data are evaluated in comparison to calorimetric data from thermal analysis as well as to crystal growth data from optical microscopy. The combination of isothermal crystallisation data from rheology with those of other methods highlight the molecular structure and flow influence on the crystallisation behaviour for a broad range of thermo-mechanical histories. Experiments and molecular theory both highlight the flow-induced effects on polymer chains of initially equilibrated Gaussian conformation that enhance the crystallisation process, for which the total deformation and rate

in relation to the time scales of molecular motions are decisive.

[1] S Saeidlou, MA Huneault, H Li, CB Park, *Progr. Pol. Sci.* (2012) 37, 1657-1677.

[2] H Tang, JB Chen, Y Wang, JZ Xu, BS Hsiao, GJ Zhong, ZM Li, *Biomacromol.* (2012) 13, 3858-3867.

[3] H Fang, Y Zhang, J Bai, Z Wang, *Macromol.* (2013) 46 6555-6565.

#### Thursday 16:30 Forum II

FI2

##### **Shear-induced crystallization of polypropylene: a rheological study with in-situ DSC and WAXD**

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Understanding and predicting structure development during flow is key in the processing of semi-crystalline polymers. Not only does the crystalline structure determine mechanical and optical properties of the solidified material, it also affects the rheology of the melt thus influencing the flow field during processing. In this work we study the rheology of crystallizing polypropylene after strong shear flows which induce highly oriented crystal structures. We present two experiments on the matter.

First, we used the novel RheoDSC device to perform plate-plate rheometry and DSC simultaneously on samples that were subjected to a shear pulse with constant shear rate, varying shear time. We show that if the shear time exceeds a certain critical value, material near the edge of the plates forms oriented crystal structures. This emerges in the DSC signal as two peaks; one from the oriented crystallization near the outer edge and one from the isotropic crystallization near the centre of the geometry. With the information obtained from DSC, we obtain a relation between crystalline space filling and viscosity for these oriented crystal structures.

In the second experiment we subject isotactic polypropylene to a poiseuille flow in a slit flow device. Combining in-situ wide angle synchrotron x-ray diffraction (with an unprecedented sample rate of 30 Hz) and the pressure signal in the MPR, we simultaneously probe crystalline structure and viscosity. It is shown that even during very short flows (0.20 s with an apparent wall shear rate of  $900 \text{ s}^{-1}$ ) the viscosity strongly increases due to the formation of crystalline structures. We used a phenomenological model to predict crystalline structure from chain stretch on a continuum level. Combining this model with the results from the RheoDSC experiment, we obtain a prediction of the pressure drop over the channel. It is shown that due to pressure gradients, crystalline morphology is strongly dependent on position along the slit.

#### Thursday 16:50 Forum II

FI3

##### **Improved constitutive model for shear-banding wormlike micellar fluids and comparison with rheology & microstructure experiments**

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Wormlike micelles are flexible cylindrical aggregates of surfactant molecules in solution. When undergoing strong shearing deformations, concentrated solutions of wormlike micelles can form localized bands with different shear rates, known as shear bands. Among the most popular constitutive models for wormlike micelles are those models originally developed for polymeric materials. A drawback of these models is that a solvent contribution is necessary in order to predict shear banding. A major advance was made through the two-species modeling approach developed by Vasquez et al. [1]. Recently, the Vasquez-Cook-McKinley model was revisited from a nonequilibrium thermodynamic perspective [2,3]. The description of the chemical reaction kinetics provided in [4] was extended to viscoelastic systems in order to account for the continuous breaking and reforming of the wormlike micelles. Fickian and stress-induced diffusion was added in a thermodynamically consistent manner using a generalized two-fluid approach. In this talk, we discuss the transient behavior of the new model during the start-up and cessation of simple shear flow and large amplitude oscillatory shear. A quantitative comparison will be made with rheometric and flow-SANS data obtained for a CPyCl/NaSal solution in a cylindrical Couette device [5,6].

[1] P.A. Vasquez, G.H. McKinley, L.P. Cook., *J. Non-Newt. Fluid Mech.*, 144 (2-3):122 -139, 2007.

[2] N. Germann, L.P. Cook, and A.N. Beris., *J. Non-Newt. Fluid Mech.*, (196):51-57, 2013.

[3] N. Germann, L.P. Cook, and A.N. Beris., *J. Non-Newt. Fluid Mech.*, submitted.

[4] A.N. Beris and E.J. Edwards, Oxford University Press, 1994.

- [5] C.R. Lopez-Barron, A.K. Gurnon, A.P.R. Eberle, L. Porcar, and N.J. Wagner, Phys. Rev. Lett., submitted.  
 [6] A.K. Gurnon, C. R. Lopez-Barron, , A.P.R. Eberle, L. Porcar, and N.J. Wagner, Soft Matter, in preparation.

Thursday 17:10 Forum II

F14

### Capillary Thinning and Elongation Induced Structure of Wormlike Micelles Solutions

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We have used the Capillary Breakup Extensional Rheometer (CaBER) to determine the elongational flow behavior of wormlike micelles (WLM) solutions in the low and high salt regime for low and high surfactant concentration. The true axial force during capillary thinning was obtained from horizontal filament stretching (tilted CaBER) experiments. Cetylpyridinium chloride/sodium salicylate (CPC/NaSal) and Hexadecyltrimethyl-ammonium bromide (CTAB)/NaSal solutions have been investigated. Both systems show two shear-viscosity maxima as the salt/surfactant ratio  $R$  is varied and behave like typical viscoelastic fluids in CaBER. They form cylindrical threads, which exhibit an exponential diameter decay characterized by an elongational relaxation time  $\lambda_e$ . WLM solutions with high concentrations and low  $R$  show elongational relaxation times smaller than the longest shear relaxation time  $\lambda_s$ , presumably due to flow-induced breakage of the micelles. In contrast, the filamental lifetime  $t_{fil}$  at high  $R$  values is only controlled by equilibrium breakage time and plateau modulus determined from small oscillatory shear experiments and  $\lambda_e \approx \lambda_s$ . Obviously, the strong elongational flow does not affect the dynamics of micelle breakage and reformation. Sparsely concentrated surfactant solutions at low  $R$  values exhibit low zero shear viscosities but a shear-induced structure formation resulting in a sudden increase of the shear viscosity at a critical shear rate. In CaBER experiments, elongation-induced structures are indicated by very high filament lifetimes (up to 10 minutes)  $10^2 - 10^5$  times greater than expected from the zero shear viscosity. Filament stretching (FiSER) experiments with constant stretching rates show a dramatic change in the diameter vs. time curve of the liquid thread when the structural change sets in at a critical Hencky strain independent of strain rate. Further stretching pulls liquid out of the reservoirs at the plates until the filaments break.

# Thursday Evening

## Conference dinner with arts and music at the ZKM

Thursday 18:30 ZKM Media Theatre

The evening starts with a concert by the award-winning KIT chamber orchestra in the media theatre of the renowned ZKM, the Centre for Art and Media Karlsruhe ([www.zkm.de](http://www.zkm.de)). Doors open at 18:00.

Thursday 19:15 - 24:00 ZKM Foyer

The conference dinner will take place in the foyer of the ZKM.

Thursday 20:30 - 22:00 ZKM

Exclusive opening of the current ZKM interactive video art exhibition. Guides will be on hand to provide information about the exhibits.

# Friday Morning

## Plenary Lecture 3

Friday 9:00 Hans-Thoma

PL3

### **Molecular rheology of entangled branched polymers using combs**

Frank Snijkers<sup>1</sup>, Helen Lentzakis<sup>1</sup>, Nikos Hadjichristidis<sup>2</sup>, Taihyun Chang<sup>3</sup>, Daniel Read<sup>4</sup>, Chinmay Das<sup>4</sup>, Giovanni Ianniruberto<sup>5</sup>, Giuseppe Marrucci<sup>5</sup>, Evelyne van Ruymbeke<sup>6</sup>, Dimitris Vlassopoulos<sup>\*1</sup>

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Since the pioneering works of Graessley in the 70s and 80s, the use of well-defined model polymers has been established as a necessary step toward understanding the physics of entanglements and eventually the rheological behavior of commercial polymers. In this spirit, remarkable progress has been made in the last 15 years toward understanding the linear viscoelasticity of well-characterized architecturally complex polymers, based on the synergy of state-of-the-art chemistry, physical experiment, modeling and simulations. This has opened the route for investigating the more challenging nonlinear rheology, which is the much-needed ingredient for tailoring and controlling industrial-scale processes. Here we present we use a particular architecture, comb polymers, as the paradigm to explore molecular rheology. This choice is justified by drawing analogies to commercial branched polymers. The progress made in linear viscoelasticity is summarized and guidelines for determining the relaxation times of branches and backbones are provided. Further, the response of entangled combs in step-strain, start-up simple shear and uniaxial extensional fields are discussed. The role of key molecular parameters is explored: molar masses of branch, of backbone and of backbone segment between branches. Further, the consequences of architectural disparity on the rheological data and modeling predictions are explored. Shear thinning and extension hardening are analyzed and molecular criteria for their onset and strength, which can serve as guidelines for developing molecular constitutive equations, are provided. The main result is that dynamic dilution of hierarchically relaxing segments is the key for rationalizing both linear and nonlinear viscoelasticity. Finally, remaining challenges to complete the puzzle, as well as perspectives in entanglement dynamics and architecturally complex polymers are addressed.

## Poster Award and Presentation of AERC 2015

Friday 10:00 Hans-Thoma

The poster award of the AERC 2014 will be presented: The three winners will be allowed to present their work. Many thanks to Europhysics Letters for sponsoring this award.

The "Groupe Français de Rhéologie" will inform us about the 10th Annual European Rheology Conference in Nantes, France, from April 14 to April 17, 2015. Nantes is a vibrant city rich in art and history situated in the heart of a dynamic region that fosters interactions between higher education, innovation and industry.

## Polymer Melts, Blends, Copolymers, and Nanocomposites - PM

Organizers: Ulrich Handge, Manfred Wagner, Dimitris Vlassopoulos, and Alexei Likhtman

Friday 11:00 Hans-Thoma

PM33

### The effect of pressure on the viscosity of miscible polymer blends: relation between free volume and pressure coefficients

Ruth Cardinals<sup>1</sup>, Lukas Polito<sup>1</sup>, Jurgen Pionteck<sup>2</sup>, Paula Moldenaers\*<sup>1</sup>

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The viscosity of molten polymers is known to depend on the processing conditions such as shear rate, temperature and pressure. The pressure dependency is however often ignored, although it can be important in polymer processing operations such as injection moulding. The main reason for the limited attention for pressure effects is related to the fact that viscosity measurements at high pressure are quite difficult. Thus, establishing and validating alternative methods to assess the pressure dependency of the viscosity can facilitate and improve numerical simulations for the design and optimization of polymer processing equipment. In literature it has been demonstrated that variations in viscosity with either pressure or temperature can be related to changes in the polymer free volume. Nevertheless, systematic investigations to unambiguously correlate free volume on the one hand and pressure and temperature dependent viscosities on the other hand are essentially lacking. In the present work, miscible PMMA/PVDF blends of different compositions have been prepared by melt extrusion to allow to systematically vary the free volume and temperature and pressure coefficients of viscosity. The melt viscosity at different temperatures and pressures was measured by means of a capillary rheometer equipped with a specially designed and in-house build pressure chamber. Based on these data, temperature and pressure coefficients of viscosity were determined. Pressure-volume-temperature data were collected by means of a high pressure mercury dilatometer. From the PVT data in the melt region, the free volume of the materials was extracted by means of fits with the Simha-Somcynski equations of state. Interestingly, unique linear relations were found between the temperature coefficients of viscosity and the pressure coefficients of viscosity as well as between the pressure coefficients obtained from PVT data and the rheologically determined pressure coefficients.

Friday 11:20 Hans-Thoma

PM34

### A rheological study of vitrimers

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Epoxyes and epoxy-based materials find applications as e.g. coatings, structural adhesives and matrices of fiber-reinforced composites due to their combination of high mechanical strength and low density. Possible self-healing properties for such systems are of great technological interest. In a series of papers Leibler's group [1,2] presented an elegant method to modify epoxy materials based on mixtures of diglycidyl ether of bisphenol A and fatty acids by the addition of an appropriate catalyst for the reversible transesterification reaction between alcohol and ester groups to impart self-healing properties to the resins. The materials, termed "vitrimers", show a strong potential in all applications of epoxyes since they can be readily prepared by mixing standard chemicals.

We studied a range of possible formulations of vitrimers. They differ in their content of mono-, di- and tri-carboxyl fatty acids thereby controlling the number of links and hence strength of the final network. We present an investigation of their curing behavior studied by rheometry and calorimetry to assess the activity of the catalyst at different cure temperatures. We further studied the linear dynamical mechanical properties of the cured vitrimers over a wide range of frequencies and temperatures. The terminal relaxation behavior could often not be reached in oscillatory tests and the frequency axis is extended by performing long-time creep and stress relaxation experiments. The relaxation time and moduli are found to depend on formulation and the "vitramer glass transition" is clearly observed in the experiments. To the best of our knowledge, this work is a first attempt at a systematic, in depth rheological investigation of vitrimers.

[1] Montarnal et al., Science 334 (2011)

[2] Capelot et al., MacroLett 1 (2012); JACS 134 (2012)

Friday 11:40 Hans-Thoma

PM35

**Assessing the phase structure of molten polymer blends using a generalized Gramespacher-Meissner model**

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Oscillatory shear rheometry is a convenient method to detect phase separation in polymer melts, as the deformation of enclosed particles will cause additional long-time relaxation processes which add to the dynamic moduli at low frequencies.

When using rheometry to investigate the phase structure of a molten polymer blend, it makes sense to avoid crystallization during sample preparation, as it induces phase separation and might therefore affect the measurement. Thus we use an experimental set-up where the compounded molten blend is transferred directly into the measuring cell of a rheometer.

If phase separation in the melt occurs, the relaxation time spectrum obtained from the measured dynamic moduli will differ significantly from the combined spectra of the pure components. By using the model of Gramespacher and Meissner [1], one can gather information about the phase structure from this discrepancy. However, the original G/M model is only valid for (near) uniform particle sizes. We therefore attempt to generalize it in order to make it applicable to broader particle size distributions. We use this model to predict the dynamic mechanical behaviour of blends with known morphologies, and, conversely, to assess the morphology from measured dynamic moduli.

Reference: [1] H. Gramespacher and J. Meissner (1992): J. Rheol. 36(6), 1127-1141

Friday 12:00 Hans-Thoma

PM36

**Phase separation dynamics in polymer blends close to  $T_g$ : aging and rejuvenation**

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We propose a model to deal with polymer blends dynamics and interdiffusion close to the glass transition. The dynamical model incorporates an extension of the Flory Huggins model to the case of compressible blends for calculating the driving forces. Spatial dynamics follows then from an Onsager like description. The model is solved on a 2D lattice corresponding to spatial scales of about a few tens to 100 nm and a resolution corresponding to the scale of dynamical heterogeneities, allowing to study inter-diffusion mechanisms of species in polymer blends close to  $T_g$ , in particular during the process of phase separation. We deal with non-entangled polymers having a degree of polymerization smaller than 50 typically. In the course of spinodal decomposition, we observe slow structures building, which coexist with fast ones. Domains are found to grow like the logarithm of the time. We study also the reverse process, after the temperature is increased again in the totally miscible range. We observe a temporal asymmetry between the aging and the rejuvenation dynamics: the slow domains melt much faster than the elapsed time required to build them during the separation process and total miscibility is recovered after a much shorter time. This approach may help preparing nano-structured polymer materials with the desired morphology.

**Non-Newtonian Fluid Mechanics and Flow Simulation - FM**

Organizers: Pier L. Maffettone and Evan Mitsoulis

Friday 11:00 Johann-Peter-Hebel

FM18

**Continuous Squeeze Flow Film Of A Structured Fluid: Non-Newtonian Effects**Edtson Emilio Herrera Valencia<sup>1</sup>, Mayra Luz Sanchez Villavicencio\*<sup>2</sup>

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In this work, the viscoelastic behavior of a complex structural fluid in a continuous squeeze flow is analyzed. This flow is generated by allowing a continuous flow of liquid into the narrow gap between two circular plates though the lower plate. In order to characterize our complex liquid, the Boek-Pearson model is used (BP). The BP model separates

the stress contributions of the structured fluid and the solvent. The solvent is modeled as a purely Newtonian liquid, and the complex fluid is characterized with the upper convective Maxwell equation coupled with a kinetic equation that describes the changes of the structures due to the relaxation and kinetic mechanisms respectively. In order to solve the set of non-linear partial differential equation, a non-dimensional perturbation scheme is suggested in terms of a small parameter, which is the ratio between two characteristic length scales (radius of the disc and gap separation between the disc). To zero order in the perturbation parameter (neglecting the inertial mechanisms of the momentum equation), it is found that the normal force on the upper disc is directly related to structure of the fluid, which is a function of the Weissenberg number. The thixotropy, shear-thinning, shear thinning, yield stress and concentrations effects are analyzed through a group of characteristic dimensionless numbers associated to structural, kinetics and viscoelastic mechanisms respectively. To first order, the effects of the rupture and structural mechanism play an important role in the elasticity. The present theory, model and computations contribute to the evolving fundamental understanding of lubrication systems through rheology and flow systems.

Keywords: Thixotropy, Continuous Flow, Boek-Pearson Model, Structured Fluid, Surfactant Solution, Load Bearing, Lubrication, Perturbation Technique

Friday 11:20 Johann-Peter-Hebel

FM19

### Periodic boundary conditions for the simulation of uniaxial extensional flow

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Periodic boundary conditions (PBCs) are often applied in molecular dynamics and other simulation techniques to allow for the simulation of bulk fluids under homogeneous flows. For example, Lees-Edwards PBCs are used for the simulation of simple shear flow [1], while for planar extensional flow the PBCs of Kraynik and Reinelt can be used [2]. A very common extensional flow in industrial applications and experiment is uniaxial extensional flow. I have recently developed PBCs applicable to this flow that allow for simulations with long duration [3]. I give a brief explanation of the technique and present results for nonequilibrium molecular dynamics simulations of some simple liquids under uniaxial extension. To conclude I discuss some further generalisations and applications of the technique.

[1] A.W. Lees and S.F. Edwards, J. Phys. C5, 1921 (1987)

[2] A.M. Kraynik and D.A. Reinelt, Int. J. Multiphase Flow 18, 1045 (1992)

[3] T.A. Hunt, arXiv:1310.3905 [cond-mat.soft] .

Friday 11:40 Johann-Peter-Hebel

FM20

### Comparison between objective and non-objective kinematic flow classification criteria

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Turbulent flows present several compact and spatially coherent regions generically known as coherent structures. It is known that the dilution of an elastic polymer in a Newtonian solvent increases the size of such structures. The understanding of these structures is closely related to the concept of vortex, whose definition is still a subject of controversy within the scientific community. In particular, the role of objectivity (the invariance with respect to arbitrary changes of reference frame) in the definition of the vortex remains a largely open question. However, three usual kinematic criteria for flow classification, namely  $Q$ ,  $\Delta$  and  $\eta_2$ , are non-objective since they all use the fluid's rate of rotation, which depends on the observer. In the present work, we propose an objective redefinition for these three classic criteria by using the concept of relative rate of rotation defined as the difference between the usual rate of rotation and the angular velocity of the eigenvectors of the strain rate tensor. We also explore two novel naturally objective flow classification criteria, which are obtained using the covariant convected derivative of the strain rate tensor. Preliminary analyses are performed with a 4:1 abrupt contraction and the analytical velocity field given by circular trigonometric functions that form the so called Arnold-Beltrami-Childress (ABC) flow. Then, all the criteria are applied to the instantaneous velocity fields obtained by direct numerical simulation (DNS) of both Newtonian and viscoelastic turbulent channel flows. The analysis will be carried out here for four frictional Reynolds numbers ( $Re_\tau = 180, 395, 590$  and  $1000$ ), emphasizing the difference between objective and non-objective identification criteria, as well as between Newtonian and non-Newtonian flows. Moreover, we try to obtain, from the results of flow classification criteria, information related to the polymer drag reduction phenomenon.

Friday 12:00 Johann-Peter-Hebel

FM21

**Use of rheology to validate a new theory for the flow through a porous medium**Mario Minale\*<sup>1</sup>, Claudia Carotenuto<sup>1</sup>, Anja Vananroye<sup>2</sup>, Jan Vermant<sup>2</sup>

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The momentum balance on the solid skeleton of a porous medium like porous rocks, foam metals or porous brushes is here theoretically derived with the volume averaging method. The equation holds in the whole porous medium and contains volume averaged stresses and velocity. For homogeneous porous media, the momentum balance on the solid skeleton is coupled with the momentum balance on the fluid within the porous medium, i.e. Darcy's equation with the first and the second Brinkman's correction, through a geometrically rescaled Darcy's term. This approach gives the opportunity to derive a new stress boundary condition at the interface between a porous medium and a homogeneous fluid stating that the stress is transferred both to the fluid within the porous medium and to the solid skeleton. A negligible stress jump is obtained that is proven to be exactly zero in simple shear flow. The theory is validated with rheological tests where the porous medium is mimicked either with a cross-hatched geometry on a ARES (TA) strain controlled rheometer, or by gluing some sandpapers on a plate-plate device of a NOVA (Reologica) stress controlled rheometer. The experiments are conducted by measuring the viscosity of Newtonian oils at different imposed gaps, in correspondence of the same applied stress in the NOVA rheometer, and at an imposed shear rate corresponding to a stress invariant with the gap, for the ARES rheometer. The viscosity always decreases with the gap and an "extrapolation length" can be inferred. This is due to the shear-induced flow through the slender porous media and the velocity at the interface is explicitly related to the extrapolation length. This velocity is used as validation parameter in the comparison with the theoretical predictions and the agreement is good.

**Colloids and Suspensions - CS**

Organizers: Matthias Ballauff and Moshe Gottlieb

Friday 11:00 Alfred-Mombert

CS33

**Shear-thinning of soft core-shell particles**

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Soft materials, including biological tissues and food systems, consist of sponge-like building blocks. These sponge-like objects are soft, porous, and they can swell and shrink by absorbing or expelling water. Our goal is to establish a relationship between the macroscopic mechanical behavior of these materials and that of the constituent sponge-like particles. To do so, we perform experiments on a model system of core-shell microgel particles, consisting of a polystyrene core with a soft pNIPAM shell; the softness of the shell can be tuned by varying the crosslinking density. At high concentrations our microgel suspensions exhibit a distinct shear thinning behavior, qualitatively different from that observed for hard particles. To elucidate this behavior, we systematically investigate its dependence on particle softness and on the suspension volume fraction.

Friday 11:20 Alfred-Mombert

CS34

**Direct observation of the formation of microstructure in drying colloidal films with in-situ vertical small angle X-ray scattering**Sunhyung Kim<sup>1</sup>, Kyu Hyun<sup>2</sup>, Bernd Struth<sup>3</sup>, Christian Clasen\*<sup>1</sup>, Kyung Hyun Ahn\*<sup>4</sup>

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Drying of colloidal dispersions to create thin solid films is a common process for various applications. When a liquid film solidifies during drying, the concentration not only of particles but also of other components increases and the

corresponding particle interaction changes over time. As a result, the structure of the solid film may be different from expectation derived from the original composition of the suspension. Therefore, the drying process needs to be understood to control the structure and properties of the final product. In-situ synchrotron X-ray scattering has proven to be one of the most promising tools in understanding the non-equilibrium phase behavior of colloids. However, conventional synchrotron beams are horizontal to the ground, thus they are not able to pass perpendicular through the colloidal suspension which intrinsically settles down in a horizontal plane due to gravity. Because of this limitation, horizontal SAXS has been applied only for a limited number of cases in drying research.

In the present work, we report a first application of novel, vertical SAXS to investigate the drying process of a colloidal suspension, overcoming gravity related restrictions. We employed a unique rheo-SAXS setup which has been developed to allow a synchrotron X-ray beam to pass vertically through the plate/plate geometry of a rheometer. After demonstrating the methodology with charge-stabilized colloidal silica, we explore the drying behavior of silica/polyvinyl alcohol suspension where the liquid microstructure is controlled by pH. The scattering intensity shows that the suspension experiences a gel to glass transition during drying at low pH, in contrast to depletion flocculation at high pH. We find that the adsorbed polymer plays a key role in the formation of the microstructure. This allows us to successfully explain the anomalous drying behavior of this suspension reported in a previous study [Kim et al. Langmuir. 2009, 25, 6155-6161.].

Friday 11:40 Alfred-Mombert

CS35

### **Microstructural origins and nonlinear signatures of yielding in heterogeneous nanoemulsion colloidal gels**

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We investigate the yielding of a colloidal gel comprised of nanoscale oil droplets in water driven by thermo-reversible interdroplet attractions. The system forms a heterogeneous gel structure that is best described as a two phase system at the micron scale containing droplet-rich domains of fractal clusters and droplet-poor domains. By combining large amplitude oscillatory shear (LAOS) measurements with simultaneous ultra-small angle neutron scattering (rheo-USANS), we characterize both the nonlinear mechanical processes and strain-dependent microstructural changes through the yielding transition. We find that the gel undergoes a broad yielding process in which the nonlinearity evolves over an order of magnitude in strain between the initial yield point and flow. By analyzing the intracycle response as a sequence of physical processes, we monitor several parameters throughout the yielding process, including the residual elasticity, yield stress and recoverable strain of the network. Frequency-dependent measurements show that the rate-dependence of the yielding process occurs primarily in the viscous nonlinear response of the material. Correlating these results with model parameters extracted from rheo-USANS data reveals that the material passes through a "top-down" cascade of structural breakdown. First, the droplet-lean domains consolidate into large voids, which saturate near the initial yield point. Second, at higher strains, cluster-cluster correlations become increasingly homogenous, with a maximum at the crossover of  $G'$  and  $G''$ , suggesting a depercolation of cluster-cluster bonds (from a network to suspended clusters) as the ultimate process determining the transition to flow. We note that all significant structural changes occur on the  $\mu\text{m}$ -scale, suggesting that large-scale rearrangements of thousands of particles, rather than the immediate rearrangement of particle-particle bonds, are responsible for the yielding behavior of heterogeneous colloidal gels.

Friday 12:00 Alfred-Mombert

CS36

### **Rheology of municipal anaerobic digested sludge: Effect of temperature on composition**

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This paper investigates the irreversible and reversible effects of temperature and thermal history on rheology of digested sludge. Digested sludge collected from one of Melbourne waste water treatment plants and its rheological properties was studied at different temperature (20-80°C) using a stress-controlled rheometer. The sludge rheological properties including flow curve, viscosity curve and yield stress were measured at different temperature and thermal histories. The experimental data was modelled using Herschel-Bulkley. In addition, the effect of temperature and thermal history on solubilized COD were also investigated to prove the observed rheological behaviour of sludge is due to composition change of sludge during heat treatment.

The result showed that thermal treatment of sludge has reversible and irreversible effects on composition of sludge which can be demonstrated by its rheological properties as an indication of this change. The sludge viscosity and yield stress decreases almost reversibly by increasing temperature and time of heating treatment below 70°C. However, at 70°C and higher temperatures, the sludge rheology showed irreversible effect as well as significant thermal history effect. In addition, by increasing the time of thermal treatment at all range of studied temperature, the sludge irreversibly became less viscous. A considerable increase in solubilised chemical oxygen demand (COD) at 70°C and higher temperature observed which induced due to transfer of organic matters from solid phase to liquid phase which was in agreement with rheological result. This result was also confirmed by measuring the liquor viscosity of sludge showing that the sludge liquor viscosity increased by increasing the temperature in which the liquor was obtained.

## Viscoplasticity and Granular Media - VP

Organizers: Philippe Coussot and Igor Emri

Friday 11:00 Clubraum

VP11

### Scaling behaviour in convection-driven Brazil nut effect

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A single large intruder embedded at the bottom of a vertically and sinusoidally vibrated quasi two-dimensional rectangular cell packed with mustard seeds rises to the top. For a range of relative density ratios, intruder sizes and bed heights, the intruder rise time,  $t$ , measured at several angular frequencies  $\omega$  and peak-to-peak amplitudes  $a$ , varies as  $t \approx (v - v_c)^{-2}$ , where  $v = a\omega$  and  $v_c$  is identified as the critical vibration velocity for the onset of convective motion of the mustard seeds. The velocity of convection of the mustard seeds at the walls is independently estimated using high speed digital video tracking and is found to be in very good agreement with the values of  $v_c$  obtained earlier. These experiments prove unambiguously that boundary-driven granular convection is responsible for the rise of the intruder in quasi two dimensions and that the peak-to-peak velocity of shaking, rather than the peak to peak acceleration, is the relevant parameter for describing the results.

Friday 11:20 Clubraum

VP12

### Coarse-grained local and objective continuum description of 3D granular flows down an inclined surface

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Dry, frictional, granular, steady-state flows down an inclined, rough surface are studied with discrete particle simulations. From this exemplary flow situation, macroscopic fields, consistent with the conservation laws of continuum theory, are obtained from microscopic data by time-averaging and spatial smoothing (coarse-graining). Two distinct coarse-graining length scales are identified, where the fields are independent of the smoothing length,  $w$ . The smaller, sub-particle length scale,  $w \ll d$ , resolves layers in the flow near the base boundary that cause oscillations in the macroscopic fields. The larger, particle length scale,  $w=d$ , leads to smooth stress and density fields, but the kinetic stress becomes scale-dependent; however, this scale-dependence can be quantified and removed.

The stress tensor is expressed in an inherently anisotropic form with four objective (coordinate frame independent) variables: (i) the isotropic pressure, (ii) the "anisotropy" of the deviatoric stress, i.e. the ratio of deviatoric stress (norm) and pressure, which is an objective measure of friction, (iii) the anisotropy distribution between the principal axes, and (iv) the difference in orientation (angle) between the stress and the strain rate tensor. Each objective stress variable is then related, via discrete particle simulations, to the inertial number,  $I$ , which represents the plane strain special case of a general, local, and objective constitutive model. The resulting model is compared to existing theories and clearly displays significant deviations from more simplified theories in all variables – on both the different length scales.

For full details of this research, see (T. Weinhart, R. Hartkamp, A. Thornton, S. Luding, Phys. Fl., 25(7), 2013). A very similar approach was recently applied to the rheology of a simple fluid without gradient due to gravity and without walls in a mixed shear situation (R. Hartkamp, B. Todd, S. Luding, J. Chem. Phys., 138, 244508, 2013).

Friday 11:40 Clubraum

VP13

**On the increase of the Mean Rise Velocity of a Bubble in a Viscoplastic Fluid Induced by an Oscillating Pressure Field**

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It has been documented experimentally [1, 2] and theoretically [1, 3] that increasing the yield stress of a viscoplastic material beyond a critical value leads to entrapment of a deformable bubble in it. This phenomenon plays a crucial role in producing desirable products in a number of processes in the food and cosmetics industries or undesirable products because air-pockets reduce the strength of concrete in the construction industry. Finally, the rate of oxygen transfer in fermentation processes is reduced when the air carrying bubbles are immobilized.

Here we examine the conditions under which an applied oscillatory pressure field in the material leads to increasing the mean rise-velocity of the bubble or induces mobilization of an entrapped bubble. Until today only one such study has been reported [4]. We have developed a dynamic finite element code to study the rise of a deformable bubble while it undergoes volume oscillations in a viscoplastic fluid. As constitutive model we have used the regularized Papanastasiou model [5]. We have examined the effect of the relevant dimensionless parameters: Bond, Archimedes, Bingham and Strouhal. The latter parameter in particular is a measure of the forcing frequency. We have found that the velocity increase is maximized when the forcing frequency of the pressure oscillations is somewhat lower than the eigenfrequency for bubble volume-oscillations in the viscoplastic material. In general the most crucial of all the problem parameters is the Strouhal number.

[1] Dubash & Frigaard, Phys. Fluids 16(12), (2004) 4319-4330.

[2] Dubash & Frigaard, J. Non-Newt. Fluid Mech., 142(1-3), (2007) 123-134.

[3] Tsamopoulos, Dimakopoulos, Chatzidai, Karapetsas & Pavlidis, J. Fluid Mech., 601, (2008) 123–164.

[4] Stein & Buggisch, Z. Angew. Math. Mech. 11-12, (2000), 827-834.

[5] Papanastasiou, J. Rheol. 31, (1987) 385-404.

Friday 12:00 Clubraum

VP14

**Influence of surface properties on the creeping flow of a yield stress fluid around spheres**

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The present experimental study focuses on the creeping flow of a yield stress fluid around spheres for which the data in the literature are scarce and fragmented, particularly when slip conditions exist. The yield stress fluid considered here consists of a suspension of deformable micro-gels (Carbopol gel). Its rheological properties, such as steady shear stress, relaxation time, first normal stresses difference... have been finely characterized. Two spheres have been considered: a "rough sphere" (resp. "smooth sphere") with a roughness greater (resp. smaller) than the characteristic size of the micro-gels. In addition, their surfaces have respectively been chosen hydrophilic and hydrophobic. These tribologic properties enable adherence on the rough sphere and slip on the smooth sphere. The slip phenomenon, specific to yield stress fluids, significantly affects both global (drag coefficients) and local (velocity fields) measurements. These measurements have been performed at high Oldroyd numbers, i.e. when plastic effects are higher than viscous effects. The observations are related to the parameters of the bulk behavior and the interfacial friction law of the gel obtained by rheometric and tribologic characterizations. These measurements have revealed a significant influence of tribologic properties. From the drag coefficient measurements, a criterion for predicting the stability of a sphere with regards to the fluid/sphere interface has been proposed. The kinematic fields obtained by PIV, have revealed a dissymmetry between the upstream and the downstream flow. They have also provided information on the shape and size of the rigid and sheared zones which highlight that the slip phenomenon reduces the influence of the sphere on the flow through more confined sheared and rigid zones. The shear rates at the wall of each sphere have been estimated in order to propose orders of magnitudes of the contribution of shear and normal stresses in the drag forces.

## Microfluidic and Microrheology - MR

Organizers: Moncia Oliveira and Anke Lindner

Friday 11:00 Forum I

MR7

### Parallel Plate Resonators for Shear-Wave Rheometry of Viscoelastic Fluids

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Mechanical resonators are devices highly sensitive to loading with mass or liquid. The linear viscoelastic parameters of a fluid in contact can in principle be derived from the shift in resonance frequency and change in bandwidth. Using micromachined cantilevers or suspended plates viscosity sensors with high sensitivity at low viscosities can be designed [1]. With increasing viscosity high damping limits the applicable range to about 0.5 Pa\*s.

We present a system of two electrodynamic plate resonators aligned parallel to each other - the sample in between - where one is used for excitation and readout, and the second for measuring only. This way the high sensitivity at low viscosities is preserved when observing the resonance of the exciting transducer. The shear-wave coupling between the two resonators increases with viscosity and elasticity of the fluid, enabling measurements at viscosities of tens of Pa\*s. The complex coupling coefficient is determined by the gap height and the product of density and viscoelastic modulus [2]. We fabricated resonators with circular plates with diameters between 6 and 10 millimeters, and spacers between 200 micrometers and 2 millimeters. The resonators are mounted in a temperature controlled block of dimensions 50x90x18 millimeters. We present measurements of liquids between 1 mPa\*s. and 10 Pa\*s and the mathematical modeling of the resonators coupled by the shear-wave in viscoelastic media.

[1] E.K. Reichel, C. Riesch, F. Keplinger, C.E.A. Kirschhock, B. Jakoby, Analysis and experimental verification of a metallic suspended plate resonator for viscosity sensing, *Sens. Act. A: Phys.*, 162/2 (2010);

[2] John L. Schrag, Deviation of Velocity Gradient Profiles from the "Gap Loading" and "Surface Loading" Limits in Dynamic Simple Shear Experiments, *Trans. Soc. Rheol.* 21, 399 (1977);

Friday 11:20 Forum I

MR8

### Elastic instabilities in the microflow of viscoelastic fluids

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Viscoelastic fluids exhibit an intermediate behavior between elastic solids and viscous liquids, depending on the time scale at which they are perturbed. Elastic instabilities may occur at vanishing Reynolds number in the flow of viscoelastic fluids and a general criterion for the onset of such instabilities can be established based on the curvature of flow streamlines and fluid elasticity (Packdel & McKinley 1996).

Our goal is to study experimentally the onset of elastic flow instabilities in viscoelastic fluids of various rheologies in microfluidic flow geometries. The main advantage of using microfluidic devices is that they allow for a perfect control of the flow curvature, via their tunable geometry. Furthermore due to their small size microfluidic devices enable to obtain high shear rates, and thus enhance the appearance of non-Newtonian effects, while keeping fluid inertia small. Recently, Zilz et al. (2012, 2013) characterized the onset of elastic instabilities of diluted PEO solutions in serpentine channels, for different channel radius and fluid relaxation times. We now aim to use semi-dilute polymeric solutions, which display significant shear-thinning behavior, in order to evaluate the influence of the non-linear rheology on the onset of the instability.

Elastic instabilities can be conveniently utilized to lead to efficient mixing at the microscopic scale. Precise understanding of the instability mechanisms will allow to use them for mass or heat transfers purposes.

[1] Pakdel, P. & Mckinley, G. H., "Elastic instability and curved streamlines". *Phys. Rev. Lett.* 77 (12), 2459–2462 (1996).

[2] Zilz, J., Poole, R. J., Alves M. A., Bartolo, D., Levache, B. and Lindner, A., "Geometric scaling of purely-elastic flow instabilities", *J. Fluid Mech.* 712, 203-218 (2012).

[3] J. Zilz, R.J. Poole, M. Alves, C. Wagner, C. Schäfer and A. Lindner, "Serpentine channels: micro – rheometers for fluid relaxation times", *Lab Chip*, 14 (2), 351 – 358 (2014).

Friday 11:40 Forum I

MR9

**Flow of power-law fluids in microfluidic bifurcating networks designed using biomimetic principles**Konstantinos Zografos<sup>1</sup>, Robert W. Barber<sup>2</sup>, David R. Emerson<sup>2</sup>, Mónica S. N. Oliveira\*<sup>1</sup>

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The flow of a non-Newtonian power-law fluid, described by the Ostwald-de Waele relationship is investigated numerically in rectangular-shaped bifurcating networks designed using biomimetic principles. Murray's law is based on the principle of minimum work and in its original form establishes the optimum ratio between the diameters of the parent ( $d_0$ ) and daughter vessels ( $d_1$  and  $d_2$ ) for circular cross-sectional networks. The relationship derived by Murray can be written as  $d_0^3 = d_1^3 + d_2^3$  [1]. The theory has recently been extended to consider rectangular cross-sectional networks containing Newtonian fluids [2]. In the present work, we demonstrate numerically the ability to customise these networks for use with power-law fluids and to generate particular resistance gradients in microfluidic distribution systems.

The problem is investigated using a fully-implicit numerical code based on the finite volume method for collocated meshes [3]. We consider isothermal, laminar flow of a power-law fluid for power law indices ranging from 0.2 to 3 to study the behaviour of both shear-thinning and shear-thickening fluids. A range of geometries has been designed to generate precise resistance gradients and initially tested using creeping flow conditions (Reynolds number,  $Re \rightarrow 0$ ), which is a reasonable approximation in microfluidics. A number of simulations using different initial channel aspect ratios and different  $Re$  were also performed to assess the flow characteristics and examine the limits of the validity of the biomimetic rule for power-law fluids under various flow conditions. Analysis of the tangential wall shear stress and flow resistance distribution shows the ability of the network design to impart the desired flow characteristics.

[1] C.D. Murray, Proc Natl Acad Sci USA 12 (1926) 207-214.

[2] R. W. Barber, D. R. Emerson, Microfluid Nanofluid 4 (2008) 179-191.

[3] P.J. Oliveira, F.T. Pinho, G.A. Pinto, J Non-Newtonian Fluid Mech 79 (1998) 1-43.

Friday 12:00 Forum I

MR10

**Microfluidic interfacial tensiometry of confined droplets in elongational flow**Rosa D'Apolito<sup>1</sup>, Antonio Perazzo<sup>1</sup>, Valentina Preziosi\*<sup>1</sup>, Giovanna Tomaiuolo<sup>1</sup>, Antonio Cassinese<sup>2</sup>, Stefano Guido<sup>1</sup>

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Microfluidic devices fabricated by using biomaterials like silicon have gathered enormous attention in the recent years[1]. The design of microfluidic systems often requires unusual geometries and the interplay of multiple physical effects, which lead to interesting variants of well-studied fluid dynamical problems and some new fluid responses. Here we exploit microfluidics to determine emulsion interfacial properties, focusing our interest on confined emulsion droplets [2] in extensional flow. A dynamic measurement, by image analysis, has been used to calculate emulsion interfacial tension in a PDMS (polydimethylsiloxane) rectangular microchannel obtained by soft-lithography technique [3]. In order to impose an extensional flow to the droplets, a pressure driven flow in a convergent microchannel has been imposed. Two different emulsions have been analyzed: i) an emulsion of water in silicone oil, ii) an emulsion of soybean oil in water stabilized by a non-ionic surfactant. Both emulsions have been prepared in a beaker by gentle mixing on a magnetic stirrer and then their fluid dynamic behavior have been analyzed in the channel where the flow has been induced by imposing a known pressure by a micropump system.

Interfacial tension measurement principle is based on the deformation and retraction dynamics of droplets under extensional flow. A dynamical interfacial tension measurement model [4] was used to fit our experimental data, thus extrapolating interfacial tension value. The influence of droplet confinement has been noticed and then a confinement parameter to adequately scale emulsion interfacial tension value has been taken into account.

[1] Whitesides G.M., Nature (442, 368-373), 2006

[2] Guido, Preziosi, Advances in Colloid and Interface Science (161), 2010

[3] Guido, Current Opinion in Colloid &amp; Interface Science (16), 2011

[4] Tomaiuolo et al., Lab on a Chip (11), 2011

[5] Hudson et al., Appl. Phys. Lett. (87), 2005

## Flow-Induces Phase Transitions and Flow Instabilities - FI

Organizers: Christian Wagner and Sandra Lerouge

Friday 11:00 Forum II

FI5

### Extensional necking instabilities in complex fluids and soft solids

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We investigate the onset and development of necking in free surface extensional flows of complex fluids and soft solids, by examining the way in which perturbations to an initially homogeneous cylindrical sample grow to different neck shapes that in turn lead to either gradual necking or sudden rupture. Previous work [1] has shown that the "Considère criterion" (of declining force with strain) fails to predict the onset of necking in most popularly studied models of polymer melts (including Oldroyd-B, Giesekus, FENE, RoliePoly and PomPom), with onset instead coinciding with an inflexion point in the evolution of the extensional stress as a function of strain.

Here we present more detailed evidence for this new inflexion-point criterion and demonstrate alongside it the existence, within a highly restricted sub-class of constitutive model, of a modified Considère-like criterion that can amplify an existing instability. (Among the above list of constitutive models, only the Rolie-poly and PomPom models, in the limit of no polymer chain stretch.) Beyond the level of linear stability analysis, we also perform fully nonlinear simulations within a one dimensional slender filament approximation. After checking carefully that the filament initially (while perturbations remain small) follows the predictions of the linear stability analysis, we then use the nonlinear simulations to explore later stages of the necking dynamics, in particular with regards a possible overshoot in the measured stress response as a function of strain. Time permitting, we will also discuss some recent results for necking instabilities in disordered soft glassy materials. For this class of materials the afore mentioned modified Considère-like criterion is of much higher importance in the growth any instability, but shows a strong dependency on sample age.

[1] Criterion for Extensional Necking Instabilities in Polymeric Fluids; S. M. Fielding (2011), PRL, 258301

Friday 11:20 Forum II

FI6

### Contraction flow instabilities in nematic polymer solutions

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Contraction flow instabilities in nematic aramid polymer solutions were studied, and compared with similar instabilities in isotropic viscoelastic polymer solutions. The flows were visualised using glass microfluidic chips with a 100:1 contraction. The used geometries, and the applied flow velocities are representative for industrial polymer extrusion processes, such as fibre spinning. The microstructure present in nematic polymer solutions enables tracer-less particle image velocimetry (PIV). Qualitatively, nematic contraction flows were observed to closely resemble isotropic viscoelastic contraction flows, with vortex-like structures near the lip of the contraction, which are greatly reduced if the contraction entrance is smoothed. The main difference is that the vortex-like structures in the nematic flow have a much flatter, elongated shape. The wavy flow structure that was reported by Bedford et al. [1], for slit flows of a hydroxypropyl cellulose (HPC) solution, was also observed in our flow cell, but was seen to disappear in the strong elongational flow near the contraction. Hence, it is believed that this wavy flow does not significantly influence the contraction flow behaviour of the nematic polymer solution. Our work demonstrates that experiments with model viscoelastic fluids can be a useful tool in the design of a production process involving nematic polymer solutions. At the same time, experiments with the target nematic polymer solution, such as described here, still remain necessary for quantitative optimisation.

[1] B. D. Bedford et al. Unstable slit flow of a liquid crystalline polymer solution. *Rheologica Acta* 36: 384-396 (1997)

**Influence of the inlet velocity on the onset of draw resonance in fiber spinning**Mathias Bechert\*<sup>1</sup>, Dirk W. Schubert<sup>1</sup>, Benoit Scheid<sup>2</sup>

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Besides other flow instability phenomena, draw resonance is a highly unwanted effect in polymer melt spinning processes. Exceeding a threshold value of the take-up velocity, or equivalently exceeding the so-called critical draw ratio, it causes oscillations of the fiber diameter around the centre line, which might eventually lead to the breakdown of the process.

In this talk, we propose for the first time a numerical correlation between the critical draw ratio and the inlet velocity. A linear stability analysis of the steady state solution is used, which is the common way to handle this problem. By using a continuation method via the software auto-07p[1], we are able to determine the critical draw ratio for various sets of model parameters. For the sake of simplicity, a pure Newtonian model is used and inertia and gravity effects are accounted for. Applying proper scaling, it is reasonable to use the Galilei number as dimensionless parameter for the stability curves. The stability analysis shows a threshold for the Galilei number beyond which unconditional stability exists. By fitting the stability curves with an appropriate empirical function, we are able to analyse the dependency of both the threshold value and the general trend of the curve on the inlet velocity of the viscous fiber. In general, this makes a quantified numerical analysis of the influence of material and process parameters on the onset of draw resonance possible and provides an easy manageable predictive tool for practical use.

[1] E. J. Doedel et al.: AUTO-07p: continuation and bifurcation software for ordinary differential equations, 2007; available to download from <http://indy.cs.concordia.ca/auto/>

**Local dynamics and first normal stress difference during extrusion flow in high sensitivity slit die via the 'hole effect'**Roland Kádár<sup>1,2</sup>, Ingo F.C. Naue<sup>1</sup>, Manfred Wilhelm\*<sup>1</sup>

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Polymer melts exhibit instabilities during extrusion flow that hinder the throughput of processing operations. For a given bulk operating temperature, with increasing Weissenberg number ( $Wi$ ) the extrusion flows experience a transition from smooth extrudate to extrusion instabilities. These instabilities are observed as extrudate patterns and range from relatively simple to chaotic structures. In this framework, our research is concerned with the analysis of local dynamics via a high sensitivity instability detection die in the presence of curved streamlines inside the die induced via the 'hole effect'.

The experimental system features a slit die equipped with four high sensitivity pressure transducers with three of them regularly placed along the channel length (Tr1-3) and the fourth (Tr4) opposing one of the other three. The position of Tr4 can be accordingly adjusted as to create the so called 'hole effect' as an estimation of the normal forces. Complementary, an online visualization system is positioned at the die exit to monitor the extrudate. The die swelling is thus determined and spatio-temporal diagrams are therewith created by extracting a line of pixels out of each movie frame. Furthermore, an axial load can be applied on the extrudate using a Rheotens accessory. Commercial samples with different molecular topologies, i.e. linear (high density polyethylene), short chain branched (linear low density polyethylene and) and branched (low density polyethylene), are investigated.

The in situ mechanical pressure data and the spatio-temporal diagrams are then used for process/flow characterization, whereas the nominal pressure difference between Tr3 and Tr4 is used to estimate the first normal stress difference. The characteristic frequencies of instabilities are determined for the analyzed Weissenberg numbers using a variety of experimental protocols. Thereafter, pressure bifurcation diagrams, reconstructed attractors, and the divergence of trajectories in this reconstructed space space, i.e. maximal Lyapunov exponent, are used to correlate the local dynamics to the extrudate patterns and the first normal stress difference.

# Friday Afternoon

## Polymer Melts, Blends, Copolymers, and Nanocomposites - PM

Organizers: Ulrich Handge, Manfred Wagner, Dimitris Vlassopoulos, and Alexei Likhtman

Friday 13:30 Hans-Thoma

PM37

### Nonlinear Rheology of Interphase: Relaxation after a Step Strain, Startup Shear and Uniaxial Extension of PMMA/PVDF Compatible Multilayers

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This work aims to examine whether or not nonlinear transient rheology of multilayered polymer structures in both shear and extensional flow are sensitive to the presence of the diffuse interphase generated at neighboring layers. For this, stress relaxation after a step strain, fast startup in simple shear and in uni-axial extension have been performed based on a PMMA/PVDF alternating multilayer with presence of robust diffuse interphase and a multilayer with no interphase as a reference. For neat PVDF and PMMA melts, in nonlinear step strain, time-strain factorability is found to occur around the terminal relaxation time. Damping functions have been determined to be type A and type B respectively for PMMA and PVDF melts, which could be fitted by different forms. In fast startup shear, typical features of stress overshoot and "strain softening" are evident for the neat melts at high shear rates. In fast startup uni-axial extension, a "strain hardening" behavior has been found for the PVDF melt whereas the studied PMMA melt displays a "strain softening". These nonlinear features are interpreted under the framework of Doi-Edwards theory incorporating "convective constraint release" and under some recent theoretical scenarios of entanglement network yielding as well as dynamic tube confinement barrier breakdown under stress. For multilayers, an original model has been developed to describe the relaxation behavior after a nonlinear step strain, which well captures main tendencies of experimental results, and is able to estimate the relaxation modulus  $G(t,g)$  of the interphase. For the un-annealed bilayers without interphase, the  $G(t,g)$  significantly falls down from their counterparts with robust interphase and the theoretical predictions after intermediate deformations, implying occurrence of an interfacial failure. This has been confirmed by their transient viscosity  $\eta^+$  in startup shear measurements as the  $\eta^+$  of bilayers without interphase is negatively deviated from their counterparts with robust interphase and the theoretical prediction at an intermediate shear rates. For the annealed bilayers, the triggered robust interphase greatly delays the interfacial failure to a larger deformation in step strain and to a higher deformation rate in startup shear. Such sequential failure at the interface/interphase, may be due to entanglement strands breakdown under stress after and/or during large external deformations, as a consequence of entanglement lack at the interface and entanglement weak intensity at the diffuse interphase. In startup uni-axial extension, presence of certain interphase that bridges the entanglement gap at the interface enhances the transient extensional viscosity  $\eta_E^+$  of the structure. After saturation, as the interphase portion is increased by mounting layer number, its weak entanglement intensity as the equivalent blend makes the  $\eta_E^+$  of the structure subtly decline. After all, the interface/interphase at multilayer structures is able to be distinguished in nonlinear rheology due to their sequential easy interfacial failure upon external deformations.

Friday 13:50 Hans-Thoma

PM38

**Understanding of the compatibilization effect of the multifunctionalized epoxy in PLA/PBAT biopolymer blends: linear and non-linear rheology, morphology and interfacial properties**Racha Al-Itry, [Khalid Lamnawar\\*](#), Abderrahim Maazouz[khalid.lamnawar@insa-lyon.fr](mailto:khalid.lamnawar@insa-lyon.fr)

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The focus of this paper is to gain a true understanding of the impact of a multi-functional epoxide (Joncryl) on the interfacial properties of biopolymer blends based on PLA and PBAT. Their effect on the shear rheological, morphological and interfacial properties of blends was investigated systematically. Different sandwich model systems (droplet/matrix) for the deformed drop retraction experiments were studied to probe the role of the epoxy-functionalized chains and to assess different scenarios of compatibilization. The decrease of the interfacial tension in the modified PLA/PBAT and the formation of the PLA-copo-PBAT were highlighted. A new relaxation peak relative to this copolymer was detected from the relaxation spectrum. Transient start-up shear and nonlinear stress relaxation experiments were carried and confirm the obtained results. Besides, the interface contribution, as introduced by the Lee and Park model, appeared in comparison with other emulsion models. Its relaxation time increased with the Joncryl amount. Hence, the co-existence of chain extension/branching chains coupled to the PLA-copo-PBAT formation have to be taken into-account to explain the improved mechanical properties.

Friday 14:10 Hans-Thoma

PM39

**Large Amplitude Oscillatory Shear of Immiscible Polymer Blends and Comparison to Predictions of Droplet and Anisotropy Models**[Abdulwahab S. Almusallam\\*](#)[abdulwahab.almusallam@ku.edu.kw](mailto:abdulwahab.almusallam@ku.edu.kw)

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Large amplitude oscillatory shear (LAOS) experiments were carried out for a model immiscible blend composed of two Newtonian components at different viscosity ratio and volume fraction values. Data for the first and third harmonic of the sinusoidal stress response were recorded and compared to the Constrained Volume (CV) model and to the Maffettone and Minale (MM) model. Various constitutive equations were tried: the Batchelor constitutive equation with the viscous term of the interfacial contribution neglected, the Peters et al. [J. Rheol. 45, 659 (2001)] constitutive equation, the Lee and Park (LP) [J. Rheol. 38, 1405 (1994)] constitutive equation and the Yu and Bousmina [J Rheol 47 1011 (2003)] constitutive equation. In addition, the MM model was used to calculate droplet dimensions during LAOS deformation, and stresses were calculated using the Batchelor constitutive equation. It was found that models that provide a description for the viscous term of the interfacial contribution to stress performed better in describing the first harmonic value in all of the tests that were carried out. On the other hand, the descriptions provided for the viscous term tended to lower the quality of agreement with the third harmonic experimental data. The exception is the LP model, where the provided correction for the viscous term is linear with respect to the rate of deformation tensor. The MM model performed poorly at low viscosity ratio values because of large droplet deformation that go outside the limits of stability of the MM model. On the other hand, the MM model predictions of the third harmonic at high viscosity ratio value are higher than those obtained from the CV model, and the experimental data fall between those two predictions. Analysis of excess shear stress predictions during a strain period reveals the growth of secondary oscillations as strain amplitude is increased. Those secondary oscillations grow faster in the MM than they do in the CV model.

Friday 14:30 Hans-Thoma

PM40

**Analysis of phase inversion composition and rheological behavior of PA6/HDPE reactively compatibilized blends**

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Control of the morphology in polymer blend is key for controlling the final properties. The model systems used for this study were PA6/HDPE blends reactively processed with Maleic Anhydride grafted HDPE. The obtained morphologies were observed by microscopy (SEM and TEM) and the raw materials viscosity was measured by a

cone-plate geometry rheometer (ARES). It has been shown that different micrometer scale morphologies could be developed in reactive extrusion process following the rules of drop break-up and coalescence: Dispersed, stretched Dispersed, fibrillar and co-continuous. Moreover, nano-inclusions which can be attributed to the compatibilization reaction, could be formed for most of our reactive blends, in addition to the micro-scale morphology. The objective of this study is to make the link between formulation/morphology/rheological properties of reactively compatibilized blends.

In the micro-scale morphology, co-continuous morphologies appear as phase inversion occurs. In this study, we show that phase inversion at the micrometer scale can be predicted from the viscosity ratio,  $R_v$ , of raw materials when  $R_v$  is calculated at a frequency representative of process conditions. A large range of viscosity ratios, from 0.1 to 450 for reactively compatibilized blends with high conversion rates, have been tested. We propose to analyse the composition at phase inversion on the basis of a modified Krieger and Dougherty model (Meijer et al. 2009), which is shown to be coherent with the Palierne's model. When  $R_v$  is very different from 1, the model gives a range of phase inversion which is consistent with observations. Thus, even though nano-inclusions represent a large volume fraction in each phase domain (since we use a large amount of compatibilizer), the micro-scale morphology formation seems to be driven by the rheological properties and more specifically by the viscosity ratios of raw materials.

Friday 14:50 Hans-Thoma

PM41

### **Characterization of compatibilized Polypropylene/Polystyrene blends via nonlinear rheological properties under large amplitude oscillatory shear (LAOS) flow**

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The large amplitude oscillatory shear (LAOS) tests are used to investigate the effect of compatibilizer on polypropylene (PP)/polystyrene (PS) blends. For analyzing nonlinear stress under LAOS flow, the nonlinearity (third relative intensities) is calculated from FT-Rheology. PP/PS blends are well known as immiscible blends. For better mixing or blending, compatibilizers are necessary. Especially, mixing protocol of compatibilizer or the kinds of compatibilizers affect the final morphologies of PP/PS blends. The effect of various mixing methods (four different mixing protocols and three different mixing times) for PP/PS/organoclay (C20A) blends was investigated using linear and non-linear rheological properties under dynamic oscillatory shear flow. Blends of 1 minute mixed (PS+C20A)/PP showed the highest values among the all protocols. Furthermore, the effect of different compatibilizers (C20A and fumed silica) concentration on nonlinear rheological properties of PP/PS blend is also investigated. In order to quantify the degree of dispersion at different concentrations, a new parameter, the Nonlinear-Linear viscoelastic Ratio ( $NLR \equiv \text{Normalized nonlinear viscoelasticity} / \text{Normalized linear viscoelasticity}$ ) was used. A relationship between NLR value and PS droplet size in the PP matrix domain was found. TEM images revealed; C20A located mostly at the interface or partially inside the PS drops and reinforced compatibilization effect. The C20A make well dispersed morphologies of PP/PS blends, however fumed silica make poor dispersed ones (agglomerated inside PS domains). Therefore the NLR values for well dispersed blends are larger than 1 (C20A) and the NLR values for poor dispersed blends are less than 1 (fumed silica). From these results, both linear rheological properties from small amplitude oscillatory shear (SAOS) tests and nonlinear ones from LAOS tests can be used to characterize the effect of compatibilizer for polymer blends.

Friday 15:10 Hans-Thoma

PM42

### **Non-linear Rheology of Well-Defined Comb Polymer Architectures with a Low and Controlled Degree of Long-Chain Branching**

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Well-defined, monodisperse polystyrene-based homopolymer comb architectures with varied number and length of the branches were synthesized and investigated under linear and nonlinear deformation to determine the effect of branching on the rheological properties. Within the linear regime, the reduced van Gurp-Palmen plot [1,2] was used to identify critical points that illustrated the influence of the branch molecular weight and number of branches on the resulting rheological properties. In the nonlinear regime large amplitude oscillatory shear (LAOS) measurements were performed to obtain the nonlinear parameter  $Q_0(\omega)$  via a quadratic scaling law from FT-rheology

[3,4]. An intrinsic nonlinear master curve based on the  $Q_0(\omega)$  parameter reflected the relaxation hierarchy and was shown to be a sensitive method to extract information on the different relaxation time scales. The nonlinear shear measurements were complemented by uniaxial extensional measurements to quantify the strain hardening effect and how the strain hardening was affected by branch relaxation. The results obtained from the uniaxial extensional measurements could be correlated to relaxation times obtained from the intrinsic nonlinear master curve  $Q_0(\omega)$ . Pom-pom constitutive model predictions were performed for the comparison with experimental data for extensional rheology with focus on the strain hardening behavior and for LAOS with focus on the nonlinear parameter  $Q_0(\omega)$  as a function of increasing number and molecular weight of the branches in the pom-pom molecule.[5]

Literature:

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- [2] van Gurp, M.; Palmen, J. *Rheol. Bull.* 1998, 67, 5-8
- [3] Wilhelm, M. *Macromol. Mater. Eng.* 2002, 287, 83-105
- [4] Hyun, K.; Wilhelm, M. *Macromolecules* 2009, 42, 411-422
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## Non-Newtonian Fluid Mechanics and Flow Simulation - FM

Organizers: Pier L. Maffettone and Evan Mitsoulis

Friday 13:30 Johann-Peter-Hebel

FM22

### Theoretical and experimental studies on the contact line motion of second-order fluid

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Studies on a contact line motion are important in many industrial processes such as inkjet printing, screen printing, coating and so on. As inks in printing processes are complex fluids containing particles and/or viscoelastic additives, we need to consider the elasticity of complex fluids in the contact line motion. In this study, we consider the contact line motion of second-order fluids theoretically and experimentally. The theoretical study shows that  $N_1$  increases the contact line velocity while the second normal stress difference ( $N_2$ ) does not affect the contact line motion. The increased contact line velocity is caused by the hoop stress acting on the curved stream lines near the contact line. The hoop stress increases the liquid pressure near the contact line, and the increased pressure results in the surface profile having the smaller curvature and smaller dynamic contact angle. For experiments, silicone oils of different kinematic viscosities (1,000-200,000 mm<sup>2</sup>/s) which are well fitted to the second-order fluid model with the positive  $N_1$  are used. The spreading rate of a silicone oil drop on a solid surface is faster than the spreading rate predicted by the theory for Newtonian fluids. As the experimental result confirms the theoretical prediction, the effect of  $N_1$  is established.

Friday 13:50 Johann-Peter-Hebel

FM23

### Numerical Simulation of two miscible fluids within a static mixer

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The turbulent flow structure and mixing performance of a simplified static mixer with and without inserted Static Mixing Elements (SMEs), where two liquid streams impinge into each other have been investigated using computational fluid dynamic (CFD) simulation. Fluent software is used to evaluate the mixing efficiency of 6 models with different cross flow angles and different Static Mixing Elements (SMEs). Hence, intensity of segregation (IOS) and 95% mixing time are used in order to characterize the quality of mixing. Numerical simulation results shows that the mixers with (SMEs) are highly efficient over static mixers without inserted elements. The changes of flow direction angle and velocity ratio between the cross flow and bulk flow have a significant effect on the mixing quality. The cross flow angle of 90° gives fastest mixing at 1 - 2ms. The enhancement in mixing performance is thought to be caused by the insertion of SMEs causing vortices that split the streams of mixture into sub-streams promoting a large several contact zone between the liquids present in the mixer. Mixing efficiency as higher as 96.8 % is reached within a

length of 15mm downstream from the first contact of the two liquids.

Friday 14:10 Johann-Peter-Hebel

FM24

### Dense semiflexible polymer brushes in flow: a model for glycocalyx layer in blood vessels

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The response of dense brushes of semi-flexible polymers to flow is of great interest in both technological and biological contexts. Examples include the glycocalyx or the endothelial surface layer in blood vessels and mucus-like layers in lungs. We employ smoothed dissipative particle dynamics (SDPD) method, a mesoscopic hydrodynamics technique, to study semi-flexible polymer brushes for a wide range of conditions including grafting density, polymer elasticity, and shear stress due to flow. Our simulation results are in good agreement with previous studies, which focused on brushes with low grafting densities. We also propose a theoretical model which describes the deformation of dense semi-flexible polymer brushes in shear flow for a wide parameter range. The model allows us to predict effective deformation (height), monomer density profile and hydrodynamic penetration depth (solvent velocity profile) within a brush. Finally, we also investigate the interactions between a modeled glycocalyx and flowing blood cells.

Friday 14:30 Johann-Peter-Hebel

FM25

### Organisation of large-scale motions in turbulent pipe flow of a dilute polymer solution

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An experimental investigation focussing on the structural organisation of large scale motions (LSMs) in fully developed turbulent pipe flow has been conducted in the Very Large Scale Pipe Flow (VLSPF) facility at the University of Liverpool using a dilute aqueous polymer solution: a 300ppm high molecular weight ( $20 \cdot 10^6$  g/mol) polyacrylamide ( $c^* \sim 1$ ). Measurements using high-speed stereoscopic particle image velocimetry in the radial-azimuthal plane at a Reynolds number of 25000 (based on bulk velocity, the pipe diameter and the viscosity corresponding to the shear rate at the pipe wall) have been made to obtain all three components of velocity with good temporal resolution. Comparison is made with a reference experiment using water and a high level of drag reduction (55%) is measured for the aqueous polymer solution.

Taylor's approximation [1] is employed to create pseudo-3D representations of the LSMs from the measured velocity data [2]. The effect of the polymer on these motions is found to be akin to a low-pass spatial filtering. Recently, the presence of a set of distinct organisational states has been identified in Newtonian turbulent pipe flow through the decomposition of the two-point spatial correlation of the streamwise velocity fluctuations by azimuthal wavenumber [3]. These states are characterised by alternating positive and negative fluctuations of the streamwise velocity around the pipe azimuth and are found to be related to a series of alternately-rotating quasi-streamwise vortices. We apply the same analysis technique to the experimental results obtained with the drag-reducing polymer solution to investigate the influence of the polymer on these flow states.

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Friday 14:50 Johann-Peter-Hebel

FM26

### Hibernating Turbulence in Newtonian Fluids and Dilute Polymer Solutions

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The upper limit of turbulent drag reduction with polymer additives – often termed Virk's Maximum Drag Reduction (MDR) asymptote [1] – is a well-known phenomenon in the turbulent flow of complex fluids. One intriguing feature of MDR is its universality. Recent direct numerical simulations [2] have identified time intervals showing key features of MDR. These intervals have been termed 'hibernating turbulence'. They are a weak turbulence state

which is characterised by low wall-shear stress and weak vortical flow structures. Here we report the results of an experimental investigation which shows that the streamwise velocity of a turbulent channel flow collapses to the MDR asymptote, even in the absence of a polymer additive, during intervals of hibernating turbulence.

Our experiments are conducted in a fully developed turbulent channel flow of Newtonian fluids and semi-dilute polymer solutions, 300 ppm of a very high molecular weight ( $23 \times 10^6$ ) polyacrylamide, at a Reynolds number of  $Re_\tau = u_\tau h / \nu = 85$ , where  $u_\tau$  is friction velocity,  $h$  is channel half-height and  $\nu$  is kinematic viscosity. We measure the instantaneous wall-shear stress with a hot-film probe, which we use as an indicator for hibernating turbulence, whilst simultaneously sampling the streamwise and wall-normal velocity components with Laser Doppler Anemometry.

We show that hibernating turbulence, which is strongly related to MDR, is a Newtonian phenomenon and could be interpreted as the weakest turbulence state for self-sustaining wall-bounded turbulence. The addition of a polymer additive entices the turbulence to enter a state of hibernation more frequently [2]. On a time-averaged point of view, this yields a large reduction in turbulent skin-friction drag, and causes the collapse of the polymer solution's time-averaged streamwise velocity profile onto the MDR asymptote.

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Friday 15:10 Johann-Peter-Hebel

FM27

### Free-surface jet of a power-law fluid near channel exit

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The jet flow of a shear-thinning power-law fluid is examined theoretically as it emerges from a channel at moderate Reynolds number. Poiseuille flow conditions are assumed to prevail far upstream from the exit. The problem is solved using the method of matched asymptotic expansions. A similarity solution is obtained in the inner layer near the free surface, with the outer layer extending to the jet centerline. An inner thin viscous sublayer is introduced to smooth out the singularity in viscosity at the free surface, allowing the inner algebraically decaying solutions to be matched smoothly with the solution near the free surface. This treatment is similar to power-law flow near the edge of a boundary layer (Denier & Debrowski 2004, Zhao & Khayat 2008). A Newtonian jet is found to contract more than a shear-thinning jet. While both the inner-layer thickness and the free-surface height grow with downstream distance, the sublayer thickness is smaller, growing with distance for  $n < 0.5$ , and decaying for  $n > 0.5$ ,  $n$  being the power-law index. The relaxation downstream distance for the jet are found to grow logarithmically with  $Re$ . The current work extends our previous study on viscoelastic-inertial jet flow near channel exit (Saffari & Khayat 2009).

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[3] Zhao J Khayat RE 2008 Spread of a non-Newtonian liquid jet over a horizontal plate. *J. Fluid Mech.* 613, 411

## Advances in Rheometry - AR

Organizers: Maik Nowak and Thomas Schweizer

Friday 13:30 Alfred-Mombert

AR10

### Influences of patterned surface in rheometry of complex fluids

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Rheometry of soft matter is dominated by the interaction between the sample and plate. The uncertainty of the boundary conditions, in particular the wall depletion phenomena and slip at the wall, are still one of the main subject of research in the modeling of soft matter rheology. The aim of our investigation is to find a correlation between the quality of the lower plate and the measurements performed at the upper smooth tool in a commercial rotational rheometer. One question we are looking for an answer is the following: For a given patterned surface, which is the minimum gap which influences the quality of the measurements? We expect to relate the measurements with the magnitude of a slip length (real or apparent) associated to smooth and patterned surfaces and to find a quantitative measure of the wall depletion phenomena. The study is focused on micro-structured surfaces with uniform heights

in the range of 20 - 50 microns. The experiments are accomplished with numerical simulations, which are previously calibrated for viscoelastic fluids with well defined rheological behavior. The samples used for experiments are lanolin creams enriched with solid particles of 1 micron diameter. The influence of concentration on the dynamic measurements is also investigated.

Friday 13:50 Alfred-Mombert

AR11

### **Correcting for Shear Strain in an Oscillatory Squeeze Flow Rheometer**

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The stress response of a viscoelastic fluid is dependent on the strain to which it is subjected. In the case of squeeze flow this strain is generally characterized as the amplitude of plate displacement divided by the gap between the two plates. While this is an accurate definition of extensional strain, it fails to take into account that, where there is no slip on the plates, fluids in squeeze flow are predominantly undergoing shear flow (as opposed to extensional flow) and that this flow is dependent on the plate dimensions in addition to the displacements of the plates. We will show that the current system of representing strain does not lend itself to comparison between different rheometers and thus a new formulation for strain will be suggested that allows for shear strain comparison between rheometers of different dimensions. This relationship will be validated by both computer simulations and laboratory experiments comparing strain sweeps of materials in various rheometers. Ultimately this work provides a relationship which allows for the characterization of a fluid's viscoelastic regime in a squeeze flow rheometer in such a way that it can be related to measurements taken on both other squeeze flow rheometers and rotational rheometers.

Friday 14:10 Alfred-Mombert

AR12

### **High strain extensional rheometry of polymer melts**

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Usually, when studies on uniaxial extension of polymer melts are performed the main concern is the achievement of the largest possible deformation with a homogeneous stretching of the sample at any given deformation rate. Therefore, it is necessary to ensure that the correct experimental conditions are achieved, which, more often than not, is not the case. In fact, despite a wealth of work available in the open literature that highlights the importance of correctness of the experimental method, many researchers still disregard basic experimental phenomena such as, for example, the almost certain discrepancy between the nominal and the true strain rates being imposed on the sample, poor sample preparation, inadequate sample dimensions and the effects of sample sagging.

In this work we build on previous works by our group and use our new CSER, a dual Controlled-Stress/Rate Extensional Rheometer based on the Meissner principle but small enough to fit in the oven of a standard rotational rheometer, to highlight the importance of truly controlling the strain rate in rate-controlled experiments in order to achieve high deformations in uniaxial extension of polymer melts. This can only be achieved by coupling the ability of the CSER to achieve very high strains while visually accessing the sample during deformation and using a feedback control loop to keep the desired rate constant. By using the control loop to compensate for the deviations in the expected cross-section evolution over time it is possible to minimize or even eliminate both slip at the rollers and the planar component of the deformation known to be present when relatively wide samples are used, e.g., to prevent sagging in SER-type devices. With proper experimental care, we have been able to perform true constant rate experiments in various polymers up to Hencky strains of more than 8, depending on the polymers. The latter case corresponds to a linear deformation of almost 4,000.

Friday 14:30 Alfred-Mombert

AR13

**Low-field NMR as a new in-situ combined method for shear rheology**Karl-Friedrich Ratzsch<sup>1,2</sup>, Christian Friedrich<sup>1</sup>, Manfred Wilhelm\*<sup>2</sup>

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Rheo-NMR has been an established method for over twenty years, however the very high apparatus effort needed has put its use outside the reach of most rheologists. New developments with permanent magnets now have shrunk NMR magnets to outlines of under 20 cm at a few kilograms [1], making it possible to integrate such a device into a conventional rheometer. As rheological samples typically are rich in hydrogen, the low NMR sensitivity at magnetic fields  $\leq 1.5$  T is unproblematic, proven by the longstanding use of low-field NMR on static samples both in industry and academia. Methods that spring to mind for use with RheoNMR are for example ones to measure quantitative composition and phase sizes in multiphase systems [2].

We have for the first time built a rheo-NMR system using a home-made magnet with 0.7 T (30 MHz proton resonance) installed in a Rheometrics/TA Ares rheometer, together with a convective sample heating reaching  $\geq 200^\circ\text{C}$ . To display the possibilities of this new setup, we would like to show our measurements on shear-induced crystallization of isotactic Polypropylene, regarding the development of the mass crystallinity and the mobility of the amorphous phase, as displayed by NMR relaxometry. The findings are compared to earlier measurements with conventional rheometry [3], and to static crystallization experiments [4].

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Friday 14:50 Alfred-Mombert

AR14

**Rheometry, NMR and Combined RheoNMR of TiO<sub>2</sub>-Filled Poly(n-alkyl methacrylates) and t-Polyisoprenes to Investigate Molecular Dynamics of Composite Materials**Volker Röntzsch<sup>1,2</sup>, Karl-Friedrich Ratzsch<sup>2,3</sup>, Gisela Guthausen<sup>2</sup>, Sabine Schlabach<sup>4</sup>, Manfred Wilhelm\*<sup>2</sup>

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Composite materials based on polymeric matrices and fillers play a key role in today's materials science. Their tunable mechanical, electrical, thermal and optical properties make them extremely useful for a broad range of applications. Although composites are commercially very important, little is known about the interaction between filler particles and polymers on a molecular scale. To investigate the influence of filler content and polymer topology on the molecular dynamics, composite model systems based on poly(n-alkyl methacrylates), trans-polyisoprene and titania (TiO<sub>2</sub>) were prepared via a solvent-free melt-mixing process. Molecular dynamics were characterized using rheometry, NMR and the new technique of combined rheoNMR.

Frequency-dependent SAOS experiments were performed and entanglement molecular weights using vGP-plots were obtained. The behaviour of the model systems under LAOS conditions was studied using FT-rheometry. Temperature-dependent NMR experiments were performed to gain information about fast molecular relaxation processes via longitudinal and transversal relaxation rates. Different pulse sequences and data models were compared based on their sensitivity and selectivity towards different side-chain lengths and filler content in poly(n-alkyl methacrylate) composites. The crystallization of trans-polyisoprene in composites was investigated using a new rheoNMR set-up and quantitative results for the crystallization kinetics by applying an Avrami model were obtained.

Friday 15:10 Alfred-Mombert

AR15

**LAOS: The strain softening/strain hardening paradox**Marius Mermet-Guyennet<sup>\*1</sup>, Janaina de Castro<sup>1</sup>, Medhi Habibi<sup>1</sup>, Nicolas Martzel<sup>2</sup>, Morton Denn<sup>3</sup>, Daniel Bonn<sup>1</sup>

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Numerous materials, from biopolymers to filled rubbers, exhibit strain softening at high strains during a strain sweep in oscillatory rheology: the modulus decreases with increasing deformation. On the other hand, if the non-linear elastic response is analyzed within a single oscillation cycle (described by Lissajous curves), these systems are reported to exhibit strain hardening. We compare strain sweeps and single cycle LAOS (Large Amplitude Oscillatory Shear) analyses of stress vs. strain on three very different materials. We conclude that the reported strain hardening is due the use of a tangent modulus in the LAOS analysis, and that the overall rheology remains strain softening. To show that this conclusion is robust, we demonstrate a rescaling of the modulus that collapses the data from all the oscillatory measurements onto a single master curve that clearly exhibits the correct strain softening behavior.

**Viscoplasticity and Granular Media - VP**

Organizers: Philippe Coussot and Igor Emri

Friday 13:30 Clubraum

VP15

**Viscoplastic dip-coating: experiments and simulations**Mathilde Maillard<sup>\*</sup>, Jérémy Bleyer, Jalila Boujlel, Philippe Coussot

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Many industrial techniques rely on interactions between yield stress fluids and solids. This is in particular the case for the coating of objects, a process widely used in painting, food or building industries. Here, we are interested in characterizing in detail the specific technique of dip-coating of a vertical plate from a bath of yield stress fluid. The key issue is to understand the formation process of the layer coated on the plate in particular to predict its thickness. We carried out such tests with Carbopol gels. Our data show that during withdrawal, in our range of fluid yield stresses and velocities, the layer coated on the plate has a uniform thickness and there is no drainage of the fluid along the plate. This thickness increases slightly with the plate velocity and strongly with the material yield stress. In particular, we observe the existence of a critical value for this thickness at vanishing velocities. Thanks to PIV technique we show that in the bath a liquid layer of uniform thickness forms along the plate while the rest of the fluid stays solid. A close analysis of the velocity fields suggests that the coated layer results from the separation of the liquid layer into two parts: one remaining in the bath while the other is stuck on the plate.

Then, we performed numerical simulations of the material flow inside the bath. The velocity fields obtained fit very well our experimental data and predicts the evolution of the liquid layer thickness with the plate velocity and the material properties.

Friday 13:50 Clubraum

VP16

**Experiments on wet granular matter: Tracing the motion of single particles and drops**Jennifer Wenzl<sup>1</sup>, Laurent Gilson<sup>2</sup>, Rene Stangenberg<sup>1</sup>, Ulrich Bröckel<sup>2</sup>, Günter K. Auernhammer<sup>\*1</sup>

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A large portion of the goods transported on earth is transported as granulates and powders. With the advances in production techniques of composite materials, the grain size of these powders tends to shrink and reach sizes in the micron and even sub-micron range. For a good processability of the powders their flow behavior is a dominant parameter. The smaller the particles become, the more dominant is the influence of the inter-particle forces on this flow behavior. The macroscopic behavior of such particulate systems is a complex interplay between the internal properties of the particles, their surface properties and the structure the particles form. 3D optical imaging of the

particle motion over time [1] can give valuable information about the internal dynamics of the system. Translation and rotation of particle are relevant [2].

In case the particles are in contact with more than one liquid, the wetting behavior (and thus the surface properties of the particles) plays the dominant role in the particle interaction. The surface energy of the particles can be tuned through the density of hydrophobic groups on a otherwise hydrophilic surfaces. When the interfacial energies allow a finite contact angle of the liquid interface on the particles. The wetting dynamics governs the microscopic as well as the macroscopic dynamics of the system.

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Friday 14:10 Clubraum

VP17

### **Influence of the yield stress on the evolution of a bubble population in a viscoplastic fluid**

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The context of this study is to predict the swelling of bitumen barrels in which radioactive salts are mixed (60% wt of bitumen and 40% wt of salts). Radioactivity generates uniform volume production of hydrogen by radiolysis of bitumen chains. Since the production rate of gas occurs on very large time scales (more than a hundred years), one needs to set up models to predict the material swelling. It has been shown that bitumen is a yield stress fluid. The present work therefore proposes to study the influence of the yield stress and the production rate of gas on the evolution kinetics of a bubble population. Usually, in a non-yield stress fluid and without gas creation, a supersaturation of gas leads to a scenario of germination, bubble growth and Ostwald ripening (growth of large bubbles at the expense of the small ones). Over long times, a self similar distribution of large bubbles is selected, independent of the initial distribution of nuclei. In this work, a new model for bubble growth in an infinite viscoplastic material is introduced. Then it is shown that there exist conditions for which the production rate of gas competes with the kinetics of ripening and where the yield stress induces hysteresis and pulsing phenomena on the kinetics of bubbles distribution. The effect of the yield stress and the initial distribution of nuclei on the final population is discussed.

Friday 14:30 Clubraum

VP18

### **Capillary rise of Yield Stress Fluid**

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Foams, emulsions, polymer gels are example of every day life yield stress fluids. What makes such systems particularly interesting for applications, but fundamentally difficult to describe, is their intermediate fluid/solid behavior. At the macroscopic scale, this behavior is well described by phenomenological laws, such as the Bingham or Herschel-Bulkley laws. Moreover, in many applications (coating, lab-on-chip, jet-printing . . .), a key role is played by the surfaces.

In this study, we consider the capillary rise of a polymer microgel, situation where both wetting and yielding are important. In particular, we show that measuring the final imbibition height allows determining both the values of the surface tension and of the yield stress. This study also highlights the strong influence of the hydrodynamic boundary conditions. Finally, contrary to the case of simple fluids, we show that the final height few depends on the capillary gap.

Friday 14:50 Clubraum

VP19

**Yield stress fluid flow in simple model porous media**Johan Paiola<sup>\*1,2</sup>, Hugues Bodiguel<sup>1</sup>, Harold Auradou<sup>2</sup>

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Fluids like heavy oils, emulsions or some polymer solutions are characterized by a yield stress. This property is, for instance, used to control the flow behavior in porous reservoir to improve the sweep efficiency. Present models of the flow at the macroscopic scale are based on the assumption that the Herschel-Bulkley rheological law applied locally. To verify this hypothesis, we performed experiments in a « simplified » porous media. The geometry is composed of two channels of different lengths or sections connected in two points. If the rheological behavior is assumed to hold, each of the two channels is characterized by a different threshold pressure gradient:  $\Delta P_+$  and  $\Delta P_-$ .

In this study, the yield stress fluid is a Carbopol (ETD 2050) solution (0.3 % per weight) containing a small amount of fluorescent glass beads (they are used to measure the velocity profiles in the channels). Initially, a sufficiently high pressure is applied so that the fluid flows into two parallel channels. We then decreased the pressure, the flow is observed to stop in one of the channels when  $\Delta P_+$  is reached and the flow completely ceases when the pressure falls below  $\Delta P_-$ . If the pressure is increased from this point, flow starts again but surprisingly at much higher pressure threshold. Using two complementary techniques: soft lithography with PDMS to obtain micrometer scale geometry or milling in transparent plexiglas plate to obtain millimeter scale channels, we demonstrate that our observations are independent of the length scale considered.

Friday 15:10 Clubraum

VP20

**The specificity of yield stress fluid flows through porous media**Thibaud Chevalier<sup>\*1</sup>, Stéphane Rodts<sup>2</sup>, Philippe Coussot<sup>2</sup>

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The flow of yield stress fluids through porous media is of interest for various applications such as injection of drilling fluids in rocks for enhancing oil recovery. Although we can suspect that the strongly non-linear character of such fluids can lead to specific effects the detailed flow characteristics in such case are so far widely unknown. It has been suggested that the flows of yield stress fluids in porous media exhibit two original trends: at a local scale as the pressure drop increases a wider region of fluid starts to flow; at a macroscopic scale the flow starts only along a specific path [1-2] and as the pressure drop is increased more flowing paths progressively form within the porous medium. From our measurements, we provide the effective trends of flow of yield stress fluids in porous medium, which strongly differ from the above assumptions.

We carried out tests by injecting a yield stress fluid (an emulsion) through model porous media (bead packings) at different mean velocities. The density distribution of velocity of the fluid inside the whole sample is measured with an NMR technique, namely a pulsed-gradient spin echo sequence. From this distribution we deduce that there is no fluid at rest in the sample even at low velocities (for Bingham number much larger than 1). This means that at a local scale there is no region at rest and at a macroscopic scale all regions start to flow at the same time.

Moreover, in our range of mean velocities, the velocity distributions are similar from that obtained for a Newtonian fluid. This means that in a porous medium the impact of the yielding character of the fluid on the flow characteristics is partly destroyed as a result of the disorder of the porous medium: in contrast with the flow characteristics in a simple geometry, the velocity distribution being independent of the rheological behavior of the fluid.

[1] M.T. Balhoff, K.E. Thompson, AIChE J. 50 (2004) 3034-3048

[2] M. Sahimi, AIChE J. 39 (1993) 369-386

## Microfluidic and Microrheology - MR

Organizers: Moncia Oliveira and Anke Lindner

Friday 13:30 Forum I

MR11

### Elastic-driven flow instability of polymeric suspension under oscillatory flow perturbations

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We study experimentally the elastic-driven flow instability of a dilute polymer solution (polyacrylamide in water) in a cross-shaped micro-channel. A constant flow rate is imposed in one branch of the cross-slot device and an oscillatory perturbation is imposed in both perpendicular branches. The flow rates imposed at the entry of the perpendicular branches have the same amplitude, but opposite phases, thus the flow rate at the exit channel is constant.

We vary the intensity and the frequency of lateral flow perturbations, up to 20 Hz, using two piezoelectric-actuators, while the main flow is driven at constant flow rate using a syringe pump.

Using a time-resolved micro-particle image velocimetry (PIV) system, we are able to measure the velocity profiles in different locations of the micro-channel, at high frequency rates, for varying values of the Weissenberg number ( $Wi$ ). We study the time-evolution of the velocity field and analyze how the flow patterns evolve downstream of the intersection region as function of  $Wi$ , and quantify how far the flow perturbation persists downstream of the intersection.

Friday 13:50 Forum I

MR12

### Visualization of micro-scale inhomogeneities in acrylic thickener solutions: a multiple particle tracking study

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Multiple Particle Tracking (MPT) has been used to quantify the degree of structural and mechanical microheterogeneity of three acrylic thickener solutions with similar main monomers but different molecular architecture due to different types and degree of crosslinking or hydrophobic side groups. We have investigated the commercial acrylates Sterocoll D (BASF-SE), Viscalex HV30 (BASF-SE) and Carbopol ETD 2050 (Lubrizol Corporation) solutions. Statistical analysis of mean square displacement data from MPT experiments and van Hove analysis, show that Carbopol ETD 2050 is heterogeneous on the micron length scale whereas Sterocoll D and Viscalex HV30 are both homogeneous materials. For these latter systems, the homogeneity of the micro-structure is polymer concentration independent indicating a uniform network structure with a mesh size well below 100 nm. In contrast, Carbopol ETD 2050 is a homogeneous viscous material at low polymer concentration but becomes more and more heterogeneous as the concentration increases. The microstructure may be that of microgel particles with a highly crosslinked core surrounded by a strongly swollen network of polymer chains. At low polymer concentration the microgel particles do not overlap and tracer particles within the polymer network diffuse freely since the high degree of swelling corresponds to a low polymer concentration. At higher concentration microgel particles interpenetrate and tracers in the overlap regions are elastically trapped. These overlap regions occur at a critical polymer concentration  $c_c$  and their thickness increases with  $c$ . As a result a heterogeneous microstructure with a characteristic length scale of about 10  $\mu\text{m}$  is observed. This structure can be directly visualized based on the spatial distribution of tracer particle mobility using Voronoi diagrams.

Friday 14:10 Forum I

MR13

### Microconfined flow-based imaging methods to study red blood cell membrane viscoelastic properties

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Red blood cells (RBCs) perform essential functions, such as gas exchange between blood and tissues, thanks to their ability to deform and flow in the microvascular network[1]. The high RBC deformability is mainly due to the

viscoelastic properties of the cell membrane, especially shear modulus and surface viscosity[2]. Since pathological alterations of RBC deformability are implicated in several diseases, RBC confined flow behavior in microcapillaries has been the subject of a number of studies. Here, we report on an imaging-based in vitro systematic microfluidic investigation of RBC suspensions flowing either in microcapillaries[3-6] or in a microcirculation-mimicking device containing a network of microchannels of diameter comparable to cell size[7]. RBC membrane rheological behavior is investigated by analyzing the transient behavior of single RBC shape in confined flow[4] and by measuring the membrane viscoelastic properties in converging/diverging microchannels[7]. The comprehension of the single cell behavior led to the analysis of the RBC flow-induced clustering. The main result is the development of a novel method to estimate cell membrane viscoelastic properties, that can be used for the analysis of pathological RBCs, for which reliable quantitative methods are still lacking.

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[5] G. Tomaiuolo, D. Rossi, S. Caserta, M. Cesarelli and S. Guido, *Cytom Part A*, 2012, 81.

[6] G. Tomaiuolo, L. Lanotte, G. Ghigliotti, C. Misbah and S. Guido, *Phys Fluids*, 2012, 24, 051903-051908.

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Friday 14:30 Forum I

MR14

### Rheology of a confined blood model

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Red blood cells are constantly confined by blood vessel walls in the microvasculature where the supply of oxygen, nutrients and the disposal of metabolic waste take place. We study numerically a vesicle suspension (a model for blood flow) in microcirculation. We find that confinement leads to unexpected behavior with volume fraction, which markedly differs from that of non-confined suspensions. This unusual behavior is explained in terms of a subtle alternation between spatiotemporal order and disorder of the suspension upon increasing volume fraction. This finding offers a new interesting line of inquiries in the field of microcirculation. It also provides a potential diagnostic tool of erythrocyte pathologies.

Friday 14:50 Forum I

MR15

### Viscoelastic behavior of cells measured in a rotational rheometer

Haider Dakhil<sup>1,2</sup>, Anette Amtmann<sup>3</sup>, Holger Hübner<sup>3</sup>, Rainer Buchholz<sup>3</sup>, Andreas Wierschem\*<sup>1</sup>

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We study the viscoelastic behavior of fibroblast cells. Therefore, we use a commercial rheometer in the parallel-disk configuration. To work at gap widths of about ten micrometers, the rheometer is modified and equipped with a sensor. The cells are fixed to the plates in a monolayer. We carried out oscillatory and unidirectional studies, covering the range from the linear viscoelastic regime to the load limit and studying the impact of biochemical treatment on the rheological properties of the cells.

Friday 15:10 Forum I

MR16

### Microrheology in biological active fluids on the basis of sedimenting beads

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We present experimental results obtained from statistics of bead positions, sedimenting in an active fluid. The activity is characterized by irregular moving microswimmers, namely the green alga *Chlamydomonas reinhardtii*. The strong

influence in classical macrorheological measurements caused by the presence of microswimmers have been published already [1,2]. The physical explanation on the basis of microscopic properties is still an open question and will be discussed in the talk, in particular from the statistical physics point of view. Our measured trajectories of passive sedimenting beads are strongly influenced from the irregular flow field in the water media. The diameter of the beads is comparable or less the diameter of the microswimmers. The alga as microswimmer has two flagella, a diameter of 10  $\mu\text{m}$  and swims as a puller with 50  $\mu\text{m/s}$ . We present extracted statistical properties of the suspended, passive bead positions, e.g. the mean square displacement or the probability density function of positions. We will compare our results from the microswimmer suspensions with the Brownian motion characteristics of sedimenting particles in very dilute systems and the characteristics in passive sedimenting particles at higher volume concentrations. In our microswimmer suspensions as well as in the sedimentation at higher volume concentrations, the hydrodynamic interaction becomes important and a non-Brownian behavior can be observed.

[1] S. Rafai, L. Jibuti, and P. Peyla, Effective Viscosity of Microswimmer Suspensions. PRL, 104:98102, (2010)

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## Flow-Induces Phase Transitions and Flow Instabilities - FI

Organizers: Christian Wagner and Sandra Lerouge

Friday 13:30 Forum II

FI9

### Elastic turbulence in the flow of wormlike micellar solutions

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Wormlike micellar solutions constitute nowadays a canonical system for the study of experimental and theoretical rheology. Their viscoelastic behavior is well-described by a single-mode Maxwell model and they typically exhibit strong shear-thinning at moderate shear rates. In the non-linear regime a coupling with the imposed flow and fluid microstructure induces the reorganization of the flow in different shear-bands.

We characterize the onset of purely elastic instabilities in the shear-banding flow of wormlike micellar solutions in a Taylor-Couette (TC) device. Our setup allows us to simultaneously measure the global stress response and the local intensity fluctuations in a vertical plane of the TC cell. We identify the transition from laminar to an elastically-driven turbulent flow regime (Fardin et al. 2010). The transition exhibits significant hysteresis which makes us presume that the bifurcation is subcritical. Furthermore, statistical analysis of the elastic turbulence reveals anomalous scaling properties.

From a microscopic point of view, and keeping in mind the reversible character of micelles, comparison of our results with previous results available in the literature for polymeric solutions (Groisman & Steinberg 2000, Burghelea et al. 2007) would enable to elicit the role of the coil-stretch transition in the elastic turbulence framework.

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[2] Groisman, A., Steinberg, V., "Elastic turbulence in curvilinear flows of polymer solutions", Nature 405, 53 (2000).

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Friday 13:50 Forum II

FI10

### Vortex ring formation in oscillatory pipe flow of wormlike micellar solutions

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The rectilinear flow of a wormlike micellar solution, CPyCl/NaSal [100:60] mM, oscillated in a vertical pipe, was studied theoretically in Ref. [1] and experimentally -by means of time-resolved 2D-PIV measurements of the flow in a

meridional plane of the pipe- in Ref. [2]. The flow was inertialess ( $Re < 1$ ) and dominated by fluid elasticity ( $De > 1$ ). The oscillatory pipe flow of a Newtonian fluid under equivalent conditions would remain rectilinear and laminar. For the micellar solution, instead, the reversing character of the rectilinear flow prompted the formation of vortex rings [3]. In this work we present results of additional 2D-PIV measurements of the formation of vortex rings in the oscillatory pipe flow of wormlike micelles. The experiments were designed to address the following questions: How relevant was the unavoidable fluid recirculation near the driving piston, at the bottom end of the pipe, for vortex ring formation? How did the typical formation numbers (ratio of piston displacement to pipe diameter) at which vortex pinch-off occurred compare to typical formation numbers of Newtonian fluids? What was the transient flow dynamics, following a step change in oscillation amplitude that made the original rectilinear flow unstable against the formation of vortex rings?

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[2] L. Casanellas, J. Ortín. Experiments on the laminar oscillatory flow of wormlike micellar solutions. *Rheol. Acta* 51 (2011) 545-557.

[3] L. Casanellas, J. Ortín. Vortex ring formation in oscillatory pipe flow of wormlike micellar solutions. *J. Rheol.* (2014), in press.

#### Friday 14:10 Forum II

F111

### Transition to elastic turbulence and mixing in a periodic array of cylinders confined in a channel

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Using Lagrangian simulations of a viscoelastic Oldroyd-B fluid based on the Smoothed Particle Hydrodynamics (SPH) method [1], we demonstrate that the flow through a closely-spaced linear array of cylinders confined in a channel undergoes a transition to a purely elastic turbulent regime above a critical Weissenberg number ( $We$ ) quantifying the liquid elasticity. The high- $We$  regime is characterized by an unsteady motion and a sudden increase in the flow resistance in qualitative agreement with experimental observations [2]. Furthermore, a power-law scaling behaviour of the velocity power spectrum as well as enhanced mixing of mass is observed. A stability analysis based on the Dynamic Mode Decomposition method (DMD) allows us to identify the most energetic modes responsible of the unsteady behaviour which correspond to filamental structures of polymer over/under-extension advected by the main flow preserving their shape [3].

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#### Friday 14:30 Forum II

F112

### Elastic instability in straight channel for shear thinning fluids induces a genuine drag reduction

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We study the flow of an highly shear thinning polymer solution in straight channel. We evidence a linear elastic instability in line with the work of Wilson and Rallison [1]. This instability differs from the one predicted by Sarlos and coworkers that describe the flow of an Oldroyd B fluid [2]. We take advantage of microfluidics to measure accurately the velocity profiles in straight channels. We point out that the velocity profiles calculated by using the bulk flow curve underestimate the flow. We evidence a genuine drag reduction. Velocity fluctuations in the gradient direction transport polymer molecules through the sample. The effective viscosity is thus determined by this mixing process. The high shear thinning behavior induces a reduction of the local viscosity. We developed a simple model based upon the linearization of the White Metzner equations to capture this behavior.

[1] Wilson, H. J., & Rallison, J. M. (1999). Instability of channel flows of elastic liquids having continuously stratified properties. *Journal of non-Newtonian fluid mechanics*, 85(2), 273-298.

[2] Morozov, A. N., & van Saarloos, W. (2005). Subcritical finite-amplitude solutions for plane Couette flow of viscoelastic fluids. *Physical Review Letters*, 95(2), 024501.

Friday 14:50 Forum II

F113

### On the nature of the first bifurcation in shear-thinning Taylor-Couette flow

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The instability of the circular Couette flow of shear-thinning fluids, between two infinitely coaxial cylinders, where the inner one is rotating and the outer one is fixed is investigated, using linear and weakly nonlinear stability analysis. The objective is to examine the effects of the non-linear variation of the viscosity with the shear-rate on the nature of the bifurcation and the torque applied at the inner cylinder. Two rheological models are used to describe the shear-thinning behavior of the fluid: power law and Carreau law models. The stability of the system considered is first studied for an infinitesimal perturbation. In the axisymmetric case, it is shown that the critical Reynolds number defined with the wall shear-viscosity increases with increasing shear-thinning effects. This is due to the reduction in the energy exchange between the base flow and the perturbation. Deviating from the threshold stability, a weakly nonlinear analysis using the amplitude expansion method is carried out up to the seventh order in the amplitude expansion, for the two rheological models. The determination of the cubic Landau constant in the amplitude equation shows that the nature of the bifurcation depends on the degree of shear-thinning measured by the derivative of the viscosity with the shear rate at the inner wall. For a sufficiently strong shear-thinning behavior, the bifurcation is subcritical. Experimental measurements are currently being carried out with a set-up exhibiting a large gap (radius ratio of 0.4) and a large aspect ratio (height to gap ratio of 40). The measurements are first validated with a Newtonian viscous fluid (glycerol). The non-Newtonian fluids then used, aqueous solutions of CMC (Carboxymethylcellulose) and Xanthan, are shear-thinning and weakly viscoelastic. The transition threshold is measured using torque measurements and Laser Induced Fluorescence (LIF) visualizations. A possible hysteresis will be highlighted.

Friday 15:10 Forum II

F114

### Onset of the Rayleigh-Bénard convection in a yield stress in relation with rheological properties close to the solid-liquid transition

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The Rayleigh-Bénard convection (RBC) has been widely studied for Newtonian fluids and corresponds to a buoyancy driven source of instability (natural convection). In spite of its practical interest, only few have considered the RBC in yield stress fluids. This is mainly due to the difficulty to deal with the two phases of the materials since viscoplastic fluids present a "solid-like" phase prior the yield stress and a "viscous-like" phase afterward. In a recent paper [Darboui et al., *Physics of fluids*, 25(2) 2013], we have shown the occurrence of thermoconvective instabilities characterized by a transition from the conductive regime (fluid at rest) to a convective one in a concentrated percolated suspension of microgels (Carbopol gels). The question is no longer whether the onset of convection occurs in viscoplastic fluids but which mechanisms govern the onset of motion. This key issue concerns directly the viscoplastic fluids behavior close to the solid-liquid transition. In this communication, we propose to consider experimentally several possible mechanisms:

- (i) a viscosity at low values of shear rates by creep measurements below the yield stress over the characteristic time of the onset of convection (concept of kinematic hardening [Dimitriou, *J. Rheol.* 57(1) 2013])
- (ii) the elasto-visco-plasticity behavior of the material below the yield stress
- (iii) a microscopic viewpoint considering the fluids as a porous two phases system

# Wednesday Evening

## Poster Session - PO

Wednesday 17:00 Weinbrenner

### P1-AR

#### Study of the effect of ultrasound on the rheological properties of polymer solutions

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An ultrasound transducer (50 W power) was adapted to the lower plate of a controlled stress rheometer (model AR-100, TA Instruments) to study the effect of ultrasound on the rheological properties of a HASE polymer suspension. The ultrasound was applied at different frequencies in a range of 1-100 Hz during small amplitude oscillatory and continuous flow time sweep tests, storage and loss moduli were monitored during the oscillatory tests and viscosity was monitored in the continuous flow tests. The time interval for ultrasound application was >5 min up to a moment were recorded parameters were considered at steady state ( $\leq 0.5\%$  change). Both moduli and viscosity were strongly affected when ultrasound was applied to the sample. Continuous flow test did not show viscosity recovery after ultrasound application. However, at high ultrasound frequencies (80-90 Hz), full recovery of both moduli values was achieved after ultrasound application. The time for ultrasound recovery is considered as a structure relaxation time as this is still under study. Repeated cycles of ultrasound and no-ultrasound were applied to test for structure sample recovery. Ultrasound frequency of 40 Hz specifically was problematic due to heating and stability issues.

[1] A.I. Isayev, Rishi Kumar, Todd M. Lewis; "Ultrasound assisted twin screw extrusion of polymer-nanocomposites containing carbon nanotubes", Polymer, 2008

[2] Gareth J. Price, Emma J. Lenz, Christopher W.G. Ansell, "The effect of high intensity ultrasound on the synthesis of some polyurethanes", European Polymer Journal, 2001

[3] Vaibhav Desai, Mohan A. Shenoy, Parag R. Gogate, "Degradation of polypropylene using ultrasound-induced acoustic cavitation", Chemical Engineering Journal, 2007

[4] Antti Grönroos, Pirkonen Pentti, Kyllönen Hanna, "Ultrasonic degradation of aqueous carboxymethylcellulose: Effect of viscosity, molecular mass, and concentration", Ultrasonics Sonochemistry, 2007

### P2-AR

#### Investigating the influence of colouring agents on the rheological characteristics of a film-coating dispersion

Thorsten Agnese<sup>1</sup>, Thorsten Cech\*<sup>1</sup>, Nils Rottmann<sup>2</sup>, Fritz Soergel<sup>3</sup>

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The intention of this work was to evaluate whether coating parameters can be used for a spraying dispersion independent of colouring agents contained. In order to investigate this, the rheological characteristics of several film-coating dispersions were tested. Based on the results recommendations for the coating process were deduced. As film-coating material a ready-to use coating system based in Kollicoat® IR was tested.

Regarding flow properties, dynamic viscosity indicates the spreading behaviour of the droplets on the core's surface, whereas extensional viscosity is an indicator for droplet formation. Both values were found to be dependent on the solid matter content of the spraying dispersion. Furthermore, as soon as concentrations of 25% were exceeded, the colouring agent also showed a distinctive influence on both rheological characteristics. These results apply for the ready-to-use formulation and for the pure polymers.

This suggested that coating parameters can be used universally and independently of the colorant. Assuming that the basic formulation (in regard to the kind and amount of polymers) is equivalent and a solid matter content of 25%

is not exceeded. In regard to higher concentrations, the pigments influence the coating properties and parameters have to be gathered separately for each individual colour.

### P3-AR

#### **Investigating the processing properties of instant release film-coating polymers in aqueous solutions by means of extensional rheology**

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This work was to investigate extensional properties and dynamic viscosity of six instant release film-coating polymers. The results were correlated with their coating properties.

Filament life-time (FLT) can be used as a measure to describe the droplet formation. The risk of spray drying effects was found to be increased with longer FLTs.

Firstly, a viscosity of 50 mPa\*s was set. Kollicoat® IR was found with the highest solid matter content - about three times higher than the two cellulose derivatives HPC EF and HPMC 6 mPa\*s. The resulting FLTs of the solutions were also markedly different. Kollicoat® IR with the highest polymer concentration resulted in the shortest FLT. PVA on the other hand, showed a FLT four times longer.

Secondly, solutions with various polymer concentrations were tested. Comparing the HPMC grades, a similar FLT was determined for low polymer concentrations, whereas huge difference could be seen with higher concentrated solutions. A similar effect could be found for Kollicoat® IR and PVA.

Best coating results can be expected for low viscous solutions allowing high solid matter contents and still yielding short FLTs. The Kollicoat® products were found to match all these requirements best.

### P4-AR

#### **Advanced CaBER technology**

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Commonly, the Capillary Breakup Extensional Rheometer (CaBER) is equipped with a laser micrometer to monitor the diameter of a thinning liquid thread. This method is suitable as long as the filament is cylindrical. For non-cylindrical filaments, an accurate determination of filament shape is mandatory for understanding deformation behavior. Therefore, we have set up an optical train including a high-speed camera, telecentric objective (1x, 5x, 20x magnification) and telecentric back-light illumination. Image analysis allows for diameter determination with accuracy up to 0.7  $\mu\text{m}$ . Characteristic values like the elongational relaxation time, the viscosity of a Newtonian fluid or the elongational yield stress can be analyzed correctly from the video images. Using the shape of a horizontally stretched liquid filament, bended due to gravity allows for the determination of the true axial force acting in the filament in a range of 0.1  $\mu\text{N}$  and 1 mN and, therefore, of the true elongational viscosity. A self constructed temperature cell unit and a thermocouple mounted next to the sample in the lower plate of the CaBER device allows for an appropriate temperature control. Using a water bath thermostat, temperatures between 5°C and 90°C with an accuracy of 0.2°C can be achieved. The temperature cell unit also serves as a solvent trap to prevent evaporation independent of temperature. In general, our setup also allows for combining other optical trains (e.g. birefringence, turbidity or light scattering) with CaBER to study the influence of an elongational flow field to molecular structures at different temperatures.

### P5-AR

#### **On the applicability of the QL-LAOS analysis to viscoelastic liquids**

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Recently we proposed a novel approach for using large amplitude oscillatory shear flow experiments (LAOS) to determine—in a simple, direct and robust manner—the mechanical behavior of soft solids. This approach is based on the observation that, as the stress amplitude and frequency are independently varied, two classes of motion are observed: (i) structure-changing motions, characterized by a non-sinusoidal response, when the stress amplitude is large enough to cause microstructural changes and the frequency is of the order of the reciprocal of the time

scale of microstructural changes; and (ii) constant-structure motions, characterized by a sinusoidal response, when either the stress amplitude is not large enough to cause microstructural changes or the stress amplitude is large enough to cause microstructural changes but the frequency is much larger than the reciprocal of the time scale of microstructural changes. For a commercial hair gel, we confirmed experimentally the existence of these two classes of motions. While at present all LAOS analyses focus on the structure-changing motions, our methodology—quasi-linear LAOS or QL-LAOS—relies for the most part on data obtained from constant-structure motions, which simplifies dramatically the experiments and the analysis, and provides material functions the physical meanings of which are quite evident. In this presentation, we present the results and conclusions of an investigation the goal of which was to verify the applicability of the QL-LAOS analysis to a viscoelastic liquid. To this end, we selected an aqueous solution of polyacrylamide. We employed both a stress-controlled (DHR-3) and a strain-controlled (ARES-G2) rheometer, with a cone-and-plate geometry. In the conference we will present and discuss the small- and large-amplitude oscillatory shear flow test results obtained for a wide range of stress amplitudes and frequencies.

## P6-AR

### **Simultaneous Dielectro/Rheological Measurements in Thermoplastics, Rubbers and Thermosets Materials**

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Rheology is, more and more, a technique that can be used coupled with other techniques. For example, Dielectric Analysis. Dielectric Analysis measures the two fundamental electrical characteristics of a material, capacitance and conductance, as function of time, temperature and frequency. Dielectric analysis is powerful technique for characterizing polar materials (with permanent or induced dipoles) such as most of polymers, foods, pharmaceuticals, etc. There is a broad range of applications where this technique is very valuable like phase separating systems, curing kinetics of materials such as epoxy and urethane systems, polymer blends, and nanocomposites. The technique involves applying an oscillating electrical field (AC Field) to measure the degree to which the sample is storing (capacitance) or transferring electric charge (conductance) through its bulk. The system used provides a frequency range of 20 Hz to 2 MHz and a temperature range of -160°C to 350°C. It can be used in stand-alone or simultaneous mechanical and dielectric techniques. A novel feature is the fact that with the DETA accessory of the DHR or ARES G2 (TA Instruments), it is possible to perform experiments with disposable plates in for example, thermosets curing materials. The disposable plates offer a unique platform for the most challenging samples such as epoxies. In this work, an EVA copolymer, a Rubber/carbon black system and an Epoxy thermoset has been characterized with this coupling techniques. The 3 applications presented here only show a portion of what simultaneous rheology and dielectric analysis can do.

## P7-AR

### **Tribo-rheology Accessory for Controlled Stress Rheometers**

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A thorough characterization of material properties at each stage of manufacturing, processing, and end use conditions is critical when designing new and novel materials. Of these, an understanding of the impact of frictional effects and long term usage on the wear on the material properties can be beneficial for improving overall product longevity. Such information is pertinent to a wide spectrum of applications including prosthetic devices, personal care creams and lotions, automotive components, and greases. The traditional approach to investigating frictional effects involves the use of a tribometer equipped with normal force and either linear or rotational displacement rate control. In this poster we introduce and discuss the application of a tribo-rheometry accessory for performing tribological measurements on commercially available DHR rheometers. The accessory exploits the superior normal force control afforded by the DHR's FRT normal transducer and the torque sensitivity of the magnetic bearing combined with excellent displacement resolution. Additionally, the ability to operate at maximum motor torque for an indefinite period and the high stiffness rheometer frame allow tribo-rheometry testing at high rates and high axial loads for extended periods of time. A number of different configurations for the tribo-rheometry accessory are presented and the versatility of the platform for measuring the coefficient of friction is demonstrated.

## P8-AR

### LAOS Characterization of TPU Nanocomposites

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The intense development of new nanocomposites, consisting of polymer matrix and inorganic filler, has recently originated a significant increase in the number of studies focused on the characterization of organic-inorganic interphases. Those studies are justified since a proper characterization of the interphase is crucial to understand the properties and behavior of the nanocomposite. Despite the utility of those studies, identification and characterization of the structure-properties relationships presented a number of difficulties depending on the features of each specific case. Particularly, most of the results are not applicable outside of the linear viscoelastic region. That is the reason why a large amplitude oscillation shear (LAOS) experimental setup is used in the present work to identify and characterize the organic-inorganic interphases of multiwalled carbon nanotube (MWCNT)-thermoplastic polyurethane (TPU) nanocomposites. The experiments were made in the Process Analyzer (RPA) (TA Instruments/Scarabeus) that is the most advanced rotorless rotational shear rheometer dedicated to the complete characterization of polymers, rubber and rubber compounds at all stages of manufacture. The fully flexible architecture of the RPA elite enables advanced testing capabilities including large amplitude oscillatory shear (LAOS).

## P9-AR

### Measurements of low-viscous liquids at high shear rates in a thin-gap parallel-disk configuration

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We modify a commercial rheometer to set-up disks with a precision in parallelity of down to about 1  $\mu\text{m}$ . At gap widths of about 20  $\mu\text{m}$ , this allows an extension of the measurement range to low viscous liquids and to shear rates of up to about  $10^5 \text{s}^{-1}$ . We show that the viscosity of low-viscous liquids such as water can be determined with the parallel-disk configuration. Comparison with measurements carried out with a capillary viscometer shows good accordance.

## P10-AR

### Evaluating the Fourier Transform Spectra of the Axial Normalforce of Polymermelts Under LAOS with a New Parameter $Q_{NF}$ and a New High Sensitive Normalforce Geometry (NoForGe)

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We measured the normal forces of polymer melts in LAOS experiments. For our investigations we used a high performance ARES rheometer in combination with the FT-Rheology of Wilhelm [1]. Its sensitivity for measuring the normal forces is limited and it has no capacity to measure normal forces under oscillatory shear.

We made two approaches to obtain the normal forces under oscillatory shear with the ARES.

1) We improved the FT-R set-up, as published by Wilhelm et al.[1-2], to measure the normal force. The normal force data can be obtained by connecting the PC directly to the hardware of the ARES. However, it is still limited to the sensitivity of the its installed force.

2) We designed a new geometry for the ARES with a highly sensitive force measurement. This special set-up contains a highly sensitive piezoelectric force transducer and was installed in the ARES:

We compared the results of LAOS measurements of these both approaches with the results obtained from the high performance shear rheometer, the ARES G2. It has initially the capabilities to measure the normal forces under LAOS. To show the advantages and capabilities of our new setup, we conducted measurements with different PS and PE melts, which have a different molecular architectures.

The higher even harmonics appear in the Fourier transform spectra of the normal force obtained from LAOS experiments. Thus, we introduce a new non-linear parameter  $Q_{NF}$  which is a function of the applied strain rate [3].

We did this in analogy to the non-linear parameter,  $Q$ , of the spectra of the shear amplitude and we use  $Q_{NF}$  and  $Q$  to differentiate between linear and branched polymers [4].

[1] M. Wilhelm. *Macromol. Mater. Eng.*, 287(2):83–105, 2002.

[2] M. Wilhelm, P. Reinheimer and M. Ortseifer. *Rheol. Acta*, 38:349–356, 1999.

[3] I.F.C. Naue. PhD thesis, Karlsruhe, 2013.

[4] K. Hyun, M. Wilhelm, C.O. Klein, K.S. Cho, J.G. Nam, K.H. Ahn, S.J. Lee, R.H. Ewoldt and G.H. McKinley. *Prog. Polym. Sci.*, 36(12):1697–1753, 2011.

#### P11-AR

##### **Rheo-optical measurements: Enhancing the image quality by using alternative illumination techniques**

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Combining light microscopy with rheometry in one instrumental setup (rheo-optics) is a powerful tool for analyzing the change of a material's microscopic structure in relation to its rheological properties. Microscopic images recorded under shear in rotational measurements reveal induced structural changes like orientation, deformation, coalescence, aggregation or disaggregation. Stress, strain or temperature dependent microscopic changes, like crystallization, can be made visible by recording images during non-destructive oscillatory measurements.

In order to extend the useable measurement range of the rheometer for rheo-optical measurements to (much) higher shear-rates an alternative illumination technique has been developed which allows for much shorter exposure times. The image quality for low contrast samples, like certain emulsion, could be significantly improved by making several modifications to the optical path of the HAAKE RheoScope module.

We will present data with sharp images for shear-rates up to around 40000 1/s as well as high quality and high contrast images acquired using rheo-optical measurements on an emulsion, which was considered to be low-contrast when using normal illumination.

#### P12-AR

##### **In-situ rheology with simultaneous X ray scattering**

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For a comprehensive understanding of a material, usually more than just one analytical technique is required. Techniques complementing rheological measurements are e.g. FT-IR spectroscopy or X-ray scattering. By combining two analytical techniques in one instrument the amount of information gathered from one single sample is maximized.

During the last six years, a novel combination of a HAAKE MARS rheometer combined with a vertical deflected X-ray beam has been developed at DESY. With the rheometer designed as open platform individual solutions can be realized to meet even the most complex demands. The presented set-up allows for the combination of in-situ rheology measurements with small and wide angle X-ray scattering experiments (SAXS/WAXS). Here, we would like to report on the possibilities of coherent scattering experiments, namely X-ray photon correlation spectroscopy (XPCS) using this unique rheology setup installed at the synchrotron source PETRA III making use of the novel LAMBDA pixel detector. XPCS measures the intensity fluctuations of a coherently scattered X-ray beam as a function of wave vector transfer. By calculating the corresponding normalized intensity-intensity time auto-correlations, it is possible to directly obtain information about the dynamics of the sample on the different length scales probed. In itself, XPCS requires a detector with a high frame rate and high signal-to-noise ratio. As coherent scattering experiments rely on the possibility to detect individual speckles of an interference pattern, a small pixel size as well as high read-out speed as provided by the novel LAMBDA detector is mandatory.

As a model sample system, we investigated the effect of shear on a colloidal system in the liquid phase, where we obtained for the first time in-situ information about colloidal dynamics using X-ray scattering under steady and oscillatory shear conditions.

Details of this unique new set-up as well as selected measuring results will be presented.

### P13-AR

#### Development of Electromagnetically Spinning Sphere Viscometer

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Among various viscometers proposed so far, the most popular one is a rotational viscometer, in which shear deformation is introduced by a rotor, and the relation between the rotor rotation speed and the applied torque gives the viscosity. However, less progress in mythology has been made in recent years to meet the growing user's demands: Requirement arises, for example, to the rapid observation, small quantity of samples, and completely closed system for the viscosity measurement.

In our presentation, we introduce a new type of a viscometer employing Electro-Magnetically Spinning Sphere (EMS) technique, which is based on the principle of non-contact driving of the rotor by the electro-magnetic interaction. It applies remote torque to the metal sphere probe in the sample in a non-contact manner; rotating magnetic field is applied to the probe, which generates the induced current in the probe and the Lorentz interaction between the current and the magnetic field gives the rotor the torque to spin following the rotation of the magnetic field. By measuring the rotational speed of the probe sphere by the laser technique, we can determine the sample viscosity. The sample can be confined in a sample tube and, therefore, the system is free from the problem of the contamination. The viscometer has other unique features, such that measurements can be carried out under hermetically sealed condition and it requires very small amount of sample volume of 0.3 mL. In addition, the viscometer has a wide measurement range of 0.1m - 1000 Pa\*s. In principle, it can measure much higher viscosity beyond the above commercially corroborated range. This novel viscometer has already been applied for medical applications, such as rheology measurement of blood and other body fluids, in which preventing sample contamination is a key issue.

We will show remarkable potential of the EMS viscometer to carry out various kinds of viscosity measurement with quite easy operations at the conference.

### P14-AR

#### Computational Rheometry – an useful tool to interpret the rheological measurements

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The term Computational Rheometry is referring to the numerical modeling of the shear experiments performed in a commercial rotational rheometer. Simple shear and oscillatory flows are simulated in controlled strain and controlled stress modes, for plate-plate, cone-plate and concentric cylinders geometries. Different constitutive models, temperatures and boundary conditions are used as inputs for calculations of velocity field in the gap, the output being the measured quantity on the upper tool: torque, respectively the strain rate. At the end, the "measured" (i.e. computed) material function (in particular viscosity) is compared with the input function. The numerical procedure emphasis not only the influence of the end effects on the measured quantities, but also the effects induced by the imposed slip at the walls. The performing of computations for un-stable constitutive models is one main goal of the study. The numerical results disclose the instability phenomena and explain with accuracy the spreading of recorded measurements in real tests. We consider Computational Rheometry not only as a complementary procedure of interpret the measured data, but also an useful tool to teach rheology at advance level.

### P15-AR

#### Curved Mooney plots: an indication of non-locality in the wall slip boundary condition?

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A common way to evaluate wall slip is the Mooney procedure. Using a capillary rheometer, the apparent Newtonian flow rate is measured with various capillary radii  $R$  and the wall slip velocity  $U_s$  is obtained by plotting the apparent shear rate as a function of  $1/R$  at constant wall shear stress. If  $U_s$  depends only on the wall shear stress then the curves must be straight lines and  $U_s$  is equal to one fourth of the slope. On the other hand, it is often observed

[1] that, for polymer melts, the apparent shear rate does not vary linearly with  $1/R$ . In particular, for pressure driven flows, Mooney plots are often curved upwards. In this work we show that the upward curvature of Mooney plots is compatible with slip boundary conditions formulated in a non-local way.

The non-local slip velocity and wall shear stress are defined as in [2] using a suitable kernel function. A characteristic length of the fluid is automatically introduced and is denoted with  $L$ . A non-local slip condition can then be formulated in terms of the non-local slip velocity and wall shear stress.

With this relation, a corrected form for the apparent shear rate can be found. This is given by the sum of three terms: two of these are the ones appearing in the usual Mooney procedure, i.e. a constant term and one that varies linearly with  $1/R$  and that contains the slip velocity. The last term is a non-linear correction that is responsible for the upward curvature and can be shown to be negligible for small values of  $L/R$ . Therefore, as  $L$  is only material dependent, in order to use the Mooney correction properly  $R$  must be sufficiently large, i.e. the Mooney plot must be considered only for sufficiently small  $1/R$  values. For completeness, a comparison with experimental Mooney plots taken from [1] is presented, and it is shown that the agreement is excellent.

[1] S.G. Hatzikiriakos, Prog. Polym. Sci. 37 624 – 643 (2012).

[2] A.C. Eringen, Nonlocal continuum field theories, Springer (2002)

## P16-BF

### Determination of gluten-free doughs structure by the fractional rheological model

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Viscoelastic properties of a biopolymers can be described using the so called fractional derivative rheological models. An advantage of the fractional rheological models is that they can describe dynamic behavior by means of a single equation which contains a number of constant parameters determining various viscoelastic properties of a material being tested. The values of the rheological parameters of fractional model give a useful information concerning the structure of biomaterial, such as total elasticity of the networks, network oscillations, gel stiffness and structure of cross-linking. Due to growing interest in gluten-free doughs, the authors have undertaken to analyze the mechanical state of structure of corn starch and amaranth flour mixture with proteins isolated from pea and plantain fibers psyllium, using the results obtained by Mariotti [1]. Experimental data presented in Mariotti [1] paper are only showing a solid elastic-like behavior of gluten-free doughs and their data are described by simple power-law model.

The aim of this study was to present that very interesting additional information could be extracted from the same experimental data if we describe rheological curves of gluten-free doughs by FLSM model. Proposed by us method of interpretation of the results of rheological measurements makes it possible to present a comprehensive evaluation of the analyzed medium structure. Application of the FLSM model to describe the viscoelastic behavior of gluten-free doughs allows to explain the influence of the amount of ingredients - Psyllium fiber and Pea protein - on the rheological properties of such biomaterials.

The fractional rheological models can be useful to control adequately the structure of biomaterial for the needs of the formed product which is particularly important from the point of view of materials science and product utility.

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## P17-BF

### Rheological Measurements on Chocolate Using the Large Amplitude Oscillatory Shear (LAOS) Tests

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LAOS, which is a rheological method carried out in the nonlinear region, is scarcely applied on foods to define the rheological properties. Up to date, this technique has been applied to determine the rheological properties of food products such as gluten dough (Ng et al., 2011), polysaccharide systems i.e. carrageenan or starch (Klein et al., 2008), whey protein isolate and  $\kappa$ -carrageenan gels, commercial cheese (Melito et al., 2013a), tuna myofibrillar protein (Liu et al., 2014). In this study, LAOS experiments were conducted on chocolate at various temperatures (20 °C, 25 °C, 30 °C, 36 °C). The relative rates of shear thickening/thinning and strain stiffening/softening properties were compared. The measurements were carried out using HR-3 Rheometer (TA Instruments) between the strain values of 0.01 to 5% at 1Hz. According to the results obtained, the chocolate sample exhibited strain stiffening and shear

thinning behavior at all experimental temperatures.

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[3] Melito HS, Daubert CR, Foegeding EA (2013b). Relationships between nonlinear viscoelastic behavior and rheological, sensory and oral processing behavior of commercial cheese. *J Texture Studies* 44:253-288.

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## P18-BF

### Study on the relation between the (fine-)structure of the protein network and the energy dissipation modes in semi-solid food gels

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Due to the growing pressure on using protein in foods, a predominant texturing component, there is a demand to understand protein-specific behaviour in the material responses during deformation, e.g. in oral processing or product manufacturing. The way a spatial protein network, enclosing an aqueous serum phase, is able to deal with external applied energy, has been shown to be a determining factor in the extend of fracturing of the material and thereby in a number of important sensory perceptions of the product related to consumer acceptance. Typically between tongue and palate deformation speeds of 20-50 mm/s are developed with contact pressures ranging from 10-30 kPa. The energy developed on the food gel can be either stored in the matrix, be used for fracturing events or dissipated via other means, like friction forces developed during the viscous flow of serum through the porous matrix during mechanical deformation. Obviously, when energy is dynamically stored in the matrix it has become inaccessible for fracture phenomena, thereby affecting the overall macroscopic responses of the product. The origin of the ability of such a spatial protein network to store energy during deformation, that becomes available again after release of the externally applied pressure (defined as recoverable energy), is the topic of this study. To this end, protein-continuous gels were prepared and their large deformation properties (fracture stress, fracture strain, recoverable energy) were determined. By using different protein sources (milk caseins, egg white protein, pork skin gelatin, soy protein isolate) a broad range of morphologies was obtained that were characterized on the micrometer lengthscale by confocal scanning laser microscopy, and at smaller lengthscales by electron microscopy and atomic force microscopy. By studying these rheological responses as a function of applied deformation strain and deformation strain rates, in combination with the (fine-) structural analysis of the structure building blocks of the protein network, allows one to hypothesize on the relation between the ability to store energy dynamically and the "structural smoothness" of the protein network in terms of their ability to dissipate energy via stress relaxation.

## P19-BF

### Mechanics of Intermediate Filament Networks

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Intermediate filaments (IF) serve as mechanical stress absorbers in eukaryotic cells. There are more than 70 different cell specific IF proteins which are divided in six different types according to similarities in their protein structure. Here we investigate IF networks of keratin 8 and 18 (K8/18) formed from the basic type I keratin 8 and the acidic type II keratin 18 in vitro that are typically found in abundance in simple (internal) epithelia. These networks show an unusually high plateau modulus (1–10 Pa at 1 g/l), which depends only weakly on concentration ( $G_0 \sim c^{0.5 \pm 0.1}$ ). After addition of the non-ionic surfactant Triton X-100 the plateau modulus decreases by more than two orders of magnitude

and follows a power law of  $G_0 \sim c^{1.9 \pm 0.2}$ . The addition of the surfactant not only alters the linear viscoelastic shear modulus, but also has a strong effect on the non-linear mechanical network response. Strain stiffening can be completely suppressed adding a sufficient amount of surfactant. In contrast, the network mesh size determined from microrheology and the bending stiffness of the individual filaments obtained from high frequency oscillatory squeeze flow experiments are not affected by the added surfactant. This is also true for the network structure revealed from electron microscopy. From these findings we conclude that attractive interactions among filaments govern the macroscopic properties of K8/18 networks and are pivotal for their linear and non-linear rheology. Networks of the type III IF protein vimentin show the same decrease in the plateau modulus and in strain stiffening after addition of Triton X-100. This suggests that these attractive interactions are controlling the mechanical response of cytoplasmic IF networks. This at least seems to hold for the major representatives and this hypothesis is further supported by the strong effect of ionic strength on strain-stiffening of vimentin reported in the literature.

## P20-BF

### Rheological behavior of chocolate with polysaccharide

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Chocolates are complex rheological system with solid particles, like cocoa and sugar, dispersed in cocoa butter which is the fat phase. The cashew polysaccharide is from exudate species *Anacardium occidentale* L., presents molecular weight  $M_w =$  approximately  $1.5 \times 10^4$ , and has characteristics similar to those of gum arabic, representing a potential substituent to various gums used in food industry. Rheology is the study of the flow of matter, in the liquid state, or as semi solid or solid, under conditions in which they respond with plastic flow rather than deforming elastically in response to an applied force. The aim was to study the rheological characteristics of chocolate added with cashew polysaccharide (1 and 3%). Dark chocolate was prepared in a pilot plant (ball mill 20 - Mazzetti, Italy), with cocoa liquor (Cargill, Brazil) + refined sugar (União, Brazil) + soy lecithin (Tovani, Brazil) + vanilla flavor (Duas Rodas, Brazil). Rheological behavior was determined in a Haake MARS II rheometer (Thermo Electron Corporation, Germany) with thermostatic bath and cone plate sensor (C35 / 1 Ti), at 40°C: rotational controlled rate test, three steps (1) 0.00 1/s a 65.00 1/s,  $t = 180$  s; (2) 65.00 1/s,  $t = 60$  s; (3) 65.00 1/s a 0.00 1/s,  $t = 180$  s. The captured points were adapted to Casson equation. Casson viscosity varied as ( $p < 0.05$ ): chocolate standard ( $4.14 \pm 0.87$  Pa.s), 1% ( $5.55 \pm 0.52$  Pa.s), 3% ( $5.77 \pm 0.70$  Pa.s). Yield stress was ( $p < 0.05$ ): chocolate standard ( $21.00 \pm 2.79$  Pa), 1% ( $128.01 \pm 49.83$  Pa), 3% ( $166.03 \pm 25.64$  Pa). The addition of cashew polysaccharide increased the yield stress and viscosity in 1% and 3% as expected. However, the variations did not interfere in the way to mold chocolates or in final quality.

## P21-BF

### Evaluation of rheological gelation kinetics in aqueous solutions of poloxamer for ophthalmic use

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The aim of this study was to evaluate the rheological behavior of poloxamer aqueous solutions (Pluronic F-127 and Pluronic F68, Sigma-Aldrich), in order to determine their potential as in-situ gelification systems for ophthalmic administration. Poloxamer solutions were prepared by the cold method, using deionized water or phosphate isotonic buffer (0.1 M, pH 7.4) as solvents. Solutions were tested in oscillatory shear flow with temperature sweeps using parallel plate geometry on a controlled stress rheometer (AR-G2, TA Instruments). Kinetics of oscillatory flow with small deformation amplitude were conducted from 10 to 80 °C with heating rate of 0.5 °C/min, deformation and angular fixed frequency of 95% and 1 Hz, respectively, with a gap of 500  $\mu\text{m}$  between the plates. Also, time kinetics were performed at temperature of ocular surface (at 36 °C). To determine gel point, evolution of complex viscosity ( $\eta^*$  vs temperature) of solutions in temperature kinetics and time kinetics at was followed. Poloxamer solutions at maximum concentration permitted by FDA for use in humans (0.1% and 0.2% for F68 and F127, respectively) and in a concentration range of 5 to 15% (w/v) were analyzed. According to our findings, we cannot say that studied solutions show actually a transition from viscous liquid to viscoelastic solid. The results suggest that these solutions produce "weak gels", which do not form a semisolid structure, but increase their viscosity with increasing temperature. Diluted solutions showed no change in rheological tests. However, solutions with higher concentrations showed, generally,

a significant increase in complex viscosity. Solutions prepared with buffer had higher viscosity than solutions in deionized water. Additionally, F127 solutions showed higher viscosity than those with F68 at the same concentration. Finally, the gelation temperature decreases with increasing concentration in all cases.

#### P22-BF

##### **Effect of waiting period on gel strength of gelatin solution: Steady shear rheological characterization during gelation**

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The main objective behind this study was to determine the effect of time on the gelation behavior of beef gelatin by steady and dynamic oscillatory shear rheological characterization. For this aim, 5% (w/v) beef gelation solution was prepared and it is put into a beaker having no cap. Steady shear and dynamic oscillatory shear rheological properties of sample were studied using a stress/strain controlled rheometer equipped with a peltier system during the gelation for 5 h at certain time intervals. Apparent viscosity value of gelation solution was recorded to be 8.0 mPa\*s at 50 s<sup>-1</sup>. After one hour later, apparent viscosity was measured to be 49 mPa\*s and after 5 h later from the beginning of the gelation, apparent viscosity value reached to 1894 mPa\*s. Oswald de Waele model was used to describe the relationship between the shear stress and shear rate by fitting to the steady shear rheological data and it was found to be enough to describe the behavior of sample until 3 h waiting. Consistency coefficient of gelation solution was calculated to be 6 mPa\*s<sup>n</sup> at the beginning of the waiting and it was determined to be 39170 mPa\*s<sup>n</sup> after 3 h later. At the end of the waiting, consistency coefficient value was calculated to be 81243 mPa\*s<sup>n</sup>, but determination coefficient was found to be 0.319 that means Oswald de Waele model can not be used for fitting after 5 h gelation for gelatin solution.

#### P23-BF

##### **Viscoelastic behavior of fat based fillings**

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Fatty fillings are components used in the confectionery and bakery products. Viscoelasticity characterization can be determined through G' parameter (elastic modulus or storage), which indicates the capability of the system to recover their original characteristics after suffering deformation, or G'' (viscous modulus or dissipation), which quantifies the dissipated energy. The aim of this study was to evaluate the viscoelastic behavior of fillings made with variation in the type and amount of fat used for the fat base of these products. Nine fat based filling formulations were developed with low trans fat, cupuassu fat and cocoa butter at concentrations of 10%, 7.5% and 5%, from standard formulation containing hydrogenated vegetable fat. The fillings were analyzed through combined oscillation and rotation analysis in a Haake MARS II rheometer (Thermo Electron Corporation-Germany), with a cone-plate sensor (C35 / 1 polished Ti). Analyzes was conducted as: oscillation with controlled tension (1 Hz, 0.01 Pa), rotational with controlled shear rate (50 s<sup>-1</sup>) and oscillation with controlled tension (1 Hz, 5 Pa) at a constant temperature of 28 °C. During analyzes images were captured through a high resolution microscopy system coupled to the equipment (RHEOSCOPE Module) and the results were obtained from the HAAKE Rheowin program (version 6.0). The fillings showed strong gel behavior by the viscoelastic system G' > G'', where the variation of type and amount of fat used did not change this result. Higher values of apparent viscosity were observed in all formulations containing vegetable low trans fat. Samples prepared with a higher fat concentration (10%) showed high elasticity and better recovery after lowering the tension in the third step of the analysis. The difference in the samples structures was also observed by the shape and orientation of the particles before and after shearing, in the images obtained during the test.

#### P24-BF

##### **Chocolate with Brazil nut flour**

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Chocolates are a suspension of fine solid particles (sugar, cocoa, milk) making about 70% in total, in a continuous

fat phase. It is increasingly about consumers weighing the health benefits, and chocolate companies seem to be leaning farther toward chocolates. Brazil nut flour has nutritional quality in terms of macro and micronutrients, making it suitable for application or use as a raw material base or in partial substitutions as a nutritional enriching compound in the food industry. The aim was to study the rheological and nutritional characteristics of chocolate added with Brazil nut flour. Dark chocolate (Nestlé, Brazil) was added with Brazil nut flour (5, 10 and 20%). Nutritional properties were determined as AOAC (2000), granulometry in sieves, and rheological properties were determined in a Haake MARS II rheometer (Thermo Electron Corporation, Germany) with a plate sensor (PP20 Ti). The analysis was performed at 40°C as: rotational controlled rate test (CR), three steps (1) 0.00 1/s a 65.00 1/s,  $t = 180$  s; (2) 65.00 1/s,  $t = 60$  s; (3) 65.00 1/s a 0.00 1/s,  $t = 180$  s. The captured points were adapted to Casson equation. Casson viscosity varied as: chocolate with 20% flour ( $2.07 \pm 0.71$  Pa\*s), 10% ( $3.71 \pm 0.35$  Pa\*s), 5% ( $1.97 \pm 1.25$  Pa\*s), dark chocolate ( $1.88 \pm 0.06$  Pa\*s). Yield stress was to 20% flour ( $35.35 \pm 7.31$  Pa\*s), 10% ( $16.27 \pm 1.88$  Pa), 5% ( $12.11 \pm 1.70$  Pa), dark chocolate ( $16.22 \pm 3.91$  Pa). Mainly protein content was improved in both samples with Brazil nut flour. It is not so easy to determine rheological parameters to products with particles. The addition of Brazil nut flour increased the yield stress only to 20%, and viscosity to 5, 10 and 20%. However, the variations did not interfere in the way to mold the chocolates or in final quality. Brazil nut fat did not interfere in rheological process, and adds to chocolate nutritional evidences.

#### P25-BF

### Interaction between hydrocolloids used in model system jam production: Simplex Lattice Mixture Design Approach to optimize the rheological parameters

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The aim of the present study was to investigate the interaction between the selected hydrocolloids (xanthan gum, carboxymethyl cellulose (CMC) and pectin) in the model system jam formulation and to determine the optimum gum combination for the use in jam manufacturing using Simplex Lattice Mixture Design. Model system jam samples were produced using sugar, tartaric acid and gums and rheological analyses of produced samples were carried out. Steady shear rheological properties of samples produced according to a certain design were characterized using a stress/strain controlled rheometer at a constant temperature and consistency coefficient, flow behavior index and apparent viscosity values were recorded. To estimate the steady shear rheological parameters, some regression models were constructed. It was concluded that the highest apparent viscosity value among the sole gum solutions was recorded for the carboxymethyl cellulose (CMC). It was measured to be 0.326 Pa\*s while the apparent viscosity values were 0.232 and 0.205 Pa\*s for the pectin and xanthan gum solution samples (0.5% w/v), respectively. Consistency coefficient of the samples increased with the increase in CMC in the gum mixture significantly ( $p < 0.05$ ). The linear effects of added hydrocolloids on the steady shear rheological parameters of model system jam was determined to be significant statistically ( $p < 0.01$ ). Increase in the pectin level in the formulation caused a decrement in the consistency coefficient and increase in the flow behavior index. Optimization study showed that the highest apparent viscosity values can be obtained by using CMC as a sole gum in the formulation. It was concluded that the CMC can be used as an alternative hydrocolloid instead of pectin in the jam production.

#### P26-BF

### Origin of anti-slip in a CTA containing CASUCOL 301

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The poster shows how a starch ether is responsible for flocculation of cement particles via a polymer bridging flocculation mechanism and thereby influences the rheological properties of cement- and gypsum-based construction materials.

## P27-BF

### Modeling of Rheological Properties of Mellorine Samples by ANN, ANFIS and Combine Design

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In this study, the effects of two different oil types (soybean and olive oil) and three different gums (xanthan gum, sodium alginate, locust bean gum and their blends) on the rheological properties of the mellorine mix were investigated. Mellorine mix samples showed Ostwald de Waele flow behaviour ( $R^2 > 0.9915$ ). The gum and oil types significantly affected rheological properties of mellorine samples. The mellorine samples including xanthan gum and locust bean gum had the highest K and  $\eta_{50}$  value and this value was the lowest for the sample including alginate. Viscous synergy index value of the xanthan and locust bean gum combination was found to be approximately 1.80. Effects of different gums on the apparent viscosity values at  $50 \text{ s}^{-1}$  ( $\eta_{50}$ ) were satisfactorily modelled by modified power law model. ANFIS model was also found to be sufficient to predict apparent viscosity values based on the oil type, gum concentrations and shear rate ( $R^2 = 0.9121$ ). According to the combined design, the optimum gum concentration was determined as 56.3% xanthan gum and 43.7% locust bean gum.

## P28-BF

### Steady shear rheological properties and textural characteristics of yoghurt/molasses blends

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In the present study, yoghurt/molasses blends were produced with the addition of molasses at three different concentrations (5, 10 and 15%) to the yoghurt and steady shear rheological properties and textural characteristics of produced yoghurt/molasses blends were characterized. Stress/strain rheometer equipped with a peltier system was used for the rheological analysis. Back extrusion test was conducted to characterize the textural properties of the samples using a texture analyzer. Oswald de Waele model was used to describe the relationship between the shear rate and shear stress values of samples and it was found that the samples showed pseudoplastic behavior. Consistency coefficient (K) and flow behavior index (n) values were calculated using Oswald de Waele model. Increase of molasses concentration showed a significant effect on the studied parameters. Consistency coefficient and apparent viscosity values decreased with the increase in molasses level in the blends. K value was determined to be  $51.1 \text{ Pa} \cdot \text{s}^n$  for the control sample (un-enriched yoghurt) while the K value of the sample added with 15% molasses was  $21.7 \text{ Pa} \cdot \text{s}^n$ . Apparent viscosity values at  $50 \text{ s}^{-1}$  and  $25 \text{ }^\circ\text{C}$  were recorded in the range of 2.47-4.31  $\text{Pa} \cdot \text{s}$ . Increase of molasses concentration in the blends showed a significant decrease in the back extrusion parameters namely firmness, consistency, cohesiveness and viscosity index values of samples. A firmness value was 316 g for the control sample while the firmness value of sample added with 15% molasses was 89 g. As a conclusion, addition of molasses caused a significant change on rheological and textural properties of yoghurt/molasses blend. These results should be taken into consideration in order to optimize and find the best quality of yoghurt/molasses blend product.

## P29-BF

### A CaBER computational-experimental rheological study on human sputum (bio-fluid)

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The main focus of this computational modelling study is to determine the extensional rheological response of sputum biofluids to provide a diagnostic tool (biomarker) for experimentally-based pathological analyses and clinical practice. This may be accomplished through advanced rheological parameterisation and characterisation of sputum samples, when considering extensional deformation flow situations that mimic sputum escalator deformation in the

lung-airways. Sputum samples have been collected from patients (male and female, fifty+ years of age) suffering from Chronic Obstructive Pulmonary Disease (COPD) at two stages of development: uninfected (stable or non-infective) state and infected (suffering exacerbations) state.

Immunoassays have been tested without any pre-treatment such as mechanical homogenisation. Experimental and numerical studies of Capillary Break-up Extensional Rheometer (CaBER) have been performed, from which comparison significant correlations are presented. Typically, the dynamic development of the mid-filament diameter is monitored during the process of necking and failure. The aim is to link this type of data with that emerging from experimental/clinical trials to provide a biomarker revealing insight on disorder treatment.

The rheology of sputum immunoassays is represented through several rheological fluid modelling approaches: (i) a kinetic Single Extended pom-pom (SXPP) model; (ii) a time-dependent thixotropic Modified Bautista-Manero (MBM) model; and (iii) a time-independent network-based Exponential Phan-Thien Tanner (EPTT) approximation. These models are sufficiently rich to enable description of both network-structure and rheological properties, exhibiting viscoelastic response (memory), with strain-hardening/softening and shear-thinning properties.

### P30-BF

#### Detection of honey adulteration by fructose and saccharose syrups using steady, dynamic and creep rheological analysis

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This study was undertaken to detect adulterants such as fructose and saccharose syrups in honey using dynamic oscillatory rheometer. Fructose and saccharose were mixed with authentic honey samples in the following ratios: 1:10 (10 %), 1:5 (20 %), 1:3.3 (30 %), 1:2.5 (40 %) and 1:2 (50 %, w/w). Steady, dynamic and creep tests were conducted to detect such adulterations at the specified ratios. The rheological analysis test results revealed that the syrup addition remarkably changed the rheological properties of the authentic honey samples. Syrup addition decreased the apparent viscosity ( $\eta$ ), storage ( $G'$ ) and loss modulus ( $G''$ ) values of the authentic honey samples. Deformation represented by the compliance ( $J(t)$ ) values was more prominent in the honey samples adulterated by fructose and saccharose syrups, as determined by the creep tests. In addition, internal viscosity ( $\eta_1$ ) values were lower in the adulterated honey samples. The results of this study suggested that the steady, dynamic and creep analysis techniques be a promising technique for detecting such adulterants in honey.

### P31-BF

#### Time Dependent Viscosity Profile of İncir Uyutması Dessert: Effect of Fig Concentration

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In recent years, consumers have tended to consume natural foods or desserts due to their awareness of relation between health and diet. İncir Uyutması is a one of the dairy based natural desserts consumed in Anatolia and Middle Asia. It is basically prepared by addition of fig pieces into the boiled milk (at approximately 40 °C) followed by homogenization, holding at 40 °C and storage at 4 °C for 5 hours. In the present study, effect of fig concentration (5.0, 7.5, 10, 12.5 and 15 %) on time dependent viscosity behavior of the İncir Uyutması dessert was studied. Apparent viscosity ( $\eta$ ) measured at shear rate 50 s<sup>-1</sup> ( $\eta_{50}$ ) decreased with time. However,  $\eta_{50}$  values increased with increase in fig concentration, indicating that resistance of the dessert to flow. Weltman and second-order structure models were used to determine the relation between  $\eta_{50}$  value and time. Determination coefficient values of the models ranged between 0.9878 - 0.9971 and 0.9979 - 0.9995, indicating the adequacy of the models. Initial shear stress and time coefficients for thixotropic breakdown and parameters of the Weltman model, were found to range between 72.96 - 16.30 Pa and 9.19 - 1.24 Pa, respectively. Second-order structure parameters, namely initial apparent viscosity, equilibrium apparent viscosity and rate constants ranged between 0.258 - 1.306 Pa\*s, 0.142 - 0.404 Pa\*s and 0.008 - 0.036 s<sup>-1</sup>, respectively.

### P32-BF

#### Rheological Characterization of Creamed Honey

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Creamed honey is prepared from honey to improve its spreadability. In the production, the conventional honey is processed to control crystallization. The main difference between conventional honey and creamed honey is that creamed honey includes a great number of small crystals while honey contains large crystals. In this study, steady shear rheological properties of the creamed honey were determined at three temperature levels (10, 25 and 45 °C). Apparent viscosity was determined to decrease with shear rate at all temperature levels, revealing that the creamed honey had also a shear thinning (pseudoplastic) behavior alike conventional honeys. Ostwald de Waele model was the best model describing flow behavior of the sample. Consistency coefficient values ranged between 9.92 – 269.67 Pa\*s and decreased with increased temperature levels. Temperature sweep tests revealed that  $\eta_{50}$  values decreased with temperature. Arrhenius equation satisfactorily described the relation between temperature and  $\eta_{50}$  value ( $R^2 = 0.9998$ ). Activation energy was determined as 36.62 kJ/mol.

### P33-BF

#### Optimization of effect of incubation time and temperature levels on dynamic rheological properties of ayran produced with EPS producing cultures

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Ayran is a traditional Turkish drink especially consumed in Middle East countries in summer. It is produced by mixing yoghurt with water and salt and incubated with yoghurt cultures under different incubation time and temperature levels. In this study, effect of different incubation time and temperature levels on dynamic rheological properties of ayran produced with EPS producing cultures was optimized using Response surface methodology (RSM). Three level and two variable (temperature: 32-42 °C, time: 3-4 hours) central composite design of RSM was used in the present study. Storage modulus ( $G'$ ) values were found to be higher than loss modulus ( $G''$ ) values, indicating that ayran samples had elastic structure rather than viscous.  $G'$  and  $G''$  values ranged between 0.30 – 35.30 Pa and 0.25 – 10.29 Pa, respectively for samples prepared by the first ayran culture and between 4.02 – 69.77 and 1.74 – 19.80 for the samples prepared by the second ayran culture. RSM was found to be adequate on optimization of  $G'$  and  $G''$  values with the  $R^2$  values ranged between 0.9387 and 0.9934. The results of this study revealed that  $G'$  and  $G''$  values increased with increase in temperature and time levels. Optimum incubation condition was found to be 42 °C for 4 hours for both ayran cultures.

### P34-BF

#### LM Pectin gels: a rheological characterisation and modeling

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Pectin is a vegetable-extracted polysaccharide mainly composed by  $\alpha$ -(1-4)-D-galacturonic acid chain which is, in a certain amount, esterified with methanol. The degree of methyl esterification (DM) classifies pectin into high-methoxyl pectins (HM), with more than 50% of esterified carboxyl groups, and low-methoxyl pectins (LM) with less than 50% degree of esterification. The main characteristic, for which pectin is addressed to a wide range of industrial uses, is the capability to structure water by building a more or less strong network typical of a gelled system. In the present work, four different LM pectin (at different degrees of Methoxylation, DM, and molecular weight, MW) were employed to produce gels, which, in turn, can be used as an ingredient of other complex systems, i.e. emulsions filled-gels, where another liquid phase can be entrapped within the structured aqueous phase. A rheological characterisation of such gels was carried out, evidencing the different properties given by each polysaccharide with its own DM and MW, and also evaluating a predictive model to relate gel rheology (in terms of complex modulus at 1 Hz got by a frequency sweep test) to pectin content.

## P35-BF

**The Effect of Chitosan Molecular Weight on the Kinetics of Sol-Gel Phase Transition for Chitosan Thermogel Systems**Piotr Owczarż<sup>\*1</sup>, Zofia Modrzejewska<sup>2</sup>, Agata Skwarczynska<sup>2</sup>, Patryk Ziókowski<sup>1</sup>, Artur Bartkowiak<sup>3</sup>

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In the technology of new drug forms of great importance are the researches aiming at the development of carriers for a controlled release of medicinal substances. Currently, one of major solutions is the use of polymer matrices which form colloidal systems. Upon activation of an inhibitor in the form of a pH change or temperature increase, a sol-gel phase transition occurs and active components present in the solution are blocked in the structure of the formed gel. Reserchers are very interested in chitin derivative – chitosan. The main test which characterizes suitability of a solution to form a thermogel system is the determination of lower critical solution temperature (LCST). Rheological studies with the use of the classical rheometry based on sample deformation in the Couette system of a rotary rheometer allow us to determine gel point of the tested solutions of chitosan salts. A review of the literature and the authors' studies have shown that in many cases the gelation temperature of a solution determined in rheometric measurements is much above the value of LCST for a given composition of the solution. The rheometric tests made for chitosan salt solutions with the same composition showed that the gel point depended not only on the temperature but also on the rate of its increase. The measurements of chitosan salt solutions with different average molecular weights, while maintaining the stability of other parameters allowed us to determine the dependence of the rate of gelation on the length of a polymer chain forming the initial solution. Since chitosan thermogels belong to the group of physical gels whose structure is formed through the change of the molecule from hydrophilic to hydrophobic and next physical bonds are formed between subsequent chains, the gelation kinetics is determined by the rate at which polymer chains approach in the solution.

The paper describes the effect of rheological properties (especially viscosity) of the initial solution on the kinetics of sol-gel phase transition for diluted chitosan salt solutions. A mathematical description of the studied phenomenon with reference to rheological properties of the initial solutions is presented.

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## P36-BF

**Steady shear rheologic properties on “masa” obtained from nixtamalized maize varying the concentration of calcium hydroxide and cooking time**Rodrigo Saavedra-Rosiles<sup>1</sup>, Gerónimo Arámbula-Villa<sup>1</sup>, Juan de Dios Figueroa-Cárdenas<sup>1</sup>, Francisco Rodríguez-González<sup>2</sup>, Rodolfo Rendón-Villalobos<sup>\*3</sup>, J. Abraham Méndez-Albores<sup>4</sup>

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The nixtamalization (corn grain treated with lime) of maize is a traditional Mexican process developed by the Mesoamerican civilizations and is still utilized in the production of maize-based food products. Still today, several Latin American countries manufacture maize food products using nixtamalization to obtain a soft dough, known as “masa”. In this work we have evaluated the effect of the concentration of calcium hydroxide (0.1 - 3.9 % w/v) and cooking time (15 - 75 min) of maize grain on the rheological characteristics during the nixtamalization process. The rheological test were carried out using a stress/strain controlled Rheometer TA Instruments (strain mode), model AR1000, using a parallel plate (60 mm of diameter) and the gap size was set as 1.0 mm during all the test. The experimental protocol was opportunely tuned to minimize water evaporation (the instrument is equipped with a solvent trap). The results showed that both the yield stress and the flow curve are influenced by the increasing calcium concentration and cooking time. The yield stress in the “masa”, increase sharply (e.g., from 12.42 to 49.37 Pa) and the apparent viscosity significantly ( $p < 0.05$ ) decreased with the increasing of shear rate, due to processing conditions and that the water retention capacity increases with temperature and particle size.

### P37-BF

#### Understanding protein-polysaccharide laminated food emulsions at multiple length scale

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Biopolymers (proteins, polysaccharides) and their complexes have a hierarchy of interactions and offer a range of functional elements that define the texture and shelf-life of most food emulsions. Food scientists have exploited protein-polysaccharide composite interactions to design new structural emulsions with promising applications in food and pharmaceuticals.

Relatively few investigations have focused on quantifying, manipulating and understanding the emulsion microstructure, and correlating them to interfacial/bulk rheology of composite protein/ polysaccharide adsorption layers. The challenge arises from the complexity and multicomponent nature of food systems and the evolution of emulsion microstructures during the formulation, storage and application.

In this study laminated protein-polysaccharide stabilized oil in water (O/W) emulsions were prepared and the effect of environmental conditions (pH and ionic strength), on emulsion stability and microstructural changes were investigated at different length scales using interfacial and bulk rheology and cryo-electron microscopy. The mechanical and flow properties of the systems were determined in the linear viscoelastic region. The mechanical stability of the adsorbed layer(s), the kinetics of surface viscoelastic evolution as manipulated by sequential addition of the protein and the polysaccharide and variation of the pH and ionic strength were studied by interfacial shear rheology. The collective results with respect to ascertaining the correlation and causation relationships between the generation of the elastic films at the O/W interfaces, microstructure of the emulsion, macroscopic behaviour and stability of the systems showed that the interactions between protein-polysaccharide are closely correlated with the microstructural variation, i.e. the microstructure influences the rheology and the local viscoelastic environment determines the evolution of the microstructure.

### P38-BF

#### The Rheological Properties of Heat-Induced Gelation of Globular Protein, Bovine Serum Albumin

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Globular protein gels are largely used in food and drug industries. It is used to control the texture and stability of the products. When globular proteins are heated above their denaturation temperature (typically 50-80°C), the protein unfolds substantially. Rheological properties are effective tools to monitor the denaturation, unfolding, and/or stability of protein. As protein molecules unfold or fold and aggregate or disaggregate, rheological properties dramatically change. With the addition of urea ( $CO(NH_2)_2$ ), protein molecules are unfolded. The extent of unfolding protein molecules affects rheological properties. In this study, heat-induced gelation of the typical globular protein, bovine serum albumin (BSA) solution was investigated by temperature ramp test and time sweep test using thermal process. Gelation temperature was measured by temperature sweep test. Time sweep test with two-steps thermal process was also carried out to monitor the gelation state. Frequency sweep test was done to compare linear viscoelasticity of BSA solutions without and with urea. The results of protein gelation without and with urea were compared by temperature ramp test. Properties of the gel state of BSA solution and effect of urea on rheological behavior and structure of BSA were also studied by comparing the results. Heat-induced gels were made with protein solutions by programmable dry bath. Rheological properties of the samples were measured at the state of the solution depending on the heating time. With gelation temperature as a function of concentration, the curve illustrated sol/gel boundary. The gelation time was more shortened, with higher concentration of urea. With further heating of the gels with urea, the gels came back to solution states. By using urea, gelation temperature, texture and transparency of heat-induced protein gel could be controlled.

## P39-BF

**Thermal, structural and rheologic behaviour of thermoplastic sorghum starch**Jose Luis Rivera<sup>1</sup>, Javier Solorza-Feria<sup>1</sup>, Edgar García-Hernández<sup>2</sup>, Rodolfo Rendón-Villalobos\*<sup>1</sup>

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Native starch and mixtures with the ratios 90:10 and 95:5 (w/w) of starch:mucilage solutions were prepared. A significant increase in starch gelatinization temperature and enthalpy, was observed with mucilage addition. Fourier Transform Infrared (FTIR) revealed physical interactions between starch and mucilage favouring the increase in enthalpy and gelatinization temperature. The Frequency starch gels profiles, increased about three times the storage modulus ( $G'$ ) and twice as much the loss modulus ( $G''$ ), in samples with 90:10 (w/w) starch:mucilage. A trend to a shear-thickening behaviour was observed in mucilage added solutions, suggesting a re-arrangement in the starch-mucilage system structure, ending up with a lower viscosity than the control.

## P40-BF

**A potential source of pectin from pomelo peels: Extraction Characterisation and Its Food Applications**Jaruwan Krongsin<sup>1</sup>, Pawadee Methacanon<sup>1</sup>, Chaiwut Gamonpilas\*<sup>1</sup>, Suk Meng Aaron Goh<sup>2</sup>

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Pectins are branched polysaccharides richly composed of the methylated ester of poly 1,4-linked  $\alpha$ -D-galacturonic acid. They are typically isolated from cell wall of higher plants and used as gelling, thickening or stabilising agents in many food products. Commercial pectins are recovered from citrus fruits or apple pomace as large quantity is available as waste from beverage industry. In this work, pomelo (*Citrus maxima* Merr.) which is a kind of citrus fruits largely cultivated in Thailand and Malaysia, has been explored as an alternative source of pectin. This is due to the large amount of its peels being disposed as waste. The extraction of pectin was performed using nitric acid at pH 2 and at 90°C for 90 min. Such extraction resulted in pectin yield of approximately  $23.2 \pm 2.8\%$  which was comparable with those commercial pectins. The average molecular weight (MW) and degree of esterification (DE) were found to be  $353 \pm 78$  kDa and  $57.9 \pm 0.6\%$ , respectively. The DE consequently indicated that such pectin was a high methoxy (HM). The structural analysis showed that the pectin was largely composed of galacturonic acid with a range of monosaccharide branching that was dominated by arabinose. Such result interestingly contradicts with those of commercial pectins from other citrus fruits or apple pomace as the latter's branches are predominantly galactose. Rheology of various pomelo pectin dispersions was also examined. It was found that they formed gel at the concentration above 0.8% w/v and exhibited shear thinning behaviour. Furthermore, they possessed calcium sensitiveness which enhanced their rheological properties when small amount of  $Ca^{2+}$  was added. Since these pomelo pectin is high methoxy, their acid-induced gelling properties were also investigated. At the same content, it was shown that the gel strength and elasticity of these pomelo pectin gels were much superior than the commercial ones with similar MW and DE. To further explore the usefulness of pomelo pectins, acidified milk drinks were prepared and their stability investigated. It was revealed that the control sample with no pectin addition showed immediate casein aggregation after acid addition while the sample with 2% w/v pomelo pectin addition showed good stability and no phase separation observed after a week storage at 4°C. Therefore, it can be concluded that pomelo peels are promisingly potential source of pectin extraction.

## P41-BF

**Gelation of different agarose-hydrocolloid systems and the impact of sucrose and trehalose**Natalie Russ\*<sup>1</sup>, Birgitta I. Zielbauer<sup>2</sup>, Thomas A. Vilgis<sup>3</sup>

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The combination of different gelling and non-gelling hydrocolloids is known to yield complex systems with a wide range of mechanical properties. In addition, high amounts of sugars influence the physical properties of hydrocolloid systems enormously, due to their mutual interactions with each other as well as with water molecules. Agarose, a typical

gelling agent, is combined with the non-gelling agents sodium-alginate and xanthan, two polyelectrolytes which differ significantly in their flexibility. The impact of the two disaccharides sucrose and trehalose on the thermo-mechanical properties of agarose based hydrogels is investigated. Material properties, such as viscoelasticity, network structure and water holding capacity can be adapted by the controlled addition of sugar and the combination with the non-gelling agents. These properties are investigated by strain dependent oscillatory rheological measurements as well as confocal laser scanning microscopy and controlled drying experiments. A phenomenological model to describe the network formation of agarose in the presence of alginate or xanthan respectively is presented and illustrates the different influences of the sugar molecules in the hydrocolloid systems. It is suggested that hydrate shells and the differences in local water binding on atomistic and nano scales have strong effects on macroscopic properties.

#### P42-BF

##### **Rheological monitoring of amidated carboxymethylcellulose crosslinking**

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Viscosupplementation is a symptomatic treatment of mild osteoarthritis in synovial joints when the lubricating and cushioning actions normally provided by the synovial fluid are sensibly reduced and can be adequately restored for a prolonged time through single or repeated injections of a viscoelastic fluid, which more frequently consists of high-molecular-weight hyaluronan (HA) and/or partially cross-linked HA.

A novel viscosupplement based on amidated carboxymethylcellulose has been developed by blending the soluble polymer (CMCAp) with its crosslinked derivative (CMCAg) in appropriate proportions and concentrations in order to ensure an optimal combination of flow behavior and viscoelastic properties. The crosslinking of amidated carboxymethylcellulose is obtained using NHS/EDC as activating agents and 1,3 diaminepropane as crosslinker (molar ratio with the polymer 0.5:1) in order to obtain a crosslinking degree of about 50 %.

The present work is concerned with the rheological study of the crosslinking reaction performed at 25°C by starting from aqueous CMCAp solutions at different concentrations. Each polymer solution has been subjected to consecutive frequency sweeps during the crosslinking process in order to describe the gelation kinetics at different frequencies with a single experimental test. Satisfactory correlations of the time dependence of the viscoelastic moduli have been provided by sigmoidal relationships and, hence, a sequence of mechanical spectra can be generated in order to describe the time evolution of the linear viscoelastic behavior occurring along the whole gelation process. Thus, the sol-gel transition has been individuated for each solution in accordance with the Winter-Chambon criterion and the dependence of both gel stiffness and relaxation exponent on polymer concentration was analysed.

#### P43-BF

##### **Rheological and mechanical properties of extruded films of corn starch plasticized with coconut oil**

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In recent years, films of starch have been highly studied due to their potential applications, mainly as packing in the food industry and as substitutes for plastic bags made from petroleum products. Starch films are advantageous compared to those from petroleum, because to their biodegradable and sustainable character. The sustainable nature of the raw materials is important because, to generate options for supply chains in rural communities. On the other hand, the biodegradable character of the materials could solve the problem of accumulation of plastic waste in landfills. However, the drawback of these materials focuses in the optimization of processing conditions and the loss of mechanical properties over time. In this work, films from corn starch plasticized with water and coconut oil were obtained by extrusion process. Previously, suspensions of corns starch and coconut oil with 50 % of water, were used for to obtain rheological curves , in the curves from viscosity in function of rate is possible to observe the effect of plasticizer (coconut oil), increasing the viscosity as the content of plasticizer was increasing. The curves of  $G'$  and  $G''$  as a function of rate for the formulations with higher amount of plasticizer are nearer than those with lower amount as consequence of plasticizer power. As expected the  $G''$  curve associated to the viscous character of the material are above the  $G'$  curve associated with the elastic character. On the other hand, films of corn starch plasticized with 15 % in weight of coconut oil showed higher mechanical properties (Young modulus and tensile strength) respect the films with 20 % and 25 % of coconut oil. Finally, Dynamical Mechanical Analysis was performed to confirm the previous results.

## P44-BF

**Rheological Properties of a Biological Thermo-Responsive Hydrogel Prepared from Vegetable Oil**

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Hydrogel is a colloidal gel in which water is the dispersion medium. The unique properties of hydrogels make this kind of materials have many utilization potentials, such as drug delivery, gene therapy, wound care products, breast implant materials, cosmetic products, and tissue engineering. Hydrogels produced from biopolymers and/or natural sources have particular superiority in vivo applications since they are more likely biodegradable, biocompatible, bioresorbable, and even edible. The rheological properties of a newly developed biological thermo-responsive hydrogel made from vegetable oil were investigated. The material named HPSO-HG is a hydrolytic product of polymerized soybean oil (PSO). HPSO-HG is a thermo-responsive gel, and it exhibited viscoelastic behavior above 2 % (wt. %) at room temperature and viscous fluid behavior at 55°C. The viscoelastic properties of HPSO-HG were strongly dependent on concentration. The analysis of modulus and concentration dependence and stress relaxation measurement indicated that HPSO-HG was a physical gel meaning the cross-linkers between the molecules were physical junctions. HPSO-HG hydrogel also showed fast initial partially recovery of its viscoelastic properties after being subject to a mechanical shear disruption. The function and behavior of the HPSO-HG hydrogel suggest that this biomaterial be a potential candidate for applications in cosmetic products, drug delivery, and wound skin care products.

## P45-BF

**Structure-Property-Relationships of Carboxymethyl Hydroxypropyl Guar Gum**

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Guar gum is a natural nonionic polysaccharide from the endosperm of *Cyamopsis tetragonoloba*. The polymer consists of a linear backbone of  $\alpha$ -1,4 linked D-mannopyranosyl units and in pairs and triplets arranged  $\beta$ -1,6 linked D-galactopyranosyl units as side chains. Branchless parts of the backbone may form segment-segment interactions, so called hyperentanglements.[1,2] The high viscosity in aqueous solutions at low concentrations is put into conjecture with the latter interactions. Guar gum may chemically be modified to broaden the range of application. Commercial derivatives may contain hydroxypropyl and/or carboxymethyl groups and are used in food, pharmaceutical, agriculture and oilfield applications. Despite the fact that these guar gum derivatives are widely used, the rheological behavior is not completely understood and remains a current research topic.[3]

A comprehensive rheological characterization of carboxymethyl hydroxypropyl guar gum gives insights into the behavior in water and the importance of hyper-entanglements. For this purpose, a homologous series was prepared by ultrasonic degradation and characterized by SEC/MALLS/dRI. Material functions were measured by steady shear flow and small amplitude oscillatory shear. Structure-property relationships were obtained in dilute and more concentrated solutions as function of molar mass and temperature. Additionally, the first normal stress difference were measured and compared with the estimated values by the empirical Laun's rule and the 2012 established AbNormal rule [4], allowing a deeper understanding of hyperentanglements.

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## P46-CS

**Modelling Capillary Break up of Particulate Suspensions**

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A diverse range of materials can be manipulated using inkjet technology, the most common being particulate suspensions. Most graphical inks contain solid pigment particles rather than dyes and in many non-graphical applications, such as printed electronics, the functional components of the ink are solid particles. However, there is relatively little known about particulate effects on the stability of jets. The presence of particles increases the bulk viscosity of a

fluid. Thus, particles are expected to retard thinning and delay the time to breakup. However, experimental measurements suggest that once the filament thins to approximately five particle diameters, the thinning no longer follows the behaviour predicted by the bulk viscosity; thinning is 'accelerated' due to the effects of finite particle size. Our hypothesis is that accelerated thinning arises from variations in local particle density. As the filament thins, variations are amplified, leading ultimately to sections of the filament containing no particles at all. Sections of the filament that have a low particle density have a lower viscosity and can therefore thin more easily. To test this hypothesis, we have constructed a simple one-dimensional model in which the viscosity is determined from the local particle density, found by tracking individual particles within the suspension. Particles only contribute to the dynamics through the local viscosity, so the direct effects of hydrodynamic interactions between particles and the effect of the individual particles on the free surface are not included. Nevertheless, our model is able to reproduce the accelerated thinning found in experiments.

#### P47-CS

##### **Rheological properties of the solutions of mixed wormlike micelles: influence of co-surfactant chemical structure**

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Adding oppositely charged co-surfactant to spherical micelles of an ionic surfactant may induce the transition to long wormlike micelles. Viscoelastic solutions of wormlike micelles find successful application in many industrial and technological fields, including oil and gas production. In the present work we investigate viscoelastic properties of mixed micelles comprised of an anionic surfactant (potassium oleate) and different cationic co-surfactants. First we investigated the influence of co-surfactant tail length on rheology. It was shown that the values of viscosity are several times higher (up to 10000 Pa\*s) for longer tail (C12), but the solutions of C12 co-surfactant do not reveal simple Maxwellian behavior with one relaxation time even at the maximum of viscosity. On the other hand, the region of phase compatibility narrows with the increase of the tail length. This result may be explained by the increased forces of hydrophobic attraction, leading to longer micelles, but also to a stronger tendency for aggregation. Then the influence of polar head chemical structure on rheology was investigated. Solutions containing co-surfactants with pyridinium and trimethylammonium polar heads show similar phase behavior and practically similar rheology, therefore, it is mostly controlled by the hydrophobic tail of the co-surfactant. In case of pyridinium polar head the viscosity is slightly higher at low molar ratios [co-surfactant]/[surfactant] and lower at high molar ratios. It can be explained by higher accessibility of charge in pyridinium head and thus its higher efficiency in screening electrostatic interactions. The difference between scission energy and electrostatic energy increases with the ratio [co-surfactant]/[surfactant]. It can be explained by the increase of scission energy due to stronger attraction of molecules within the micelle, as well as by the decrease of electrostatic energy due to higher screening.

#### P48-CS

##### **Rheology of heavy crude oils with asphaltenes**

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Nowadays the energy demand has increased dramatically and petrochemical companies are focusing on the so-called unconventional oils. The latter are characterized by unconventional extraction methods, because of their high viscosities, principally imputable to the presence of asphaltenes within the oil. Asphaltenes are polar macromolecules classified in terms of solubility in organic solvents: They are defined as toluene-soluble and heptane-insoluble. The asphaltene microstructure is still debated. Generally, they are oil-dependent polyaromatic molecules, constituted of six or seven benzene rings with aliphatic tails and heteroatoms. Asphaltenes can stack in piles and/or aggregate in clusters thus forming a microstructure that has a strong effect on the crude oil viscosity and viscoelasticity, conversely rheology results to be a very sensitive tool to investigate this microstructure. In this paper, we study three oils coming from the same well and taken from the very same tank in different moments. They show the same TGA (thermo-gravimetric analysis), DSC (differential scanning calorimetry) and UV spectra. Despite this, their viscosity results quite different. Thus, to investigate in details the origin of this behavior, we have fully characterized and then compared their viscoelastic response at different temperatures, thus indirectly testing the intermolecular interactions

strength. Moreover, we studied the effect of dilution in organic solvents (e.g., gasoline) so to probe the effectiveness of the microstructure to thicken the solution and, finally, we added small quantities of an organic acid, able to interact with the asphaltenes.

#### P49-CS

##### **Bentonite suspensions in polymer solutions: modeling of the solid-liquid transition**

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Bentonite dispersions in polymer solutions often display a gel-like behavior. Under shear, a solid-liquid transition occurs when the stress exceeds the yield stress. The determination of the yield stress is always a difficult problem, especially for time-dependent systems. A model is proposed to fit the answer of such materials to a stress ramp. The model reduces to the Herschel-Bulkley equation above the yield stress. Below the yield stress, we take in account an elastic behavior of the material. The parameters are determined for different polymers, polymer concentrations and molecular weights. The interpretation of the results is related to the change of the microstructure under shear.

#### P50-CS

##### **Orthogonal superposition rheometry of hard sphere glasses**

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Hard sphere colloids above a critical volume fraction are caged giving rise to non-ergodic states glassy states. At rest stresses in such states relax only partly by in-cage diffusion through Brownian motion while long-time out-of-cage ( $\alpha$ ) diffusion is largely suppressed. Under shear out-of-cage diffusion is induced leading to glass melting. Using conventional linear viscoelastic tests it is not possible to capture the shear induced  $\alpha$  relaxation. Here we present orthogonal superposition rheometry[1,2], a novel experiment on colloidal glasses, where Small Amplitude Oscillatory Shear is superimposed orthogonally on the rotational steady shear in colloidal glasses. In this way the shear-induced out of cage relaxation is measured as a function of shear rate for Hard Sphere particles and star-like micelles at different volume fractions. The orthogonal storage and loss modulus provides intricate details of these systems out of equilibrium. The crossover frequency of  $G'_{orth}$  and  $G''_{orth}$  depends linearly on the applied shear rate for hard sphere glasses and sublinearly for soft micellar glasses. Based on these experiments a shear rate frequency superposition is proposed and its universal character for concentrated colloidal suspensions and glasses is discussed.

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#### P51-CS

##### **Quantifying Large Amplitude Oscillatory Shear (LAOS) within a period**

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There has recently been a large surge in interest to understand non-linear rheology using Large Amplitude Oscillatory Shear (LAOS). Quantification of linear regime using Small amplitude oscillatory shear (SAOS) is well established and a big effort has gone into trying to quantify LAOS in a similar manner. We review current approaches using Fourier Transform or similar type analysis and the use of higher harmonic related moduli [1,2,3]. Moreover we introduce a new set of moduli  $G'_{inst}$  and  $G''_{inst}$ , which are defined within a period of LAOS, derived with no symmetry constrictions imposed.[4]  $G'_{inst}$  and  $G''_{inst}$  are used to calculate the elastic and viscous stresses within a period during LAOS and in turn reproduces the Lissajous Bowditch plots. We compare these with a similar type quantification of LAOS introducing local moduli,  $R'$  and  $R''$ , within the period.[5] An extensive comparison and discussion of the physical meaning

of the different approaches is presented by applying them on well defined rheological models and experimental data of model hard and soft sphere colloidal glasses.

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## P52-CS

### Shear thickening suspensions based on nanosized silica

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Suspensions based on nanosized silica and oligomers presented various behaviour under shear stress depending on the oligomer chemical structure and molecular weight. Different volume fraction and size of silica particles also affect the rheological properties of the fluids. It has been indicated, that the increasing volume fraction of a solid phase causes stronger dilatancy effect. Shear thickening fluids are able to obtain higher viscosity value at lower temperature. The best combination of the properties (high viscosity, obtained at high shear rate) represents the material composed of the FS and PEO300, although the highest viscosity value was obtained for the material composed of FS and PPG400. Addition of polymeric microspheres enables tailoring the density of the STF. The shear thickening fluid obtained was tested in the composite system, consisting of paraaramide fabric with colloidal insert, for the bulletproof properties, against parabellum 9mm. Improved flexibility of such armour was demonstrated.

## P53-CS

### Connecting the final properties of PDMS with rheological data of the base components

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Depending on the desired features the wide variety of polydimethylsiloxanes (PDMS) types with different properties (viscosity, hardness, elongation modulus) and applications makes it necessary to select the used type properly. Additionally, knowledge about the crosslinking behavior of PDMS is very important for scientists dealing with it or its composites.

During this work different types of PDMS were investigated to find a fully crosslinked PDMS with the desired properties. Therefore the base components (PDMS and crosslinker) were characterized very well and the crosslinking behavior was examined with Rheometry.

Several different rheological measurements were carried out with an ANTON PAAR UDS 200 Rheometer. The base components were examined via frequency sweeps whereas there are different ways of following the curing via Rheometry, namely strain-controlled time resolved frequency sweeps (=time-resolved mechanical spectroscopy = TRMS) and stress-controlled time tests. The TRMS measurements were done at a frequency range between 0.1 and 100 rad s<sup>-1</sup> (both at 25 °C), the stress-controlled tests with constant stress = 75 Pa and constant frequency = 1 Hz. We found a reasonable accordance between these two ways. Through the rheological data we can predict the final properties of the cured PDMS and additionally gain parameters after which we can select the appropriate PDMS for our application.

## P54-CS

### Influence of Brownian motion on particle's settling velocity in non-Newtonian fluids

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Sedimentation of suspension is a process of great practical importance for industry, lying at the core of water pu-

rification, particle classification and separation or even for medical diagnostics. While theory for sedimentation in Newtonian fluids seems to be developed, there is urgent need to extend it towards non-Newtonian media, as sedimentation in such a media is a common practice.

Although a lot of work has been done during last decade in this area [1], most of the effort has been focused on sedimentation of non-Brownian particles. Therefore the implicit boundary of the non-Brownian regime, where the velocity fluctuations due to thermal energy can be neglected and the available models for settling velocity applied, is an important issue. While in Newtonian fluids many authors defines this regime in terms of Peclet number being ratio of convection to diffusion, the influence of Brownian fluctuations on settling velocity of sedimenting particle in case of non-Newtonian fluids remains mainly untouched.

In current work we will investigate this issue by means of passive optical rheology. Using Leica 2000B optical microscope we will trace the movement of model, round polystyrene particles of diameter between 0.1 and 2  $\mu\text{m}$  (Sigma Aldrich) in non-Newtonian solvents (PEO, CMC).

In expected results we will answer if the simple Peclet limit of approximately 200 taken from literature translates directly to non-Newtonian solvents, discussing the validity of existing models. In addition we will present the methodology allowing for direct, experimental validation of models in case of particular sedimenting system using passive optical rheology.

Work is supported by The National Science Centre (project N N209 764640).

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### P55-CS

#### **Experimental Study of the thixotropic behavior of bentonite - water systems**

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This work is devoted to the experimental study of thixotropy in terms of equilibrium loops. The studied Bentonite suspensions are used in the formulation of drilling fluids with different concentrations (4%, 5%, 6%, 7%, 8%). A Physica MCR 301 rheometer was used for measuring rheological properties. The thixotropic character of these suspensions is revealed by hysteresis loops. The equilibrium loop is obtained, firstly when the cyclic shearing is repeated sufficiently and secondly by varying the duration of shearing (the time of charge - discharge). A phenomenological model based on the equation of the flow curve  $\tau = f(\dot{\gamma})$  coupled to a differential equation describing the kinetic of structuration of the fluid, allowed us to correlate and interpret experimental results.

### P56-CS

#### **The effect of flow history on the rheological properties of flocculated carbon black dispersions**

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We investigated the rheology of dispersions of fractal carbon black particles with attractive interactions in apolar media. It has been reported that these systems display strong dependence of gel modulus on the preshear stress and shear thickening behavior driven by hydrodynamic breakup of densified flocs. (Osuji et al., 2009) It has also been demonstrated that the yield stress can be tuned to arbitrary value by applying an appropriate flow history. (Ovarlez et al., 2013) To characterize the state of the materials obtained as a result of shear history, we observed not only the linear viscoelastic moduli but also the "intrinsic" flow curves which are achieved by collecting the instantaneous viscosities reached after the step changes in shear flow. After applying preshear on a sample, the rheological properties became identical to another sample with different volume fraction, as if the volume fraction of the presheared sample has been changed. In spite of the difference in the amount of solid contents, those samples were indistinguishable from each other by the rheological properties such as the "intrinsic" flow curve, the dynamic yield stress, and the frequency-dependent linear viscoelastic moduli. From these results, it can be suggested that the rheological properties of the flocculating fractal carbon black dispersions can be described in terms of the effective volume fraction of the aggregates. Our results also imply that it is possible to tune the microstructure precisely to an arbitrary state by adjusting the preshear condition.

### P57-CS

#### **Rheological characterization of transparent suspensions by means of the velocity profile from PTV/PIV measurements**

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A lot of rheological research is done with classical equipment like high pressure capillary and rotational rheometers. To investigate highly filled suspension with these integral methods a correction is necessary because some standard assumptions are not correct. With this procedure the origin of the rheological behavior is not clear and it is not always possible to transfer the results to complex geometries. A direct insight in the velocity profile of a suspension during a rheological analyses provides more detailed information for the flowing process and so the rheological properties which are derived from the flow profile. Combined with a local pressure measurement it is possible to visualize even local viscosities.

A simple method to get the velocity profile of a flow is Particle Image/Tracking Velocimetry. Simple means the low demands for the measurement environment and the mobility of system. Through thoroughly performed investigations relating to the index matching between a matrix fluid and particles we obtained transparencies for suspensions ( $\phi=0,4$ ), including tracer particles, up to 80%. This level of transparency enables us to look at a plane up to 20mm deep in a rectangular slit die (30mm x 2mm). To obtain reliable and useful results it is necessary to take care of a lot of parameters concerning the practical and theoretical side. The PIV/PTV algorithm has to be chosen well considered with reference to amount of tracer particles and their visibility, which is in a direct conflict with the transparency of the suspension. The spatial resolution is connected to the light sheet thickness, magnifying factor and the camera resolution. When the matrix fluid is dyed it is possible to directly observe the particle migration. Even with good preparation a systematic statistical analysis is inevitable. These investigations aim for a deeper comprehension of rheology of suspensions and the enhancement of rheological models in the near future.

### P58-CS

#### **Effect of humectants, polymers and silicas on the rheological properties of toothpastes**

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A dentifrice is a dense suspension formed by over 20 ingredients which act as dental cleaning agents, abrasives, humectants, thickeners, gelling agents, stabilizers, aromatics and preservatives. Controlling rheological parameters is necessary in order to guarantee the easy extrusion of the paste from the tube, the capability of being sheared, the physical stability during storage time or the rapidity to restructure after shearing. Moreover, it is also important in controlling the pressure needed to pump the paste through the pipe system, from the standpoint of manufacturing the product.

The aim of this work was to study the effect of components with most relevance in the rheological properties of toothpastes, such as sorbitol, glycerin, polyethylene glycol (PEG), thickening and abrasive silicas, carboxymethylcellulose (CMC) or xanthan gum (XG). As a first step we have analyzed the liquid base in different concentrations and then how solid components affected this base. Flow curves and oscillatory measurements have been carried out at 20 °C in a controlled stress rheometer DHR-1 (TA Instruments) with a Peltier plate for temperature control. Crosshatched parallel plates sensors have been used.

Preliminary results showed that 1% of CMC conferred shear thinning character to the Newtonian mixture formed by sorbitol and water. The viscosity of this blend increased exponentially with the increase of sorbitol, but it did not affect yield-stress. Adding 10 % of abrasive silica had no effect on the viscosity curve, but thickening silica in the same concentration caused an increase of four orders of magnitude on zero viscosity.

## P59-CS

**Effect of antimony trioxide ( $Sb_2O_3$ ) on shear and extensional rheology of ultra high molecular weight polyacrylonitrile concentrated solution**

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Acrylic fiber industry has a global production capacity of 2 billion tons/year. Incorporation of additives can give acrylic fibers properties such as strength, flame retardation and etc, but additives may bring problems in industrial process and influence drawability of solution.

Aim of this study is to investigate effect of adding antimony trioxide ( $Sb_2O_3$ ) submicron sized to ultra high molecular weight polyacrylonitrile (UHMWPN) concentrated solutions. Rheological behavior of UHMWPN solution doped by  $Sb_2O_3$  was investigated using Malvern Gemini 2 rheometer and HAAKE CaBER extensional rheometer respectively. Concentrated solution was prepared by dissolving certain amount of UHMWPN in pre-mixed dimethyl acetamide (DMAc) solution. Pre-mixed solutions were prepared by mixing different amount of  $Sb_2O_3$  and DMAc in advance. Results of shear rheological tests showed that addition  $Sb_2O_3$  to UHMWPN concentrated solution lowered level of viscosity and dynamic shear rheology measurements showed shift of storage modulus-loss modulus ( $G'$ - $G''$ ) cross point to lower frequency in comparison with that of for solution without  $Sb_2O_3$ . Results from Cole-Cole plot ( $G'$ - $G''$ ) showed little influence of  $Sb_2O_3$  on homogeneity of UHMWPN solution. It was observed from extensional rheological test that adding  $Sb_2O_3$  enhanced drawability of the solution and increased rupture strain.

## P60-CS

**Parallel between suspension rheology and dry coating layers structure**

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Paper coating suspensions are complex mixture of polymers, pigments and other additives. Temperature responsive polymers can be used in water-borne suspension coatings applied onto large area substances such as paper, plastic films, etc. Temperature controlled interactions can be utilized in order to control porosity of coatings and to create 3D features by printing processes. This work focuses on porosity control and to gain understanding of the general relation between rheology of suspensions similar to those used in paper coating operations and the structure of the dry coatings.

The system in this research work contained potato starch and colloidal silica particles. The silica particles carried negative charge at the investigated pH ( $pH \approx 9$ ), and had a narrow particle size distribution with a BET area of  $40 \text{ m}^2\text{g}^{-1}$ . The used temperature responsive polymer was Pluronic F127 (PEOn-PPOm-PEOn). Addition of the temperature responsive polymer led to a dramatic change in suspension state by increasing the temperature within a narrow range ( $20^\circ\text{C}$  to  $25^\circ\text{C}$ - $30^\circ\text{C}$ ). This allowed us to perform rheological experiments above the gelation threshold at minimum residual stresses in the dispersions originating from sample loading. To determine colloidal interactions, rheology experiments (e.g. amplitude and frequency sweeps) were carried out above the gelation threshold. Significant differences in the system behavior (storage modulus, loss modulus, critical strain, etc.) were observed between  $20^\circ\text{C}$  and  $25^\circ\text{C}$ - $30^\circ\text{C}$  and were due to different colloidal interactions created by Pluronic F127 in the wet suspensions. To understand the relation between suspension rheology and dry coating structure, coatings on hydrophilic polyester film were produced by drying at  $20^\circ\text{C}$  and  $25^\circ\text{C}$ - $30^\circ\text{C}$  and low relative humidity. Differences in silica particles distribution in the dried structures and porosity were observed with increasing temperature and volume fraction solid phase.

## P61-CS

**Investigation of the dynamical slowing down process in soft glassy colloidal suspensions: comparisons with supercooled liquids**Debasish Saha\*<sup>1</sup>, Yogesh M. Joshi<sup>2</sup>, Ranjini Bandyopadhyay<sup>1</sup>

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The primary and secondary relaxation timescales of aging colloidal suspensions of Laponite are estimated from intensity autocorrelation functions obtained in dynamic light scattering (DLS) experiments. The dynamical slowing down

of these relaxation processes are compared with observations in fragile supercooled liquids by establishing a one-to-one mapping between the waiting time since filtration of a Laponite suspension and the inverse of the temperature of a supercooled liquid that is rapidly quenched towards its glass transition temperature. New timescales, such as the Vogel time and the Kauzmann time, are extracted to describe the phenomenon of dynamical arrest in Laponite suspensions. In results that are strongly reminiscent of those extracted from supercooled liquids approaching their glass transitions, it is demonstrated that the Vogel time calculated for each Laponite concentration is approximately equal to the Kauzmann time, and that a strong coupling exists between the primary and secondary relaxation processes of aging Laponite suspensions. Furthermore, the experimental data presented here clearly demonstrates the self-similar nature of the aging dynamics of Laponite suspensions within a range of sample concentrations.

## P62-CS

### **On The Non-Newtonian Properties Of Metal In The Liquid State And Its Impact On Semisolid Metal Suspensions**

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Semisolid metal slurries show pseudo-plasticity, thixotropy and yield-stress. With according preparation, the material is a suspension of globular particles in liquid metal. Since this was discovered [1], the liquid matrix is supposed to be Newtonian [2, 3]. Recent measurements however, showed pronounced shear thinning with high viscosities (several Pas) at low shear rates in liquid metals [4]. This gave the impulse to investigate the impact of this property on the flow properties of semisolid metals.

Flow-curves of liquid and semisolid aluminum and steel alloys were measured with Searle rheometers at up to 1500°C. Considering the power-law parameters of the resulting flow curves, it is remarkable that the flow exponent  $n$  is not significantly different in the liquid and semisolid state. The samples were quenched after the experiments to analyze the microstructure.

With the gained particle size distributions (40-300 $\mu\text{m}$ ), suspensions were synthesized of various materials. Suspensions of 0 to 50%<sub>vol</sub> in a Newtonian liquid matrix (e.g. glycerin, oils) show flow exponents of min. -0.2. These suspensions do not show a yield stress or pronounced thixotropy. Employing shear-thinning matrices (methylcellulose, latex) leads to flow exponents around -0.85 and in the case of Latex-PMMA suspension even to yield-stresses and thixotropy, just as in semisolid metal alloys.

The non-Newtonian characteristics of semisolid metal alloys are not caused by the solid phase microstructure only. In fact, the liquid phase is a dominating factor as for any suspension. Consequently, rheological models of semisolid metal alloys should consider the non-Newtonian nature of the liquid matrix.

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## P63-CS

### **An Innovative Injection Molding Process for Highly Porous Ceramics**

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Introducing capillary forces in ceramic suspensions via addition of a small amount (< 5 vol%) of a secondary, immiscible fluid is a new technique to create precursors for highly porous ceramic materials [1]. Adding an appropriate secondary liquid phase changes the rheological behavior from fluid-like to gel-like due to the formation of a sample spanning network of flocculated particles bound together by capillary bridges consisting of the added the secondary phase. This network is much stronger than a network controlled by attractive van-der-Waals forces, it does not collapse upon removal of the bulk fluid, and therefore can serve as a precursor for highly porous sintering materials.

The yield-stress and low shear viscosity of such so-called capillary suspensions increases drastically with increasing amount of secondary fluid [2]. But with respect to processing of ceramic capillary suspensions in low pressure injection molding especially the flow behavior at high shear rates is important to examine. Ceramic suspensions designed for this process are based on a molten wax as bulk fluid. Corresponding capillary suspensions with different particle loading and secondary fluid volume fraction were examined at high shear rates using capillary rheometry. The influence of the mentioned parameters on the rheological behavior in the wet state will be discussed. It will be shown that

the observed changes have serious effects on the microstructure of the sintered body. Pore size and porosity can be influenced directly by the composition of the capillary suspension in the wet state.

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#### P64-CS

##### **The nonlinear rheological behavior of PVA/Silica/Cu-Nanowire Suspension under the Large Amplitude Oscillatory shear(LAOS) flow**

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The poly (vinyl alcohol) (PVA) exhibits the good performance to make a film due to the transparent, non-toxic, and water soluble properties. In this study, the PVA based silica/Cu nanowire suspensions were investigated by using rheological measurement, especially the Large Amplitude Oscillatory shear (LAOS) test. Through the data from LAOS test, nonlinearity (third relative intensity) can be calculated by the FT-rheology. First of all, the effects of PVA concentration were investigated using the SAOS and LAOS test. By increasing the PVA concentration, the gelation occurred and shear thinning effect can be detected. When the concentration of PVA was increased, nonlinearity shows overshoot and fluctuation. It means that there are differences in the internal structure. Next, the effects of stirring time were investigated by change the mixing time from 5 days to 10 days. The suspension become more elastic with increasing stirring time, even the LAOS results shows similar trends. Finally the effects of silica concentration were investigated. The suspension which contains 15 wt % PVA/10 wt % silica/ 0.1 wt % Cu nanowire shows gel property. It also shows overshoot and fluctuation on high silica concentration.  $G^*$  values were calculated for check the particle-particle interaction. In some literatures,  $G'$  can be influenced by not only the hydrodynamic effect and viscoelastic effect but particle-particle interaction effect in the polymer composite system. From the  $G^*$  graph, the slope difference were confirmed and we can suppose that there are particle-particle interaction in the low frequency range. Through the results of linear and non-linear rheological measurements, the different rheological properties are correlated with the internal structure of polymer/particle or nano-wire suspension.

#### P65-CS

##### **Internal deformation and rearrangement in magneto-responsive hybrid materials**

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Magneto-responsive hybrid materials consist of magnetic particles and a carrier liquid (magnetorheological liquid) or an elastomer (magnetorheological elastomer). In a magnetic field, the magnetic particles will have dipole-dipole interaction, which can induce internal stress and cause rearrangement of the particles. This can change the mechanical/rheological property of the material. In our study we focus on (1) the kinetics of rearrangement of magnetic particles under magnetic field and (2) relationship between arrangement of magnetic particles and the magnetorheological properties.

The laser scanning confocal microscope (LSCM) is used to image the internal structure of the hybrid materials. It can be combined to mechanical testing devices, such as nanoindenter and piezorheometer. Thus, the internal structure and the mechanical properties of the hybrid materials can be detected at the same time [1-3]. A Halbach magnetic array is used to offer a tunable homogeneous magnetic field. In our study the magnetic particles are fluorescent-labeled in order to be visible. We also use the fluorescent-labeled tracer particles to track the deformation of the matrix material.

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## P66-CS

### Rheological analysis of functional templates for the construction of mesostructured materials

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Phosphorescent materials incorporating iridium(III) complexes are extensively researched as functional molecular materials for practical applications in a wide variety of industries ranging from optoelectronics to biomedicine [1]. In particular, ionic iridium(III) complexes are promising active materials in solid state lighting devices (SSL) [2]. A fine and uniform dispersion can be achieved by mixing the iridium(III) emitter with the precursor template system (lyotropic phase formed by common surfactants in water).

The position of the iridium(III) emitter in the lyotropic phase of common surfactants can be determined by using combined spectral and time-resolved photophysical techniques and rheological methods.[3] Indeed, from one side the phase diagrams of the surfactants are very sensitive to external stimuli such as functional guest molecules, and on the other hand also the iridium(III) chromophore 'feels' the environment significantly modifying its observed spectroscopic features.

Herein, the investigation of the dynamic system formed by an iridium(III) ionic complex (Figure 1) embedded in F127-water system by rheological and photophysical analysis will be presented. This approach will allow the synthesis of functional mesostructured materials with well-dispersed iridium(III) emitters, in which the position of the chromophore may be predetermined, yielding materials with functional pores or walls, as a function of the position of the chromophore in the initial lyotropic template system.

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## P67-CS

### Waxes effects on the bitumen mechanical properties

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Rheological effects of adding different types of waxes to bitumens were studied using Dynamic Mechanical Analysis (DMA). Also commercially available waxes was used in the study. The results show that the magnitude and type of effect on bitumen rheology depend on the bitumen and type of wax. Effects due to wax shown in DMA temperature sweeps are well related to the corresponding effects shown in DSC thermograms. The relative slope of the complex modulus between 25°C and 60°C is introduced as a possible proper factor for predicting rutting sensitivity due to wax content

## P68-CS

### Direct Observation of a Suspension's Time Dependent Apparent Wall Slip in a Plate-Plate Rheometer

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Rheometrical measurements of a suspension's flow behavior often lack transferability to other flow situations. The complicated interplay of various phenomena, such as apparent wall slip and particle migration, distort viscosimetric findings. Wall slip and particle migration need to be considered, since they are governed by the experimental setup as well as the suspension's properties. Particle migration is a transient effect that causes the particle concentration to decrease in areas of high particle collision frequency. This decrease influences the apparent slip velocity, because it only occurs due to pronounced particle concentration differences over the cross section. A corresponding time dependence of the slip behavior is the result. However, little experimental work has been conducted towards any useful description of this interrelationship. Our work included the measurement of the velocity profile of an index

matched suspension in a plate-plate rheometer via particle tracking velocimetry (PTV). Additionally, we dyed the matrix fluid instead of adding tracer particles and used the PTV setup to map the particle distribution in the gap and the changes thereof during the course of a plate-plate experiment. Combining the results of the two experiments, we were able to calculate the average thickness of the slip layer as a function of time at a given radial position in the gap. The main advantage of this combination of techniques was that we did not have to resort to model equations such as Phillip's model in order to account for particle migration when we extrapolated the experimental velocity profile to the immediate vicinity of the wall. We were therefore able to obtain an entirely undistorted record of the time dependent apparent slip behavior.

#### P69-FI

### Flow-induced phase transitions in liquid-crystalline polymer solutions

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Phase LC transitions and the structure of solutions based on cyanoethyl cellulose with DMA and DMF, poly-( $\gamma$ -benzyl-L-glutamate) with DMF, and hydroxypropyl cellulose with ethanol, acetic acid, DMA, DMF, and water have been studied under static conditions and in a mechanical field. With decreasing molecular mass of the polymer, the boundary curves separating isotropic from anisotropic solutions are shifted to higher concentrations and lower temperatures, in agreement with the Flory theory. When solutions are deformed, the cholesteric type of liquid crystals is transformed into the nematic type; this process is accompanied by the formation of domains in solutions, and the corresponding temperature-concentration boundaries of the LC phases are changed. As the molecular mass of the polymer increases, the ability of macromolecules to orient under the shear field decreases.

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#### P70-FI

### Global Phase Rheological Diagram for self associative systems

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The Bautista Manero Puig model, in spite of its simplifications, gives predictions that are in good agreement with the experimental rheological behavior exhibited by complex fluids such as the self-associative systems over a wide range of surfactant, electrolyte and additive concentrations, temperatures, stresses and velocities of deformation. No also shear thinning, shear thickening, thixotropy or rheopexy can be described, the shear and vorticity banding flows are predicted, too. Additionally, the non equilibrium critical phenomena is of properties can be predicted, i.e., all possible rheological behaviors of self associative systems and its transitions are systematically constructed using the general properties of the extended Gibbs free energy as a function of three pairs of relevant rheological variables. We systematically explore the model parameter space to demonstrate how the features of these rheological phase diagrams change as function of the relationship between zero shear viscosity and at high shear rate limit; the structure characteristic time and breaking-reformation kinetic constant; and the intensity parameters of the shear banding in the gradient direction and in the vorticity direction. Which depend on the composition, pressure and temperature. We have constructed these phenomena corresponding to different numbers of degrees of freedom in the extended thermodynamic parameter space, and have shown how features at each level map to the parameter space of the model, i.e. to its global phase diagram. We have argued that our approach provides a basis to construct a classification scheme for rheological global phase diagrams of self associative systems. It is similar to the scheme of van Konynenburg and Scott for binary mixtures.

P71-FI

**Spatiotemporal stress and microstructure evolution in dynamically sheared wormlike micellar solutions using rheo- and flow-SANS**

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Worm-like micelles (WLMs) are models for understanding polymer physics as well as of technological interest across a broad range of applications ranging from enhanced oil recovery to many consumer products. Prior investigations have elucidated many aspects of steady shear banding, yet few investigations have been made regarding the dynamic rheology of WLM solutions. To address this, large amplitude oscillatory shear (LAOS) measurements are used in this work to understand the spatiotemporal stress and microstructure of WLMs during deformation using newly developed instrumentation implemented on small-angle neutron scattering (SANS) beamlines at the ILL in Grenoble, France. A well-characterized formulation of 6 wt% cetylpyridinium chloride (CPCI) and sodium salicylate (NaSal) (1:1 molar ratio) with 0.5 M NaCl in D<sub>2</sub>O is studied. We present time and spatial resolved microstructure measurements during oscillatory shear flow. Measurements made in the velocity-velocity gradient plane of shear are used to quantitatively define the microstructure by the micellar segmental orientation ( $\phi_0$ ), and an alignment factor ( $A_f$ ). The shear stress measured by rheology is successfully predicted using these microstructure parameters and the stress-SANS rule derived from complementary steady-shear data. Thus, for the first time, we successfully define the time-evolution of the local microstructure and corresponding local stress for shear conditions corresponding to shear banding and metastable states. Complementary rheo-SALS experiments show butterfly patterns characteristic of shear-induced de-mixing as predicted by E. Helfand and G. H. Frederickson. Phys. Rev. Lett. 1989, 62, 2468. Quantitative measurements of spatiotemporal structural evolution and rheology are used to test constitutive models and learn more about the rich dynamic rheological behavior of shear-banding WLM solutions.

P72-FI

**Efficient heat transfer by elastic turbulence**

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An experimental study of the efficiency of the heat transfer in a regime of elastic turbulence is presented. Time resolved measurements of the temperature distribution between the rigid plates of a von Karman swirling flow system of a dilute solution of a linear and flexible polymer performed at various Weissenberg numbers indicate that the transition to elastic turbulence is accompanied by a significant increase of the efficiency of the heat transfer. By analysing the statistics of the temperature fluctuations within the flow it is found that these fluctuations decay exponentially in time somewhat similarly to the decay of the fluctuations observed for a passive scalar (put here the refs to my papers on the decay of the mixing). Corresponding to the efficient heat transfer regime, the temperature fluctuations de-correlate during characteristic times comparable to the largest polymer relaxation time and their probability distribution functions deviates significantly from the Gaussian distributions observed in a laminar regime.

P73-FI

**Experimental investigation of the Rayleigh-Bénard convection in a shear thinning fluid**

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An experimental investigation of the Rayleigh-Bénard convection in a shear thinning fluid uniformly heated from below is presented. The degree of shear thinning of the solutions is varied in a wide range by using several grades of carboxymethyl cellulose (CMC) at various concentrations. The transition to convective states is investigated by both integral measurements of the integral temperature gradient and local measurements of the convective amplitude. The nature of the bifurcation is assessed by monitoring the reversibility of these measurements upon increasing/decreasing powers. The scaling properties of the convective onset with the rheological properties of the solution are discussed in the framework of existing theoretical predictions.

## P74-FI

**Birefringent Strands and Structures in Strong Flows of Polymer Solutions**

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Birefringent strands are key to understanding non-Newtonian rheological effects in strong flows of polymer solutions. The elastic strands of highly-oriented polymer molecules, that are frequently associated with flows near stagnation points at Weissenberg numbers  $Wi > 1$ , represent localized regions of enhanced extensional viscosity. They can behave as internal stress boundary layers in a flow field and thus their appearance can significantly modify the very flow field that first gave rise to them. The resulting mechanism of feedback between localized fluid viscosification and the flow field can result in the formation of rich and complex birefringent structures (perhaps most famously the "birefringent pipes" observed in the axisymmetric opposed-jets device) and can drive the onset of elastic instabilities. In this poster, I will review historical experimental observations of birefringent strands and structures in strong flows of polymer solutions around cylinders and spheres, within contractions, and also in flows with a free stagnation point such as the opposed-jets and cross-slot devices. The review will be brought up to date with some recent experimental work performed with monodisperse polymers in a highly idealized planar extensional flow generated within a microfluidic Optimized Shape Cross-slot Extensional Rheometer (OSCER) device.

## P75-FI

**Flow of Wormlike Micellar Solutions in Rectangular Channels**

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We characterize the flow of a non-shear-banding wormlike micellar solution within two different high-aspect ratio rectilinear microchannels. We use micro-particle image velocimetry to obtain streamwise velocity profiles across the channels over a wide range of imposed volume flow rates. For the lowest and highest rates tested, pseudo-Newtonian velocity profiles are observed, which develop over a period of several minutes following the startup of flow and agree well with the predictions of a generalized Newtonian fluid model. However, over a wide range of intermediate flow rates stable and predictable flow is never observed on the timescale of the experiments (up to several hours of continuous flow at each imposed flow rate). Here the flow profile across the channel is typically characterized by spatiotemporally unstable "jets" of high velocity fluid amid surrounding regions of virtually stagnant fluid. We have not yet determined the reason for this flow instability, but it has important implications for a number of industrial applications as well as for microfluidic rheometry of complex fluids.

## P76-FI

**Inhomogeneous flow of wormlike micelles: a kinetic network model approach**Octavio Manero\*<sup>1</sup>, Juan Paulo García<sup>2</sup>, Fernando Bautista<sup>2</sup>, Jorge E. Puig<sup>2</sup>

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In this work, the rheological behavior of micellar solutions is analyzed under non-homogeneous velocity and stress flow conditions. The framework is based on the transient network formulation coupled to the underlying kinetics embodying two relevant processes: formation of wormlike chains from a free-micellar solution through a thermally-activated process and their flow-induced degradation. The second kinetic process consists in the formation of entanglements from the free wormlike chains and their flow-induced breakage. The elastic segments (here modeled as linear springs between entanglements or nodes) form a micellar network. The flow-induced change in the network complexity is modeled as a coupled kinetic scheme constituted by a set of reversible kinetic equations describing the evolution of the three microstates (free micelles, wormlike free chains and entangled wormlike chains). In this regard, microstates reflect the complexity of macromolecular interactions. In the case of a global stoichiometry and with linear spring force, the model allows the configurational distribution function to depend on time and space. The derived constitutive equations involve the kinetics, mass flux and contain diffusive terms in the stress. In special cases, such as absence of diffusion, a non-monotonic constitutive curve under simple shear flow is predicted, in addition to results of normal stresses, birefringence and extinction angle.

### P77-FI

#### **Simultaneous appearance of gradient and vorticity shear bands in wormlike micelle solutions**

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Under appropriate physical and chemical conditions surfactant molecules self-assemble into long and flexible chains, which are called wormlike micelles. Aqueous solutions of such aggregates show a viscoelastic flow behavior. In particular, with increasing shear stress the solution changes from Newtonian to shear thinning flow behavior. Above a critical shear stress the solution becomes suddenly shear thickening and the shear rate starts to oscillate. During this viscosity-oscillation a strong alignment of the micelles takes place, forming visible alternating transparent and turbid stripes of so-called shear bands. According to their orientation, it is distinguish between two types of band. Vorticity shear bands appear horizontally and perpendicular to the Couette axis, whereas gradient shear bands are seen vertically and thus concentric to the Couette axis [1, 2]. Our studies of wormlike micelle solutions, prepared with the surfactant cetylpyridinium chlorid (CPCI) and different salts of salicylate in an equimolar ratio, show that the appearance and number of vorticity and gradient shear bands is determined by temperature, type of counterion, and salt/surfactant concentration. In general, vorticity shear bands dominate the visual appearance, while gradient shear bands always coexist. Also, depending on the environmental condition, only gradient shear bands appear without the appearance of vorticity shear bands. Our studies revealed insights into the sequential appearance of shear bands and offers a model for the resulting macroscopic viscosity-oscillation in shear-thickening surfactant solutions.

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### P78-FI

#### **Viscoelastic turbulence in square duct flows - bifurcation scenario, stability and vortical flows**

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Viscoelastic fluids represent the majority of fluids involved in biological and technical processes, hence it is important to develop an understanding for their basic properties. In our research, we have focused on (visco-)elastic turbulence. Due to the generally negligible  $Re$  in these cases, we use the Weissenberg number  $Wi$  to describe the flow. We investigated the flow of a Polyacrylamide solution in a channel with a  $2 \times 2 \text{ mm}^2$  square cross section and 80 interconnected half rings (functional units). The velocity field inside the functional units and a straight stretch of the channel adjoining them has been investigated using digital particle imaging velocimetry (DPIV). Of interest to us was an insight on the bifurcation scenario, particularly the identification of a critical Weissenberg number  $Wi_c$  for the transition from laminar to turbulent flows to occur, an investigation of the spatial genesis and decay of turbulence and an analysis of the temporal spectra. Furthermore, we investigated Dean-flow like vortices which have been suggested from theoretical stability analyses, but so far, never been investigated quantitatively.

### P79-IR

#### **Coating and drying of non-newtonian lithium-ion battery electrode slurries**

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In addition to research on new materials, a fundamental understanding of the interrelations between processing, electrode morphology and performance has the potential for improved cell efficiencies and cost reduction. Process optimization will be a key factor for the development of new generations of lithium-ion batteries. Slot die coating is state of the art for casting electrode pastes. Advantages are high precision, applicability over a wide range of paste viscosity, low dead volume and the possibility to realize a closed, continuous working process.

The group „Thin Film Technology“ (TFT) at KIT investigates limits of the coating and solidification step with the aim to produce defect free electrode coatings, with large coating area, and improved morphologies at decreased production

times. Research focuses are multilayer coatings with innovative slot die designs and the development of advanced, adapted process concepts. In a close cooperation with the working group "Applied Mechanics" the special demands of the non-Newtonian and viscoelastic flows of the electrode slurries were investigated. Drying of electrode layers and solidification during solvent removal is an important and limiting process step. In this process step, the formation of the electrode morphology is governed by the process parameters and the limiting boundary conditions. Different measuring techniques can be applied at laboratory scale to analyze the drying step. The results are utilized to develop a model-based description that is transferred and verified at a pilot scale production line. The combination of fundamental drying models, morphology characterization of dried samples and performance data is the basis for an up-scale of the electrode drying process for lithium-ion batteries and the optimization of the overall process.

#### P80-IR

##### **Rheological properties of starch-based adhesives modified by tannin addition**

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Biopolymer-based adhesives have become more and more interesting in recent years because they are based on renewable polymers and offer a wide variety of functional characteristics; starch is probably one of the most important industrial biopolymers in the adhesive field, with a number of uses in the paper industry, mainly in corrugated paper-board production where the adhesive has a direct effect on both the quality of the finished board and the process efficiency.

With the aim of producing high quality board at low cost, making paperboards more competitive with different packaging based on plastic materials, improvements in adhesive characteristics should be obtained. Therefore starch modifications or additive addition are becoming frequent to obtain the macroscopic properties desired for specific uses. In this work the effects of the addition of four different tannins on a typical adhesive, adopted for corrugated paperboard production, were investigated by using fundamental rheological techniques, both in dynamic and steady conditions.

The onset of starch gelatinisation, one of the relevant technological parameters, was estimated as the knee point of the storage modulus in a dynamic temperature ramp test and it was observed that tannin addition increase it with respect to the neat adhesive. This result is due to the interactions between tannin and starch that affect the gelatinisation and retrogradation reactions. On the other hand it was observed that tannin is able to decrease the steady shear viscosity, improving the adhesive flow properties.

Tannin, therefore, has shown itself able to modify technological properties such as gelatinization temperature and viscosity and it could be used to adapt adhesive characteristics to specific applications, potentially improving starch-based adhesive competitiveness with respect to different adhesives.

#### P81-IR

##### **Chemorheology of an Unsaturated Polyester-Styrene Resin Filled With Aluminum Hydroxide**

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The chemorheological behavior and curing of a composite of unsaturated polyester-styrene resin filled with aluminum hydroxide particles was investigated, using dynamic time sweep test at 0.1 Hz frequency and different temperatures, between 60 and 170 °C. The complex viscosity,  $|\eta^*|$ , as well as storage,  $G'$ , and loss modulus,  $G''$ , during curing were measured. Curing of the composite was taken place with or without peroxide, which was used as an initiator. Obviously, the rate of curing was 100 times faster in the present of initiator. After starting the curing, complex viscosity versus time followed a power-law behavior [1] and the power indexes for compounds with and without initiator were 4 and 10, respectively. Gelation time was defined as the time of crossing of  $G'$  and  $G''$  [1,2]. Coloration of gelation time and temperature showed an Arrhenius behavior [3]. The calculated Arrhenius kinetic activation energy for compounds with and without initiator was 92 and 120 kJ/mol, respectively. To investigate the effect of temperature on the viscosity as a function of frequency, before starting of curing, dynamic frequency sweep tests were performed on the composite without initiator, at different temperatures between 30 and 90 °C. Time-temperature superposition analyses of dynamic frequency behavior of the compound showed an Arrhenius behavior having activation energy of  $90 \pm 5$  kJ/mol.

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#### P82-IR

### **Detection of Meltflow Instabilities in the Extrusion of Polymer Melts- The Sharkskin Die vs. the Advanced Image Analysis**

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During the extrusion of polyethylene (PE) and other polymer melts, visible surface distortions (also called melt flow instabilities (MFI)) of the extrudate appear at increasing shear rates. At a defined range of shear rates the surface distortions show a characteristic behaviour and are classified as e.g. shark-skin, stick-slip or melt-fracture. During the extrusion occur pressure fluctuations inside the die; preliminary studies [1-2] showed that those fluctuations seem to correlate with the MFI.

For this purpose two different approaches to study the MFI were performed from us. The first one is to measure the in-situ pressure fluctuations inside the extruder die via the sharkskin die and the Fourier transform (FT) analysis of the time-dependent pressure fluctuations  $p(t)$ . The second is to analyse the MFI after the extrusion via FT image analysis.[3] Both methods are used on the same test runs and their results are compared.

The FT of the time-dependent pressure fluctuations and the FT of the grayscale images, provide similar results about the characteristic frequencies of the MFI. The advantages of the FT of the time-dependent pressure fluctuations are the online measurement inside the die, before the extrudate leaves the die, the better sensitivity in case of weak MFI and the more detailed frequency spectrum of the MFI. The advantages of the FT of the grayscale images are the better sensitivity (except for weak MFI) and the obvious indication of the frequency contributions. Typically, this FT is strongly dominated by one characteristic frequency.

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#### P83-IR

### **On-line rheological measurements for industrial process monitoring and control of complex fluids**

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Industrial-scale production of many liquid or semi-solid products, like foods and cosmeceuticals (shampoos, moisturising lotions, toothpastes) is often performed batch-wise, historically enabling flexibility for production of high-value consumer products. As volumes increase and profit margins tighten due to more competition in the marketplace, leaner manufacturing routes are becoming more important - in particular for products which have become high-volume, lower-value consumables (e.g. shampoo, chocolate, toothpaste). Batch-wise production of these materials has become challenging due to increasing demand which often outstrips existing production capacity.

Production bottlenecks include Quality Control/Quality Assurance (QA/QC) measurements in the laboratory, often adding an hour to the production cycle. Operator-to-operator sample handling differences and continuous evolution of products post-sampling result in too-wide QC criteria for the product, and there can be operator safety concerns during sampling. Moving to a continuous processing strategy reduces or removes bottlenecks, variability and safety concerns, as well as increasing existing capacity.

To change to a continuous process and maintain QA/QC integrity it is vital to provide the operator with a go/no-go mechanism directly from the process. In processes where rheological parameters are used as release criteria current process control technologies have often proven difficult to apply because they measure at high effective shear rates, where similar recipes tend to be least sensitive to change and production errors are not detected, or they require installation in a process side-stream. The evolution of on-line oscillatory squeeze flow has been shown to have value for online process monitoring of these products in the process pipeline (Königsberg et al, Appl Rheol, 23, 35688). In this work we use process conditions representative of those encountered in industry to explore the on-line squeeze flow technique under a variety of process flowrates and temperatures for a series of complex fluids. We suggest a

framework for interpretation of the results, and provide comparative measurements using current industry-standard laboratory QA/QC measurement techniques - Brookfield viscometry and a research-grade rheometer.

#### P84-IR

##### **Viscosity of Drilling Fluids under Increased Pressure**

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During the drilling of an oil or gas well, drilling fluids perform several functions, essential for the successful creation of the well. Examples are the removal of cuttings, the stabilization of the wellbore and the lubrication of the drill. Corresponding with the large number of function, drilling fluids are complex water-based or oil-based fluids consisting of suspended particles, polymer and electrolytes and other components.

With increasing depth the temperature and pressure in the well increase significantly compared to the conditions at surface level. Subsequently, the rheological properties under downhole conditions differ considerably from those measured at surface level temperature and pressure.

To get relevant data for downhole behaviour, different drilling fluids have been tested using a rheometer (HAAKE MARS, Thermo Fisher Scientific) equipped with a pressure cell capable of running tests under pressures up to 400 bar and 300 °C using a coaxial cylinder measuring geometry or a vane rotor. The influence of pressure on shear rate dependant flow and time dependant flow is shown for two different drilling fluids. The pressure dependant viscosity data shows excellent correlation with data calculated with the Barus equation.

#### P85-IR

##### **Pressure Dependency of Fuel Oils and Recycled Fuel Oils**

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High-pressure viscosity measurements have extensive practical importance in a variety of applications such as high-pressure synthesis, molten polymer processing, enhanced oil recovery, and lubrication. The viscosity is also a significant factor that influences phase separation processes, heat transfer processes and transport of fluids and plays a very important role in many engineering calculations.

Measurements on different intermediate fuel oils and recycled fuel oils (RFO) will be presented. This rheological study was performed using a controlled stress rheometer (HAAKE RheoStress 600, Thermo Fisher Scientific) in combination with a pressure cell and coaxial-cylinder measuring geometries.

Steady-state flow and oscillatory shear measurements at different differential pressures (up to 400 bar) and temperatures (between 0 and 60 °C) were performed in the control rate mode. One sample of the intermediate fuel oils exhibits a Newtonian flow behaviour in the whole pressure range tested (1-400 bar). Whereas sample number two shows a shear-thinning behaviour, showing a power-law dependence on shear rate.

In addition the evolution of the steady-state viscosity with pressure for the recycled oil and the heavy residue/oil samples was studied. At constant temperature, viscosity increases exponentially with pressure in the range of pressure tested.

Measurements on a RFO were performed in a temperature range between 0-60 °C and at different pressures in the range 0-400 bars. The Fillers-Moonan-Tschoegl (FMT) takes into account the combined effect of temperature and pressure on the rheological properties for a variety of materials from high viscosity melt polymers to low viscosity oils. It will be show that this FMT model fits excellently well the experimental results obtained in the whole differential pressure range studied.

## P86-IR

### Structure Related Shear Thinning Of Pastes For Thick Film Deposition

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Thick film pastes are used in many fields of hybrid technology and micro systems packaging. Permanent development trends are fabrication of fine line structures as well as deposition of films with high aspect ratios (height/width). Nowadays not only a continuous improvement of established technologies like screen printing is pursued but also new deposition technologies as co-extrusion print arise. These different deposition techniques put different requirements on the rheology of thick film pastes.

In general, a thick film paste is a suspension consisting of an organic matrix fluid and an inorganic powder (which forms the final thick film) dispersed in this matrix. The organic fluid is fabricated from a solvent in which a fraction of a polymer compound is dissolved to attain a basic viscosity. The addition of inorganic powder particles increases the flow resistance of the matrix. The shear thinning of a thick film paste is influenced by at least the polymer concentration, the polymer chain length, and the solids fraction in the matrix fluid. To study effects of these parameters on the shear thinning behavior, model thick film pastes were fabricated (solids content of 76-90 wt%). The rheological characterization is of interest at the shear rate range of a particular deposition technique. Hence the shear thinning behavior was chosen to investigate by the rotational viscosimetry (0.1-1000 rad/s) and by the capillary viscosimetry (1000-6000 /s). It was found that at increased solids content the thick film pastes exhibit a similar shear thinning behavior as that of partly network plastic melts. A heuristic flow law, called CARPOW [1], which is a combination of the power law for a yield stress and the Carreau model, was used to fit the measured flow curves. The introduction of an effective viscosity allowed describing well the experimental data in a whole range of studied solids contents.

[1] K. Geiger, "A new heuristic flow law", 21. Stuttgarter Kunststoffkolloquium, 2009.

## P87-IR

### Investigating the thixotropy of coarse grained oxide ceramic slips with a modified falling sphere viscometer

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Generally ceramics for high temperature applications (refractories) consist of a coarse grain fraction with particle sizes exceeding 1 mm embedded in a fine particle matrix. The combination of this fine and coarse grain fraction improves the thermomechanical, corrosion and erosion properties of these ceramics.

Many refractories are produced by casting processes. A new casting technology for refractories is pressure slip casting, because until recently it was used only for fine particle ceramics. For refractories it is a way to produce complicated near net geometries. Further advantages of pressure slip casting are the possibility of automation, faster production, higher densities and better quality of the process and the product therefore.

An important property during casting is the thixotropy, because it often determines the inner surface quality of hollow ware and also affects the filtration behavior.

However, the rheological characterization of such concentrated coarse grain suspensions is quite difficult because the gap size of conventional shear rheometers is not sufficient. Therefore we designed a modified falling sphere viscometer, which measures especially the acceleration of the sphere in the suspension.

With the help of this viscometer it was possible to optimize the thixotropy of the coarse grained slips and finally to improve the casting properties of the ceramic bodies. As influencing factors we investigated the particle size distribution and the water, surfactant as well as the binder content by statistical design and analysis of experiments.

## P88-IR

### Following Thermal Curing Reactions with Rheometry and Simultaneous FTIR-Spectroscopy

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In this contribution a unique combination of a rheometer and an FTIR-spectrometer is presented. The so-called Rheonaut module allows the coupling of the Thermo Scientific HAAKE MARS rheometer platform with an

FTIR-spectrometer. With this set-up, samples can be characterized rheologically using cone/plate- or plate/plate-geometries while IR-spectra are being recorded simultaneously.

To proof this concept, thermally induced polymerization and cross-linking reactions have been followed with the combination of HAAKE MARS and the Rheonaut module. Depending on the chemical nature of the components involved, the disappearance of the starting material's reactive group and/or the appearance of chemical groups, which are characteristic for the product can be monitored and correlated with the development of the mechanical properties. Details of this unique instrument set-up as well as selected results will be presented.

#### P89-IR

##### **Rheology and the Crystallisation of Filling Fats**

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In confectionery products, the rheological properties of fat crystal networks need to be controlled to achieve good quality end products. The mechanical behaviour of fats is difficult to control due to the formation of mixed crystals and various crystal polymorphs. Rheology has become an important tool to provide information at many levels from quality control to research and product development. The aim of this study is to develop rheology as a standard method to monitor the final product properties as well as the processing behaviour of confectionery filling fats, using a range of cooling and shear rate conditions.

The rheological study was carried out with a typical fat using a Bohlin CVO rotational rheometer with cone and plate geometry. Using oscillatory rheology, the rheological profile gives information about the crystallisation behaviour of filling fats when cooled down naturally. Three different regimes were characterised by the rheological behaviour during 24 hours of crystallisation as the temperature fell from 70°C to ambient temperature.  $G''$  value was greater than  $G'$  during the first 2 hours which showed that the fat exhibited essentially liquid characteristics when the temperature was decreased to 24°C. With a further decrease in temperature and as the fat solidified,  $G'$  became greater in value than  $G''$  (characteristic of a weak viscoelastic solid). The ratio between  $G'$  and  $G''$  values (tan delta) was relatively constant until at around 8 hours when both moduli separated further and eventually the parameters reached a plateau when the formation of crystals had reached a limiting value. These changes in rheological data were supported and further studied using differential scanning calorimetry, X-ray diffraction and microscopy.

#### P90-IR

##### **Rheological and Mechanical Properties of ABS/SBS Composites and Nano-Composites**

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ABS is an engineering plastic widely used in industry owing to its good processability and dimensional stability. Although some grades of ABS have not appropriate impact strength. The main objective of this paper is to investigate the rheological and mechanical properties of ABS/SBS composites and the effect of clay on these properties. The blends were prepared by melt blending technique. Mechanical tests show that the tensile at yield decreased with increasing SBS content and also impact strength improved at low extent of SBS and then decreased with increasing of SBS. Also, the elastic modulus, loss modulus and complex viscosity of blends increased with increasing of SBS and damping factor decreased.

#### P91-IR

##### **Effect of Rheological Parameters on Power Characteristics of Thermoforming Equipments**

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Thermoforming is a well known technique in polymer processing due to its interesting features. The dynamic value of driving-force for the stretching process is determined based on equilibrium equation. It is used for calculation of the required theoretical work, and power of a thermoforming process. By using a viscoelastic rheological model in the proposed mathematical model, its validity was examined by performing experimental tests on ABS and PP sheets. An analysis of the presented results specifies that required process force is of interaction between the plug equipments

and the polymer sheet. It is determined by using geometrical parameters of the sheet, the velocity of the plug, the surface area of its contact with the stretched sheet, and the rheological parameters of the polymer. This force is practically applied on the plug-assist thermoforming machine components. Also, it may be used in evaluation of the machine required power. Experiments on ABS polymer sheet establish validity of the proposed model. Optimum operation of the mentioned process by setting proper values of parameters in the implemented technology secures all of its requirements.

#### P92-IR

##### **Qualitative modelling of starch products expansion by extrusion**

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In spite of the versatility, soberness and safety of extrusion process, and of the industrial importance of the area, the design of extruded foods still relies predominantly on empirical approaches. Although tools are available to transfer scientific knowledge, like Ludovic©, a software for simulating twin screw corotative extruder, there is a lack of generic model to predict cellular structure from extrusion and material variables. A bottle-neck with that regard is the modelling of the expansion phenomenon, during which the starch melt material acquires its glassy cellular structure. It is a transient process of a triphasic medium, rather challenging to address with deterministic models and too complex to be coupled with Ludovic©, in order to predict in line the cellular structure of the starch foam. Conversely, there is a strong knowledge background relying on experimental studies on the kinetics of expansion, and the role of thermorheological properties (extensional and shear viscosity, glass transition temperature) on expansion and final cellular structure. Furthermore, it is possible to model complex processes by integrating expertise and scientific knowledge using qualitative modelling approaches, as done for dough mixing, the first operation of breadmaking. So, this work aims to achieve the coupling of a qualitative model of expansion with an existing mechanistic model of extrusion. In this purpose, a qualitative model of the mechanisms of cell structure creation of starch foam is built, taking into account the thermodynamics of starch expansion at the die of an extruder. The coupling of the two models, written in different formalisms, i.e. expert rules and mechanical model, requires translation from symbolic to quantitative space of calculus. The reverse translation can also be performed, to optimize the process conditions for the desired cellular structure of the starch foam.

#### P93-IR

##### **Characterization of petroleum coke water slurries**

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As a byproduct of the oil refining industry, petroleum coke is a fuel of low price and increasing production, having high heating value, low moisture and ash content. These additional advantages are compensated by its low volatile content and high contents of sulfur, nitrogen and high volatility metals so that its use as primary fuel still represents a challenge. The present work is concerned with the preparation of concentrated petroleum coke water slurry (PCWS), suitable to be pumped and combusted and to solve partly problems related to handling and burning ground petroleum coke. PCWS of different concentration and particle size distribution have been prepared by petcoke wet milling for different times and using naphthalene sulfonate and polyacrylamide as dispersing and thickening agents, respectively. Various experimental test have been performed with controlled stress and controlled rate rheometers under steady and oscillatory shear conditions in order to characterize the rheological properties of PCWS and their dependence on previous shear history. All the systems exhibit negligible time-dependence and remarkable shear thinning-shear thickening behavior which are satisfactorily described with a modified version of the Sisko equation. The model parameters can be profitably used to examine the effects of changes in the formulation and preparation parameters on shear thickening onset and other aspects of the shear-dependent behavior.

## P94-IR

**Fluid flow of adhesives in hybrid-bonding processes**

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Lightweight design in modern transport industry requires joining different materials to one component. For this purpose adhesive bonding is increasingly being used. The combination of adhesive bonding with other joining technologies is called hybrid bonding. Hybrid bonds combine the high strength of adhesive joints using areal load transfer with fast point wise mechanical or thermal joints. These assemblies provide high strength and stiffness, corrosion resistance and excellent energy absorption in crash.

The current process for hybrid joining of two substrates has four steps. In the first step the liquid adhesive is applied on the first substrate. The second substrate is then placed and fixed in the correct position. The third step is the mechanical joining of the two substrates before the curing of the adhesives takes place as the last step. The demand to increase the stability of the industrial hybrid bonding process requires the understanding the fluid flow of the adhesive during a mechanical joining operation in the above mentioned third step. Most commonly the liquid adhesive exhibits a non-newtonian flow behavior. The flow is driven by the non-linear deformation of metal under very high pressures. Different mechanical joining technologies like clinch-bonding, riv-bonding and hemming can be observed. The fluid flow of the adhesive has a significant effect on the joint's strength, the final geometry and quality of the assembly [1]. To generate information about the fluid flow the material behavior of the liquid adhesive must be measured using different rheological methods. The parameters of the hybrid bonding process must be investigated and variations must be studied in detail. The oral presentation outlines rheological measurements, simulations and experimental work observing the hybrid joining processes.

[1] R. Neugebauer, M. Israel, B. Mayer, H. Fricke; Numerical and Experimental Studies on the Clinch-bonding and Riv-bonding Process; Key Engineering Materials Vols. 504-506 (2012) pp 771-776

## P95-SF

**Interfacial behavior of fluid under compression on fibrous structures**

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When a fluid drop is deposited on a solid surface, its shape depends on the solid-liquid interactions and is characterized by a contact angle. The surface roughness of the material induces different configurations of the drop. Wetting properties depend on a combination of surface chemistry and surface roughness. High and multiscale rugosities facilitate the trapping of air under water droplets inducing high hydrophobic surface behavior. Controlling the wetting behavior has recently attracted a great attention due to the wide applications in technologies (medical, printing, cleaning processes. . .). What happens when the fluid is submitted to stress? In our experiments, a liquid drop is deposited on different hydrophobic fibrous materials located in a horizontal plane. A plunger is moving down and up at a constant velocity so that the liquid is submitted to a given pressure. One observes the drop after such a cycle. Several phenomena occur: a transition of wetting (the quantity of air trapped under the drop decreases), a capillary flow of a part of the liquid within the fibrous structure and the deformation of this structure. Different textile materials are used as solid substrates. The results are discussed with respect to the different geometric scales of these substrates.

## P96-SF

**Shear and dilatational interfacial rheology of protein and polysaccharide systems**Noemi Baldino\*<sup>1</sup>, Domeni Gabriele<sup>2</sup>, Lucia Seta<sup>1</sup>, Francesca Romana Lupi<sup>1</sup>, Bruno de Cindio<sup>1</sup>

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Proteins and polysaccharides are often present in food emulsions and foams and their interactions play a relevant role in the final structure of many processed foods. Proteins are characterised by relevant interfacial activity which promotes droplet formation and stabilisation; polysaccharides are commonly used as bulk structuring agents able to increase the viscosity of the dispersing phase and, therefore, to improve the system stability. Anyway even polysaccharides can adsorb at the interface, modifying the interfacial structure and affecting protein behaviour, for this reason

it is of high importance to investigate protein-polysaccharide interactions at the interface with the aim of properly designing new multiphase systems with controlled properties. In the present work the shear interfacial rheological behaviour of  $\beta$ -casein and commercial citrus pectin, biopolymers typically present in dairy systems. They were investigated with small amplitude oscillations in both dilatational and shear conditions following the evolution with time of dynamic moduli at air-water interface. These methods are complementary and focus on different aspects of the interfacial layer, therefore their combined analysis can allow a better understanding of the effects of the studied biopolymers on the interfacial structure and on the behaviour of the layer in real conditions.

Protein-pectin mixtures were prepared and their behaviour was compared to that of pure components with the aim of investigating the potential interactions. It was observed that protein have an appreciable surface activity, even though at concentrations larger than that of proteins, and their presence significantly affects the protein behaviour at interface.

#### P97-SF

##### **Effect of co-surfactant molecular structure in surfactant mixtures on interfacial and rheological properties of highly concentrated emulsions**

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The effect of molecular structure of two different groups of surfactant mixtures on processing, interfacial and rheological properties of highly concentrated water-in-oil emulsions is presented. The surfactant used to form emulsions consisted of a polyisobutenyl succinic anhydride-based surfactant (Pibsa-Mea) mixed with oil soluble (Span20, 40, 60, 80 and 85) and water soluble (Tween20, 40, 60, 80 and 85) sorbitan derivative fatty acid ester surfactants. All Span and Tween samples have similar tail structure but different head groups. Interfacial characteristic of the surfactant systems were first measured by Kruss tensiometer using Wilhelmy plate method. The regular solution theory by Rosen was applied to investigate the effect of the head and tail groups of Span and Tween molecules on synergism of the surfactant mixtures. All emulsion samples were manufactured using Horbart mixer. The rheological parameters such as plateau modulus, creep compliance and yield stress were determined from the rheological measurements. Results showed that the degree of synergism in surfactant mixtures had a significant effect on emulsion refinement time. It has been found that the rheological parameters such as Plateau Modulus, Yield Stress and Equilibrium Compliance are strongly affected by the co-surfactant tail structure. Pibsa/ Tween mixtures have lower Plateau Modulus and the Yield Stress compare to Pibsa/Span mixtures with similar tail structure.

#### P98-SF

##### **Surface tension of a viscoplastic gel measured by a static method**

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Viscoplastic fluids are widely represented in industry and daily life (food, cosmetics. . .), and it is often necessary to take into account their surface tension to model their behavior when confined in thin layers or small droplets. However, this measurement is generally not simple because of significant viscous effects even at very low shear rate. We used a static method using Laplace's law on a droplet to measure the surface tension of a viscoplastic gel (Carbopol), with no effect of the yield stress on the measurement. The droplet is indeed small enough for the bulk energy associated to yield stress to become negligible with respect to the surface energy. This way, the droplet has a regular capillary bridge shape and the surface tension is directly given by the droplet curvature.

This method can also be used on any fluid, since the size of its constitutive elements is small compared to the size of the droplet. We also investigated the influence of concentration on the surface tension of the gel.

#### P99-SF

##### **Wet fibre-laden foams in axial mixing with macro-instabilities**

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Wet foam is an excellent carrier phase to produce particle or fibre structures [1]. Thus, it is important to know how particles or fibres affect foam properties. We study foams generated by axially agitated mixing with 60-80% air

content. The shear rate and resulting capillary number in mixing are very high compared to similar parameters in typical foam rheology studies. Onset of a flow macro-instability is observed at high rotation speeds both with and without cellulose fibres. The air content of the foam is strongly affected by this instability. By describing the effect of the air content on the stability of bubble interfaces [2], we explain the bubble size for broad ranges of rotation speed and surface tension. Added fibres usually reduce the bubble size for a fixed rotation speed. After the flow macro-instability, not only the air content but also the bubble size increases with reduced surface tension. Beyond the instability, the effect of fibres on foam properties becomes minor.

[1] J. Lehmonen, P. Jetsu, K. Kinnunen, T. Hjelt, Potential of foam-laid forming technology for paper applications, *Nordic Pulp Paper Res. J.* 28 (2013) 392-398.

[2] A. M. Al-Qararah, T. Hjelt, A. Koponen, A. Harlin, J. A. Ketoja, Bubble size and air content of wet fibre foams in axial mixing with macro-instabilities, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 436 (2013) 1130-1139.

## P100-SF

### Rheological characterization during hydrate formation in water-in-oil emulsions

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Hydrates of natural gas are crystalline solids, formed by the association of water molecules and molecules of a certain gas in an organized structure. Its occurrence is a natural concern for the Oil & Gas Industry, given the potential risk to flow assurance, and large investments are made in order to prevent it. Nevertheless, ever-challenging scenarios are encouraging the search of risk assessment methodologies, seeking to identify conditions where hydrates will form, but with little possibility of plugging. In this context, the understanding of hydrate rheology is a key element, for which the first step is the evaluation of the rheological properties of a model hydrate slurry. The model system is a water-in-oil emulsion within which hydrates are formed at atmospheric pressure and low temperatures, whereas in the actual case both high pressures and low temperatures are needed for the hydrate formation. In this work we analyze the effects of water and surfactant concentration on the viscosity, and on the storage and loss moduli of these emulsions. The hydrate formation at room pressure is induced with the addition of cyclopentane to the emulsion. Rheological data are obtained for several combinations of the emulsion components, and their mechanical behavior are related to hydrate formation.

## P101-SF

### Pectin-and-olive-oil-based emulsions filled-gels: a cosmetic and pharmaceutical application

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The proposed emulsions are based on pectin gels filled with olive oil droplets. Emulsions filled-gels are structured systems characterised by a particular rheology which allows them to be used in a wide range of industrial fields. Four different low-methoxyl pectins were used to structure the dispersing aqueous phase, which is mainly responsible of the mechanical properties of emulsions filled-gels. Unlike other biopolymers, the used pectins are able to structure water even at room temperature, and, as a consequence, they can create the typical gel network structure without damaging potential thermolabile additives. Cosmetic emulsions are often enriched with natural components such as olive oil, well-known for its emollient and skin care properties and, with the purpose to maintain a "clean label" formulation, citrus pectins were used for the aqueous phase formulation. A rheological characterisation of the obtained O/W emulsions was carried out with small amplitude oscillation tests, analysing emulsions properties at room temperature (frequency sweep tests) and getting stability information with temperature ramp tests (time cure). A non-linear empirical model was formulated to relate complex modulus at room temperature with gel characteristics (pectin content) and oil fraction.

### P102-SF

#### **Effect of pH, Surfactant Concentration and Temperature on the Rheological Behavior of Oil-in-Water (O/W) Emulsions**

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The present work reports the results of an experimental study which was carried out to examine the effects of pH, surfactant concentration and temperature on the rheology of 30 (v/v, %) oil-in-water (o/w) emulsion. The o/w emulsions were prepared using light petroleum oil with an anionic surfactant (SDBS) and deionized water. The surfactant concentration, pH and temperature were varied in the range of 0.5-2 (w/w, %), 2-12 and 10-50 °C, respectively. All the experiments were performed using a controlled-stress cone and plate rheometer. In dynamic rheological experiments, oscillatory measurements were performed to investigate the viscoelastic properties of the emulsions. The amplitude sweep tests were used for determining LVR and dynamic yield point. Frequency sweep tests were carried out to obtain storage modulus ( $G'$ ), loss modulus ( $G''$ ) and complex viscosity. Oscillatory time and controlled shear rate time sweep tests were performed to investigate the changes in the stability of the structure of the o/w emulsions. The dynamic shear flow study showed that the emulsion passes through a transition from elastic behavior ( $G' > G''$ ) to viscous behavior ( $G' < G''$ ) via a cross over region ( $G' = G''$ ) as the frequency changes from high to low. From the steady-state rheological measurements, it was found that the apparent viscosity of the emulsions changes significantly with a change in pH, surfactant concentration and temperature. Experimental shear rate vs shear stress data have been fitted to different viscosity models using non-linear regression analysis. The emulsions show non-Newtonian, shear thinning pseudoplastic behavior with an increase in pH and surfactant concentration. At higher pH (12-10) and surfactant concentrations (2 w/w %) o/w emulsion showed a characteristic yield point and gradually diminished as both pH and surfactant concentration decreased. The degree of shear thinning and viscoelasticity increases with an increase in pH and surfactant concentration.

### P103-SF

#### **Evaluation of rheological behavior of Brazilian heavy crude oil with polysaccharides**

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Heavy oils are identified by their high viscosity, high density and can be defined as viscous oil, aliphatic, dense (low °API) and which have a high content of asphaltenes. Generally heavy oils are high in carbon, sulfur and metals and low in hydrogen content. One of the important challenges in the study of heavy oils is their rheological behavior, during the heavy oil's outflow from the production fields till the processing plants. Some research mentioned the use of polysaccharides to enhance rheological behavior of heavy oils, since in aqueous systems, polysaccharide particles can absorb water, which results in partial or complete dissolution. Depending on the ionic form of the system or the conditions of pH and temperature, the polysaccharides can form gels or be soluble in water. One of the interesting properties of polysaccharides is that they have the capacity to modify the rheological behavior of water or aqueous systems, even when used in small concentrations. The aim of the present work was to investigate the rheological behavior of Brazilian heavy crude oil (17°API), P2, in dispersions with two polysaccharides, xanthan gum (C) and gellan gum (H) in concentrations of 10, 100 and 1000 ppm, for both. Rheological characterization of the dispersions at temperatures of 25, 40, 50 and 60°C, in a steady state, showed that the dispersion P2C100 exhibited the highest value of viscosity, around 5 Pa\*s, at 25°C between all samples. However sample P2H100 showed the lowest value for viscosity, around 2 Pa\*s, at the same temperature and shear rate from 0 to 200 1/s. At 60°C two dispersions, P2C1000 with xanthan and P2H100 with gellan samples were more effective to reduce viscosity exhibiting values lower than 0,2 Pa\*s, during the shear rate sweep. The study of the rheological behavior of heavy oils with polysaccharides becomes interesting due to the direct relationship between the concentrations and temperatures influence.

**P104-LC****Simultaneous Rheometry and Polarization Microscopy for Pharma HME Formulation and Process Development**Fritz Soergel\*<sup>1</sup>, Francesca De Vito<sup>1</sup>, Fabian Meyer<sup>1</sup>, Klaus Oldörp<sup>1</sup>, Thorsten Cech<sup>2</sup>

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More and more newly developed Active Pharmaceutical Ingredients (APIs) are crystalline and their bioavailability may therefore be low. In case the APIs cannot be solved in liquid solubilizers, the pharmaceutical industry faces the challenge to find the right polymeric solubilizers, additives and processing equipment/parameters (e.g. Hot-Melt Extrusion - HME) to be able to process them and obtain products (e.g. an amorphous solid solution) with high bioavailability, long term stability and good drug release characteristics.

Initially, such new crystalline APIs are often available in small quantities only. To investigate pure polymers, pure APIs and formulations of those (also with plasticizers and additives), simultaneous oscillatory rheometry and polarization light microscopy (with well-defined temperature profiles up to 300°C) can be used (Thermo Scientific HAAKE MARS Rheometer and RheoScope Module). Even with a very small amount of API, this rheo-optical method reveals, whether an amorphous solid solutions (or amorphous or crystalline dispersions) is formed and whether a re-crystallization occurs either during the cooling run or with the storage time (stability).

Simultaneous rheometry and polarization microscopy delivers efficiently significant and well-correlated rheological data and microscopic images. It provides on the one hand an efficient screening tool for HME formulation development and makes on the other hand rheological parameters for process development and optimization, as well as for modeling calculations for compounding and extrusion available.

Results with pure polymer (Soluplus®), pure API (Ibuprofen) and with mixtures of API and polymer (Theophylline, Soluplus®) will be presented.

**P105-PM****Printed (Hybrid-) Biosensors – Characterization of coating solutions concerning their rheological properties**Anna-Lena Riegel\*<sup>1</sup>, Jürgen Hubbuch<sup>2</sup>, Philip Scharfer<sup>1</sup>, Wilhelm Schabel<sup>1</sup>

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Biosensors offer a unique operating system, the so called “induced-fit” concept, which might constitute a key to innovative and pioneering technologies. The integration of a bio-active receptor molecule into a sensor allows the transformation of a specific substrate. Thus, the existence of a certain analyt can be proved. The aim of this research is to develop a coating process for such sensors in which the active film is applied as a thin layer. In addition, a promising way to accelerate the transfer of a signal and to achieve greater storage stability is the direct immobilization of the active component into a polymeric matrix which is conductive. In this context, wetting and flow behavior as well as rheological properties play an important role since they have a great impact on the quality of the coated film. For the development of a proper coating process, it is inevitable to thoroughly characterize the coating solution of question. With regards to the poster, experiments of a model system, consisting of the generic protein bovine serum albumin (BSA) and the conductive polymer poly(3,4-ethylenedioxythiophene/polystyrene sulfonic acid) (PEDOT:PSS), will be presented. This model system is analyzed with regard to parameters which are important to coating and drying aspects. In particular, these are the viscosity and the surface tension studied as a function of shear rate, temperature and composition of the solution. Furthermore, the obtained coating results will be discussed and correlated to measured rheological properties.

**P106-PM****Effect of viscoelasticity and surface tension on the foaming ability of zein dough**

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The purpose of this project was to focus on the experimental influence of rheology and surface tension properties on

foaming of a melt system composed of the maize protein. A dough was obtained mixing zein protein, maize starch and water and this mixture was heated between two temperature controlled parallel heat plates in order to simulate foaming during the process of baking. Citric acid was used as plasticizer to investigate the effect of viscosity on bubble formation and the melt surface tension was varied by adding surfactants. Properties as strain hardening and extensional viscosity, known as important parameters in foaming, were investigated using a Hyperbolic Contraction Flow experimental setup. Zein doughs showed strain hardening properties (expressed as strain hardening index) and a reduction in extensional viscosity (expressed as steady state extensional viscosity) with increasing extension rate or amount of plasticizer. The surface tension was estimated by means of contact angle measurements of fluids on the dry dough surface using a goniometer. The mechanistic understanding of zein foaming during baking would help to develop a commercial zein containing gluten-free bread and to optimize the way the production steps of mixing, proving and baking are performed in a manufacturing environment.

#### P107-PM

### **Iron-Mediated Photodegradation Of Polyethylene: A Molecular Approach Based On Rheological Characterization**

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Polyethylene (PE) is one of the most widely used materials in the world, and accumulated in the environment due to their very low biodegradability. However, to increase the biodegradation rate, metal salts used to promote the oxidation resulting in microfragments of PE, which is an important stage for potential biodegradation, and metals which will remain in the environment carry no risks of pollution.

This study investigates the influence of iron ions (Fe(II) and Fe(III)) on the photo-oxidative degradation process of low density polyethylene (LDPE) under accelerated test conditions. LDPE mixtures with 1% w/w of iron were prepared by using HAAKE MiniLab twin-screw micro compounder. Samples were initially exposed to varying times of UV radiation and periodically analyzed by means of spectroscopic and rheological tools. The chemical evolution of these samples was examined by monitoring the photo-oxidation products by FT-IR with the ageing times. Moreover, the UV-vis spectra suggest a reduction of Fe(III) into Fe(II) during sample irradiation. Then changes in the molecular structure of samples were followed by an original methodology based on melt rheology. It is well known that the evolution of the rheological material properties directly reflects changes in molecular parameters. The linear viscoelastic properties in dynamic experiments are sensitive both to the chain scission and to the three-dimensional network formation. Thus, melt rheology allows the prediction of the particular behaviour due to the competition of chain scissions and recombination reactions occurring through ageing.

The results demonstrate that neat LDPE samples did not exhibit significant changes during the evaluated period. On the other hand, the iron ions used as a photosensitizer play an important role in the decomposition of hydroperoxide and have a very strong influence on the photodegradation behaviour of LDPE which accelerate the UV induced photo-oxidative degradation. The occurrence of a heterogeneous oxidation in blends films through photo-ageing was observed, scissions/recombinations counterbalance and the photoageing could involve successive steps. At last, chain breakdowns are predominant. The efficiency of Fe(III) addition was more important than Fe(II) to accelerate the photodegradation of LDPE. Finally, the obtained results were compared to samples analyzed with a UV coupled melt rheology (UV in situ irradiation) which is even less common way to assess photo-oxidation of polymers. The results showed that iron ions are a very powerful way to obtain controllable-degradation PE.

#### P108-PM

### **Evaluation of molecular structure - conductivity relation of injection molded polycarbonate hybrid nanocomposites filled with carbon black/carbon nanotube**

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The effect of mixed filler system consisting of carbon black (CB) and multi-wall carbon nanotubes (MWCNTs) on electrical properties and molecular rheology of melt compounded injection molded composites with polycarbonate (PC) was investigated. Pure CB or MWCNTs or mixtures of CB and MWCNTs in mass ratio 50/50 were added to PC using injection molding process to prepare the samples with filler concentrations between 0.5, 1 and 2 wt %. SEM observations on thin sections demonstrated a suitable distribution of fairly small CB aggregates and good dispersion

of the MWCNTs in nanocomposites. Composites with pure MWCNTs were shown a lower electrical percolation and higher melt viscosity due to the nature of these nano-materials. Because the samples did not show a lower electrical percolation than calculated from the values of pure nano fillers in PC, no synergistic effect between CB and MWCNTs could be found in the samples. Linear rheological investigations were done on the samples and it was observed that rheological properties were more influenced by MWCNTs than CB. Linear rheological measurements at low frequencies were shown that Carbon black aggregates influenced the structure of MWCNTs in the system, which may influence the electrical and reversibility of the MWCNTs orientations too. Because the changes and reversibility in the MWCNTs states are very critical in the electrical applications, the effect of CB in the systems must be investigated. In order to find the effect of CB on reversibility of the MWCNTs orientations in the process non-linear rheological measurements were done on the nanocomposites. It was also observed that these hybrid nanocomposites showed suitable electrical properties compared to the pure ones and this has an economical advantage of using less amounts of MWCNTs.

#### P109-PM

##### **Rheological characterization of hot melt adhesives based on EVAK copolymers**

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The results of measurements of rheological properties of five hot melt compositions based on polyvinyl acetate-polyethylene copolymer are presented. The compositions tested differ in the content of tackifying resins. Their properties were studied under the steady shear and dynamic conditions (DMA analyser, Haake MARS rheometer). From the DMA, the glass transition temperatures of compositions were determined. The measurements of flow curves, oscillatory, creep&recovery, and tack tests of melted samples were performed in the temperature range of 120-180°C.

It was found that all the melts tested behave as slightly shear thinning and thixotropic fluids. The viscosities, degree of shear thinning, and thixotropy decrease with the increasing temperature. Due to the wax and resin content, the viscosity of the compositions is significantly lower than that of the basic EVAK components. A semi-empirical equation was proposed for the estimation of composition viscosities. From the oscillatory tests, the storage modulus  $G'$ , loss modulus  $G''$ , and complex viscosity were evaluated. At lower values of frequency, loss modulus prevails, which predicates that the wetting and adhesive flows can be sufficient to form good contact with the substrate.

The results of creep and recovery tests document that the melts exhibit only insignificant degree of linear elasticity at the measurement conditions.

The tack was estimated according to the maximum magnitude of the normal force reached in the test. It was verified that this force increases with the increasing speed of lifting and decreasing temperature (increasing melt viscosity).

The rheological behaviour of the all compositions tested is not significantly influenced by the kind of tackifying resin and its content in the studied limits.

##### Acknowledgements

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#### P110-PM

##### **Molecular Modeling of Cavitation in model Polyethylene Networks**

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A molecular-level understanding of cavitation in polymer networks upon imposition of mechanical stress is still lacking. Molecular Dynamics simulations of crosslinked amorphous Polyethylene (PE) were conducted in order to study cavitation as a function of the prevailing stress. We present a methodology for predicting the cavitation strength and understanding its dependence on cohesive interactions and entropic elasticity. Our simulations show that experimental observations and predictions of continuum mechanics analysis, which relate the critical stress for cavitation to the Young's modulus of the rubber, are in agreement with the observed tensile triaxial stress below which a pre-existing cavity cannot survive in a cavitated sample. We further show that this stress is of entropic origin, in agreement with the continuum mechanics analysis of heterogeneous nucleation.

Reference: Polymer Science, Ser. C, 55, 212 (2013)

#### P111-PM

### **A Microscopic Description of Entanglements in Polyethylene Networks and Melts: Strong, Weak, Pairwise, and Collective Attributes**

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We present atomistic molecular dynamics simulations of two Polyethylene systems where all entanglements are trapped: a perfect network, and a melt with grafted chain ends. We examine microscopically at what level topological constraints can be considered as a collective entanglement effect, as in tube model theories, or as certain pairwise uncrossability interactions, as in slip-link models. A pairwise parameter, which varies between these limiting cases, shows that, for the systems studied, the character of the entanglement environment is more pairwise than collective. We employ a novel methodology, which analyzes entanglement constraints into a complete set of pairwise interactions, similar to slip links. Entanglement confinement is assembled by a plethora of links, with a spectrum of confinement strengths, from strong to weak. The strength of interactions is quantified through the fraction of time for which the links are active. By weighting links according to their strength, we show that confinement is imposed mainly by the strong ones. A self-consistent scheme for mapping topological constraints to specific, strong binary links, according to a given entanglement density, is proposed and validated. Our results demonstrate that slip links can be viewed as the strongest pairwise interactions of a collective entanglement environment. The methodology developed provides a basis for bridging the gap between atomistic simulations and mesoscopic slip link models.

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#### P112-PM

### **Nanolatex based nanocomposites: control of the filler structure and reinforcement**

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By adding nanoparticles to polymer melts, nanocomposites with improved mechanical and thermal properties are obtained. For a given polymer-filler couple, the improvement of properties appears related to the filler size, volume fraction and dispersion. Nevertheless no universal model is established at the present time. Whereas the filler size and volume fraction are determined by the formulation, the dispersion is more difficult to control and investigate.

Firstly we will show how we can tune the particles dispersion in model nanolatex systems (polymethacrylate-silica) using different strategies: the control of the filler charge, the modulation of the latex/filler size ratio (R) and the use of different polymer chain length. Using small angle scattering and TEM analysis we will demonstrate that repulsive aggregates of varying size can be obtained playing with the pH of the casting solution [1]. A good filler dispersion is obtained for  $R = 1$ , whereas a network of well-organized silica particles around the latex beads is highlighted for high latex/filler size ratio. Finally, decreasing the polymer molecular weight, fractals aggregates of increasing size are generated. The effect of these various structures on mechanical properties will be discussed. The mechanical properties of nanocomposite materials are controlled to a large extent by the filler-filler interactions, nevertheless, another important contribution - less well understood - is due to the polymer chain-filler interactions. In a second part, we will display results of an investigation of the polymer chains in such nanocomposites [2]. Small angle neutron scattering experiments performed in zero average contrast conditions (mixing hydrogenated and deuterated latex beads) enabled to follow the latex beads dissolution using an original model. Experimental results demonstrate that the dissolution dynamic of polymer chains is significantly slowed down by the presence of silica nanoparticles.

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## P113-PM

**Effect of the kind of carbon-based nanofiller on the rheological melt behavior of polypropylene composites**Cristhian Garzón<sup>\*1</sup>, Humberto Palza<sup>2</sup>, Manfred Wilhelm<sup>3</sup>

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Recent interest in the use of nanoparticles for the manufacture of polymer composites has arisen due to the striking improvements in some properties achieved at lower loadings compared to micrometer fillers. In particular, derivatives of graphite (G), such as sheets of graphene and thermally reduced graphite oxide (TrGO), emerge to replace expensive carbon nanotubes (CNT). G-based particles are used today as a filler in various polymer matrices due to its amazing electrical transport properties and low cost, achieving a significant improvement in electrical properties at low percentages of incorporation (0.5-5.0 wt. %) [1]. Moreover, these structures are able to dramatically change the melt behavior of the polymer matrix, especially when a network is developed through the nanocomposite (percolation process). In the present study, the effect of type of carbon structure (TrGO, G, and CNT) on the melt behavior of polymer nanocomposites prepared by melt-mixing was analyzed.

Our results show that the different carbon-based particles modify the elastic and viscous moduli of the polypropylene. While PP melt and composites with low filler content behave as traditional viscous liquid material, composites with high content show an elastic solid-like behavior due to the rheological percolation process [2]. Noteworthy, the percolation threshold for CNT is around 2 vol % meanwhile for TrGO and G particles this threshold is around 4 vol % and 13 vol %, respectively, showing the relevance of the kind of carbon-based particles on the melt behavior. The same tendency is also observed in the electrical behavior of the samples.

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## P114-PM

**Properties of injection- and compression-molded recycled poly(ethylene terephthalate)/poly(butylene adipate-co-terephthalate) blends**

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The mechanical and morphological properties of recycled poly(ethylene terephthalate) (R-PET)/poly(butylene adipate-co-terephthalate) (PBAT) blends were investigated. R-PET was melt mixed with five loadings (10, 20, 30, 40 and 50 wt%) of PBAT on a twin screw extruder. The extrudates were pelletized and then molded into test specimens by injection- and compression-molding. Of the five R-PET/PBAT blends evaluated, the 80/20 blend exhibited the highest tensile strength, but a lower stiffness and thermal stability compared to that of the neat R-PET. Scanning electron microscopy analysis confirmed the better compatibility of this 80/20 PLA/PBS blend. However, the extent of such depended upon and varied with the processing technique. The injection-molded specimens exhibited a higher tensile strength and elongation at break, and a lower Young's modulus and thermal stability, than the compression-molded specimens of the same blend ratio. It can be concluded that the toughness and processability of R-PET were improved by melt blending with an appropriate amount of PBAT and processing technique.

## P115-PM

**Stress relaxation in the non-equilibrium state of a partially entangled polymer melt**Ele de Boer<sup>1,2</sup>, Efren Andablo-Reyes<sup>1,2</sup>, Sanjay Rastogi<sup>\*1,2</sup>

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Linear rheology of equilibrium polymer melt states is well-understood in terms of existing theories, such as those based on the tube model. Non-equilibrium melt states, however, are not yet well understood. Recent studies have demonstrated that on melting polymers with reduced number of entanglements in solid state, the non-equilibrium melt that is initially obtained progresses to the equilibrium state considerably slower than expected when considering a simple chain explosion process [1,2]. This slow entanglement formation is observed as a build-up of the elastic modulus  $G'$  with time. By means of linear rheological techniques, this transition to equilibrium state after melting

of "disentangled" ultrahigh molecular weight polyethylene is investigated. Oscillatory rheology shows that Rouse dynamic is increasingly hindered during the transition to equilibrium state. The existence of a plateau region in  $G'$  shows that, even in non-equilibrium conditions, the presence of entanglements confines chains, thereby forcing them to renew their configurations by renewing their constraints. Presumably this renewal process proceeds by chain reptation in a similar way as it occurs in the equilibrium melt state. Step-strain experiments allow us to study the relaxation process related to constraint renewal. Relaxation modulus,  $G(t)$ , shows that as the melt elasticity increases, stress relaxation becomes slower. Surprisingly,  $G(t)$  obtained at different stages of the modulus build-up (including equilibrium state) collapses onto one single curve when using the build-up kinetics to rescale  $G(t)$ . This shows a clear relation between constraint renewal processes in the non-equilibrium melt state and its relaxation towards the thermodynamic equilibrium. These findings can be extended to non-equilibrium polymer melts in general.

[1] C. Teng et al. *Macromolecules* 45, 6648 (2012)

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#### P116-PM

##### **Viscoelastic properties of tailor made isotactic Polystyrene compared to atactic and syndiotactic PS**

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Whereas atactic Polystyrene (aPS) represents a prominent commodity, semicrystalline isotactic (iPS) and syndiotactic Polystyrene (sPS) are specialty engineering plastics which exhibit improved stiffness and higher dimensional stability. In comparison to sPS, which precipitates immediately as soon as it is formed, iPS does not crystallize during polymerization and stays soluble. Subsequently, during melting compounding or by annealing iPS crystallizes. Investigations on rheological properties of polystyrene with various tacticities is a challenge by means of synthesis especially for iPS. With reactor blend techniques we were able to synthesize tailor made iPS with defined  $M$  and PDI[1]. These products can be compared to aPS synthesized by anionic polymerization and sPS published by Wang et al[2]. We will present an overview to thermorheological properties of all PS modifications.

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[2] C. L. Huang, Y. C. Chen, T. J. Hsiao, J. C. Tsai, C. Wang, *Macromolecules*, 44, 6155.

#### P117-PM

##### **Polypropylene structural foams: measurements of the core, skin and overall mechanical properties, evaluation of predictive models**

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Structural foams (SF) have received an increasing attention mainly because of their specific mechanical properties (strength to weight ratio) as well as lower in-mold residual stresses. Injection molding of SF is one of the most suitable approaches to produce parts having a foamed core sandwiched between two un-foamed skins. Predicting elastic properties from the foam structure or even better from the processing parameters is critical to optimize the performance of the plastics parts.

Therefore, this study focuses on the prediction of the tensile, shear and flexural moduli of polypropylene structural foams prepared by injection molding under various processing conditions, especially as far as thickness is concerned. Injection molded SF were machined to remove the skins and to recover the core only. The tensile and shear moduli of each layer were measured and compared to the predictive models. Measurements of tensile, shear and flexural data were also performed for the overall SF and compared to predictions of models for cellular materials and polymer composites. For the tensile and flexural data, classical models of the literature were used, while for the shear modulus, a new model was proposed, taking into account the amplification of shear strain due to the negligible effect of the sandwich skins.

The models were found to be predictive and they provide a reliable tool for a fine tuning of the process parameters to obtain the desired properties.

## P118-PM

**Melt Rheology as a tool to assess influence of polylactic acid photo-ageing onto biodegradation kinetic**

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During service life, polymer materials aged and mainly if they are exposed to UV light. These degradations impact the material properties and leads to the waste production. Biodegradable polymers are the focus of many researches to limit impact of our waste on environment. Poly(lactic acid) is a good candidate to respond to this problematic, because it is compostable and furthermore it is bio-based.

Degradation in compost is a complex process with unclear mechanism. Two periods are suspected: in the first step, PLA is hydrolyzed and in a second step, polymer assimilation by micro-organisms. Methods are standardized but they don't consider sun impact while UV alter polymer structure. Some recent papers seems to point out some doubts about the entire biodegradable character of polymers after UV ageing and try to correlate the decrease in biodegradation with the gel content increase in the case of UV crosslinking evolution. During biodegradation tests, samples previously photo-aged or not are taken off and analyze in rheology.

Melt viscoelasticity is used to assess the molecular evolution of the materials biodegradation and photo-ageing. Viscoelastic data are plotted in the complex plane to obtain Cole-Cole plots at different composting time. The kinetic of the molecular weight decrease during biodegradation is checked by means of the decrease of the Newtonian viscosity. After only few days burying in compost, Newtonian viscosity decreases sharply meaning that the most important part of chain scission appear at the beginning of experiment. But double molecular mass distribution observed on ColeCole representation proved there was also a chain recombination mechanism. Rheological behaviour of PLA photo-aged and not are compared. Lower viscosity is measured during biodegradation after photo-degradation, so chains scission rate was higher and PLA seems to appear more biodegradable after photo-ageing.

## P119-PM

**Aging processes in recycled polyethylene and fly ash blends**

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This report represent current state in studies of industrially recycled polyethylene with fly ash blends. Polymer is a mixture of different types of polyethylene collected and homogenized, ash taken from capturing system of shell-oil power plant. Ashes have very high water absorbtion ability what in combination with ash inorganic contaminants brings to acid creation. We study changes in rheological properties of blended materials, and estimate aging effects on processability and permanence.

## P120-PM

**Poly(styrene)-b-poly(vinylpyridine) and gold nanoparticle compounds**

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This work was done in order to gain a deeper understanding of the orientation processes of diblockcopolymers. The different blocks in blockcopolymers tend to microphase separate into nanoscale structures. The various morphologies as well as their dimensions are dictated by the degree of polymerization, the volume fraction of the blocks and the imiscibility of the blocks. The blockcopolymers themselves as well as selectively incorporated nanoparticles lead to new and exciting materials.

Computational Chemisty is able to simulate the behaviour of blockcopolymers for different experimental parameters [1-3]. This may help to understand mechanisms for microphase alignment stated in experimental works [4]. In order to provide information about the behaviour of blockcopolymers actual diblockcopolymers were investigated.

Different polystyrene-b-polyvinylpyridine systems were synthesized using sequential anionic polymerization. The samples were characterized by GPC, NMR, light scattering (SLS and DLS) and DSC. The influence of oscillatory

shear stress was monitored by rheology, FT-rheology and dielectric spectroscopy. The morphology was examined via small-angle X-ray spectroscopy.

Further work on this topic might include the use of other Polymers such as PMMA, PDMMA, PAN or PpMS. Additionally other techniques can be used to strengthen the achieved results.

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#### P121-PM

##### **Nanocomposites of plasticized-poly(vinyl chloride) with nanosilica and poly(methyl methacrylate)-encapsulated nanosilica**

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In this study, either nanosilica ( $n\text{SiO}_2$ ) or poly(methyl methacrylate)-encapsulated nanosilica (PMMA- $n\text{SiO}_2$ ) synthesized via in situ differential microemulsion polymerization was used to improve the mechanical and thermal properties of plasticized poly(vinyl chloride) (PVC). PVC, plasticizer (40 phr), heat stabilizer (2 phr) and lubricant (0.2 phr) were melt-mixed with varied amount of the  $n\text{SiO}_2$  and PMMA- $n\text{SiO}_2$  (3, 5, 7 and 9 phr) on a two-roll mill, followed by compression molding. The results showed that the tensile strength, tensile modulus, tear strength and thermal stability of the obtained plasticized PVC nanocomposites were improved by the inclusion of either an appropriate type or amount of nanofiller, whilst the elongation at break decreased with increasing amount of the nanofillers. However, the PMMA- $n\text{SiO}_2$  with a core-shell structure exhibited reinforcing efficiency superior to  $n\text{SiO}_2$  at the same nanofiller loading. This is due to the PMMA molecules grafted onto the  $n\text{SiO}_2$  surfaces that enhanced the interfacial adhesion between nanofiller and PVC, leading to a better dispersion of the PMMA- $n\text{SiO}_2$  in the PVC matrix.

#### P122-PM

##### **Properties of injection- and compression-molded recycled poly(ethylene terephthalate)/poly(butylene adipate-co-terephthalate) blends**

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The mechanical and morphological properties of recycled poly(ethylene terephthalate) (R-PET)/poly(butylene adipate-co-terephthalate) (PBAT) blends were investigated. R-PET was melt mixed with five loadings (10, 20, 30, 40 and 50 wt%) of PBAT on a twin screw extruder. The extrudates were pelletized and then molded into test specimens by injection- and compression-molding. Of the five R-PET/PBAT blends evaluated, the 80/20 blend exhibited the highest tensile strength, but a lower stiffness and thermal stability compared to that of the neat R-PET. Scanning electron microscopy analysis confirmed the better compatibility of this 80/20 PLA/PBS blend. However, the extent of such depended upon and varied with the processing technique. The injection-molded specimens exhibited a higher tensile strength and elongation at break, and a lower Young's modulus and thermal stability, than the compression-molded specimens of the same blend ratio. It can be concluded that the toughness and processability of R-PET were improved by melt blending with an appropriate amount of PBAT and processing technique.

#### P123-PM

##### **FT-Rheology of linear Homopolymer Melts: Basic research on the intrinsic nonlinearity Q**

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In rheology, dynamic oscillatory shear is a wide used technique to research the behavior of polymer melts. With introduction of FT-Rheology in combination with oscillatory shear[1] a wide range of possibilities was opened to research the influence of structural effects of the polymer chains on its overall material properties.

Hyun et al. introduced an intrinsic nonlinear parameter  $Q(\omega)$ , which was found to show a correlation to the number

and length of side chains of a comb-like polymer topology.[2][3] However, no simple systems and only two different polymers were examined.

To evaluate the basic capacities of the Q parameter, samples of different molecular weights and dispersities for a variety of linear homopolymers were investigated. The results help to understand the influence of these characteristics on the intrinsic nonlinearity and to establish the Q parameter as a potent analytical parameter for polymer materials.

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#### P124-PM

### **A Thermo-Rheological Study on the Structure Property Relationships in the Reinforcement of Nylon 6-POSS Blends**

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In recent years POSS (polyhedral oligomeric silsesquioxanes) has been used in polymers as a copolymer, graft or as melt-blend filler. Due to its hybrid organic-inorganic nature, POSS has the advantage of providing molecular reinforcement, while its variety of functionalization schemes allows for reactions and/or other interactions with the matrix polymer. For example, various works in the literature have shown that strong POSS-polymer interactions exist that reduce shear viscosity and improve mechanical properties and thermal stability. Previous studies have shown the ability of POSS to reinforce polymers when incorporated through grafting or copolymerization, but there is a lack of work on the understanding of how POSS works as an additive. The main aim of the present work is to shed some light on this issue, using Nylon 6 as the matrix polymer. Nylon 6 is a semicrystalline thermoplastic polymer with an interesting morphology and hydrogen bonding ability that can be applied on a variety of applications. This ability is expected to lead to high levels of POSS-polymer interaction. In this work we focus on POSS AM0265, which has its primary amine in the aminopropyl group. Previous work showed significant increases in mechanical properties when nylon 6-POSS were melt-spun, while recently Jana and co-workers showed that the incorporation of POSS leads to a decrease in melt-viscosity. In this work we will focus on understanding the dynamics of POSS AM0265-nylon 6 interactions by performing a full spectrum of thermal, chemical, viscoelastic and processability studies, with the focus on the thermo-rheological behavior of the blends. In particular we will explain the reason for the maximum reinforcement to happen at a 2.5% w/w incorporation content of POSS in the Nylon 6 matrix.

#### P125-PM

### **Analyzing the effect of bond constraints on polymer viscoelastic properties obtained from equilibrium computer simulations**

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The goal of the present contribution is to cast light on the effect of employing bond constraints in molecular models on the prediction of viscoelastic properties of polymers, such as the stress autocorrelation function and the viscosity, through equilibrium molecular dynamics simulations. Two unentangled linear polymer systems with different molecular structure are investigated: polyethylene, described at an united-atom level, and polystyrene, described at an all-atom level. Both a fully constrained and a fully flexible version of polyethylene at five different temperatures are studied. A fully flexible and three partially constrained versions of polystyrene at a given temperature are also investigated, thus quantifying the effect of constraining different parts of the molecule on the dynamic properties of a polymer. The effects are analyzed at two different levels: an atomistic one based on the concept of the atomic level stresses and an molecular one based on the variations of the pressure tensor. Investigation of the distribution of the atomic level shear stresses and the atomic von Mises stress reveals that the stress anisotropies and the uncertainties of the atomic level based quantities are reduced. The effect on viscosity is quantified both by direct analysis of the stress autocorrelation function and by employing an expansion of the Green-Kubo formula in terms of the atomic level stress autocorrelation function [Levashov et al *J. Chem. Phys.* 138 (2013) 044507]. We thus argue that constrained molecular models are useful in calculating polymer viscoelastic properties through equilibrium molecular simulations.

### P126-PM

#### **Melt Rheology and Thermal Behavior of Hyperbranched Polyethers Depend on Site-selective Modification**

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Thermo-rheological properties and investigation of the glass transition temperature ( $T_g$ ) of selectively functionalized hyperbranched polyglycerols (hbPG) are presented in this study. Hyperbranched polyglycerols are easily accessible in a one-pot reaction with controlled molecular weights, tunable amount of hydroxyl functionalities, a well-defined degree of branching (DB) and consistent polydispersities (PDI). In this work, we employed a synthetic strategy for the selective modification of linear and terminal units of hbPG. This approach can be viewed as a preferential modification of functional groups located in the core region and functional groups that are more likely in the periphery of the hyperbranched macromolecules. On the other hand, we investigated the influence of several protection groups (benzyl, methyl and acetonide) located at the core or in the periphery with regard to the linear viscoelastic properties and their  $T_g$ . A remarkable observation is the trend of the glass transition temperatures of the polymers. Although hbPG exhibits clearly fewer linear than terminal hydroxyl-groups, the linear units mainly affect the flexibility of the polymer. In addition, the different protection groups show a significant effect on the glass transition. Nevertheless, the zero shear viscosity is not as much affected by the protection groups as by the amount and locality of the OH-groups. This work provides for the first time elementary insights into the thermo-rheological properties of hbPG in dependency on type and location of their functional group.

### P127-PM

#### **Coupled electrical and rheological experiments as a tool to study the aggregation kinetics of carbon black in polymer melts**

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The electrical conductivity of composites containing conductive fillers reacts very sensitively on changes in the morphology of the conductive phase during the processing. Therefore, so-called coupled electrical and rheological measurements provide a powerful tool to investigate the electrical properties of such composites under defined shear deformations. In this work the kinetic aggregation behaviour of carbon black filled polymethylmethacrylate under quiescent conditions was studied theoretically and experimentally. Therefore, a novel three phase model based on two different aggregate sizes is proposed leading to manageable fit functions, which are able to describe the experimental data. In order to test the model, the time-dependent electrical conductivity of the composites was monitored prior and after a short shear step using coupled electrical and rheological experiments. It was found that the shear step leads to a significant change in the conductivity and influences the aggregation kinetics of the system which is in agreement with our physical model proposed. Moreover, it could be shown, that the model has a much higher accuracy in describing the experimental data compared to the existing aggregation models where only one aggregate size is considered.

### P128-PM

#### **Rheological behavior of natural fibers composites obtained by twin screw extrusion: effects of botanical origin and fiber morphology**

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As the use of polymer composites has grown over the past decades in many industrial fields (e.g. automotive) and with the modern urge to produce "greener" and cheaper materials, new reinforcement components are more and more considered in order to replace traditional ones (e.g. glass fibers). Natural fibers like hemp or flax are thus increasingly used for this purpose as they are easily available and come from renewable resources. However, one must ensure that the mechanical properties remain sufficient for the intended applications.

Besides single fibers' mechanical properties, important compounding effects play on the whole material strength.

When compounded in extrusion process, these fibers undergo large strains. Due to a complex structure, their sizes and shapes are modified. Lengths and diameters change, impacting final properties. We propose in this contribution to study these morphological evolutions for a broad range of fibers (hemp, flax, sisal, miscanthus). These different species present various size distributions and are thus particularly adapted to conduct experiments with different initial conditions. A laboratory extruder is used to prepare PP/fiber samples which are then characterized by rheological means. However, precautions must be taken regarding the way samples are prepared; at mixing temperature (180°C), thermal degradations occur, as rheological measurements demonstrate. Some fibers are more impacted than others certainly due to their cellulose/lignin ratios. We thus choose to analyze the samples using multi-frequency strains in order to acquire proper mechanical spectra.

#### P129-PM

##### **Mapping the electrical conductivity of carbon black filled composites prior to and after shear**

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Recently, there has been increasing interest in coupled rheological and electrical experiments because the electrical properties of conductive polymer composites (CPCs) react very sensitively on changes in the structure of filler networks induced by mechanical deformation. On the other hand, the electrical properties of CPCs depend on many factors such as the size and shape of the fillers and their spatial distribution. Moreover, due to the strong intermolecular van der Waals interactions among the carbon black (CB) aggregates, it is very difficult to disperse CB in a polymer matrix uniformly. Accordingly, this leads to the question if there is a certain dependence of the electrical conductivity on the radial distribution for disk-shape CPCs samples. However, to our knowledge, the study on this subject is rare in available literatures. To answer this question, in this work, the electrical conductivity of disk-like Polymethylmethacrylate/ CB composite samples was investigated prior to and after a shear step. Novel electrical conductivity maps of the samples as a function of the position were obtained. It was found, that the electrical conductivity after angular averaging of the static (non-sheared) sample is, as expected, independent of the radius and CB concentration. In comparison to that, the angular averaged electrical conductivity of the samples with a shear history is decreasing as a function of the radius due to the linear increase of the deformation from the center to the rim of the samples. It is shown, that this effect is less pronounced increasing the composite concentration. A simple model is proposed to explain this behaviour. The results obtained in this study are in a very good agreement with the investigations performed via coupled electrical and rheological measurements and provide a deeper insight into structure changes in conductive polymer composites induced by shear deformations.

#### P130-PM

##### **Functionalization Effect on the Viscoelastic Behaviour of Multi Walled Carbon Nanotube/Epoxy Polysulfide Nanocomposites**

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Epoxy polysulfide (EPS) is a type of hybrid resins which is synthesized from polysulfide resin and a material contain oxirane group. This polymer because of combination properties of epoxy and polysulfide resin are used for coatings applications. In this research we used multi walled carbon nanotubes (MWCNT) to study the mechanical and viscoelastic properties of epoxy polysulfide nanocomposite. Generally, it has been found that the mechanical and viscoelastic properties are affected by the degree of dispersion of MWCNTs in composition. It is necessary to chemically functionalized MWCNTs for suitable dispersion of nano particles in polymeric matrix. For the first step we were treated MWNTs with  $H_2SO_4/HNO_3$  solution to make a COOH group on MWCNTs. FTIR results for functionalized MWCNTs in comparison to pure MWCNTs showed bands which is attributed to the C=O stretching vibration of carboxylic groups. Then four nanocomposite samples with different percentage of MWCNT (0.05, 0.1 and 0.5% w/w) were prepared by sonication and mixing of them in epoxy polysulfide. SEM results were performed to considering dense of MWCNTs in nanocomposite network. DMA test results in increasing tensile strength and modulus and decreasing elongation at break with increasing MWCNTs percentage. Also, changes of storage modulus ( $E'$ ) and loss modulus ( $E''$ ) and glass transition temperature ( $T_g$ ) by DMTA were studied.

### P131-PM

#### **Preparation and analysis of PET with additives in a micro compounder and rheometer**

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PET samples with several additives and plain resin have been mixed for a specific time. During the mixing period the composition / decomposition was measured in the integrated slit capillary. When the mixture was ready it was transferred to micro injection molding machine in order to prepare disc shaped test specimens. With these discs rheological tests were performed afterwards on a rotational rheometer of the polymer melt. A correlation of the chain breaking, extension and cross linking effect of the additives in the results of the micro compounder and rheological tests is discussed.

### P132-PM

#### **Size effect of silica particles on the rheological properties of Polylactide**

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In order to get a fundamental knowledge of the process ability of the polymer and their composites, it's significant to study these materials' rheological properties under molten state [1,2]. There are several experimental modes have been used to investigate the rheological properties, such as dynamic-mechanical experiments, creep and creep-recovery experiments, stressing experiments and relaxation experiments.

Biodegradable polylactide (PLA)-based systems composed of various size silica particles (nano and micro-sized) were prepared by melt mixing method and solution method. Three particles of different size (7 nm, 40 nm and 9  $\mu\text{m}$ ) but similar geometry were chose to reinforced PLA at different filler content. The oscillation experiments and creep and creep-recovery experiments up to the steady state were performed to investigate the rheological properties of neat PLA and composites. The rheological differences induced by particles size were investigated. For microparticles filled PLA, the oscillatory properties nearly unchanged by increasing the filler addition, as well the creep compliance. However, the recoverable compliance increased gradually with filler loading. While the rheological properties of nanoparticles reinforced PLA were strongly influenced by the addition of nanofillers. The nanoparticle which is smaller than the radius gyration of PLA (19 nm) can affect the rheological properties more significantly. The results can be explained by assuming different interactions between the particles and the polymer molecules [3]. When the nanofillers content exceed a critical value, a solid-like behavior arose, and it was account for the strong interactions between nanoparticles and formation of silica network at this concentration.

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### P133-PM

#### **A new understanding of Entanglements in Polymers: Applications to Rheology and Processing**

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The phenomenon of 'sustained-orientation' is observed by submitting polymeric melts to Rheo-Fluidification processing conditions, which combine pressure flow, cross-lateral vibrational shear flow, and expansional flow in an annular die: melt orientation can be preserved above  $T_g$ . Sustained -Orientation appears to challenge the present understanding of visco-elasticity and entanglements in polymer melts, the corner stones of polymer physics. The current understanding of polymer physics is based on the description of the properties of a single chain embedded in a sea of average interactions from the other chains that disturbs its properties. This classical view appears satisfactory to deal with "linear" phenomena, resulting from the deformation at low strain and low strain rates. Yet, problems and questions of polymer physics arise, and are still far from being fully answered, in the deformation range of non-linear visco-elasticity, which is the case when Rheo-Fluidification conditions apply and 'sustained orientation' is observed.

In this research I consider the statistics of a system consisting of a set of interactive conformers belonging to all the chains put together at once. I no longer attribute to a mean field the influence generated by the other molecules on the configurational properties of a single chain (defining its entropy and enthalpy), I attribute a “grain-structure” to the field that describes the result of interactive coupling, i.e. I consider the existence of an inhomogeneous density of state due to local fluctuations of the interactions. The evolution with time of the state of interactions between the conformers, when the system is submitted to a mechanical force or to a temperature variation describes the change of the physical properties. This new statistics, called the Grain Field Statistics, leads to the elaboration of a different understanding of visco-elasticity, rubber elasticity, and of the concept of entanglement of the macromolecules.

#### P134-PM

### Large Amplitude Oscillatory Shear and Uniaxial Extensional Rheology of Blends from Linear and Long-chain Branched Polyethylene and Polypropylene

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In this research work, normal stresses were measured in addition to shear stresses in oscillatory shear flow at small and large deformation amplitudes. New material parameters were then introduced based on Fourier Transform (FT)-Rheology and Stress Decomposition (SD) analysis of normal and shear stress measurements. Furthermore, uniaxial extensional measurements were performed and compared to simulation results using the Molecular Stress Function (MSF) model. Different behaviours were observed for the PE and PP type blends, which are believed to arise from the different types of long chain branching (LCB) present on each of the systems. The use of the new material parameters proposed and described within this work has the potential to allow a better understanding of structure-property relationships in industrial LCB materials.

#### P135-PM

### A differential constitutive equation for polymer nanocomposites based on principles of non-equilibrium thermodynamics

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Polymer matrix nanocomposites (PNCs) are hybrid organic/inorganic composite materials formed by adding nanoparticles (NPs) to a polymer matrix with at least one of the dimensions of the filler phase at the nanometer scale. As a result, the composite material can have significantly improved properties compared to the polymer itself. In the present work we have tried to construct a rheological model for PNCs with spherical NPs based on non-equilibrium thermodynamics, particularly the Generalized bracket formalism of Beris and Edwards [Beris and Edwards, *Thermodynamics of Flowing Systems with Internal Microstructure*, Oxford University Press, New York, (1994)]. Our aim is to generalize a recent rheological model for polymer melts [Stephanou et al., *J. Rheol.*, 53, 309 (2009)] which has been shown to accurately describe the results of atomistic non-equilibrium molecular dynamics or thermodynamically guided Monte Carlo simulations to account for the presence of NPs. Following previous attempts for nanofibers [Rajabian et al., *Rheol Acta*, 44, 521 (2005)] and nanoclays [Eslami et al., *J. Rheol.* 51, 1189 (2007)], we have first derived the rheological model for NPs of arbitrary shape by assuming two structural state variables in the framework of the Generalized Bracket: the first is the conformation tensor  $c$  for polymer chains and the second is the orientation tensor  $a$  for the NPs, together with suitable expressions for the free energy of the PNC, and the Poisson and Dissipative Brackets. The model addresses NPs of spherical shape by constraining the orientation tensor to be always equal to its equilibrium value. We will present results for the prediction of the new model for the phase behavior of PNCs and their rheological properties in shear and extension. In all cases, the results will be directly compared against experimentally measured data for unentangled polymer melts filled with NPs [Anderson and Zukoski, *Macromolecules* 41, 9326 (2008)].

### P136-PM

#### **Structural development of Polystyrene-grafted graphene nanocomposites during shear stress at elevated temperature**

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Polystyrene graphene nanocomposites were produced by solution blending of commercial polystyrene (PS 158 K) with polystyrene grafted, organophilic modified graphite oxide. Grafting was enabled by means of free radical in-situ styrene polymerization. Besides, composites containing un-grafted graphene were used as reference system.[1]

LAOS and SAOS experiments between 135 and 255 °C showed the existence of a time- and temperature dependent graphene particle network. The solid-like behavior in the terminal regime, expressed by the respective particle-network modulus, dramatically increased with higher temperatures and enduring shear stress. Kinetic investigations of the developing structure resolved two separable processes with different time constants. Dielectric analysis showed an enormous increase in the electrical conductivity of about 6 decades during the shear and temperature treatment, combined with low electrical percolation threshold of 0.5 wt.-%. Morphological investigations using SEM images of the nanocomposites revealed a growing graphene-domain size as well as an additional exfoliation accounting for the increasing conductivity and elasticity.

As a result, polystyrene-grafted graphene polymer-nanocomposites showed a unique development in elasticity, electrical conductivity and particle network formation during prolonged shear exposure at elevated temperature, which was exclusively observed when grafting was present.

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### P137-PM

#### **Semicrystalline Poly(styrene)-Poly(L-lactide) Block Copolymers**

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Raw material scarcity and climate change lead to a search of new materials like biobased polymers [1]. At the moment biopolymers can substitute conventional polymers only in small application areas due to the limited production capacity and the current high production cost. We create block copolymers based on petrochemical poly(styrene) (PS) and renewable poly(L-lactide) (PLLA) to improve the sustainability. The influence of block copolymer properties with regard to the rheological properties and the crystallization behavior is here presented exemplarily on one PS-PLLA block copolymer [2]. The block copolymer morphology can be aligned during large amplitude oscillatory shear (LAOS), while the corresponding alignment kinetics can be monitored by the G'' modulus and the nonlinearity parameter  $I_{3/1}$  [2,3]. The best here achieved, parallel orientation showed no reflex in normal direction. The type of crystallization (hard or soft confinement) influences the changes to the lamellar microstructure. Under soft confinement conditions, we observed a partially symmetry loss of the lamellar periodic pattern with an increase of the domain spacing of about 18%.

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### P138-PM

#### **Living Polymers under Thermal and Mechanical Stress**

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Controlled/living radical polymerization (CLP) techniques have been extensively employed for the synthesis of well-

defined polymers for academic purpose [1]. Especially atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization are highly versatile and efficient controlled/living radical polymerization techniques, allowing for fine control over the molecular architecture, molecular weight and polydispersity of synthetic polymers [2]. Combining these techniques with recent advances in modular and orthogonal polymer ligation protocols [3] presents a powerful toolset which permits the synthesis of well-defined polymers with controlled functionality. The most prominent modular ligation reactions widely adaptable to polymer chemistry include the Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC).

Recently, we examined the stability of linear polystyrene (PS) carrying a RAFT-functionality (trithiocarbonate) in the middle of the polymer chain with various chain lengths ( $M_n = 20 - 150$  kDa) under both mechanical and thermal stress [4]. In the present study, the behavior of linear polystyrene (prepared via ATRP) under thermal and mechanical stress carrying terminal bromide functionalities at the end of the polymer chain as well as a triazole functionality generated by CuAAC in the middle of the polymer chain is investigated.

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### P139-PM

#### **The rheology of Poly(vinyl acetate/Poly(vinyl alcohol) random and multi-block copolymers – generality and peculiarities**

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We prepared series of poly(vinyl acetate/poly(vinyl alcohol) random and multi-block copolymers with well characterized monomer units distribution along a chain and compared their rheological properties. Samples under study also had different composition vinyl acetate/vinyl alcohol unit ratio. The objective of this work was to understand what the minimal block length is which demonstrate the difference in its rheology with random copolymer.

Experimental part of the work included measurements of dynamic properties in a wide temperature-frequency range, relaxation, and rheology in flow of melts and solutions. It was shown that the principle of temperature-frequency superposition is valid for random copolymers, while the including of blocks with even 4-5 homogeneous units leads to impossibility of superposition. The terminal zone is clearly distinguished for random copolymers while it is absent for block copolymers. DSC method shows that multi-block copolymers demonstrate transition in the 209 to 220 °C temperature range obliged to crystallinity (though not clearly detected by the X-ray method), while this effect is absent for random copolymers. The dependencies of the glass temperature are also observed for copolymers of different molecular structure.

Strong difference in flow properties were observed for copolymers of both types, especially for dilute solutions. For multi-block copolymers, concentration dependence does not obey standard rules due to the effect of block ordering. Multi-block copolymers also demonstrate the existence of the yielding even in rather dilute solutions. Difference in the rheology of random and multi-block copolymers was found for their solution in some solvents. For instance, the difference in the structure strength (characterized by the yield stress) at -20 °C reaches four decimal orders. Structure formed by multi-block macromolecules demonstrates temperature-thixotropic character which is absent in random copolymers and so on.

### P140-PM

#### **Rheological behavior of nanomodified asphalts binders with montmorillonite**

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The study of the behavior of asphalt binders becomes interesting due to the direct relationship between pavement quality and performance of the binder. Although the asphalt coating is a mixture of asphalt binder with the aggregate, and may or may not have a modifier additive, the function of the binder is to combine the aggregates, conferring

resistance properties and durability to the pavement. Around 88% of the petroleum asphalt cement manufactured worldwide is designated to act as binder in mineral aggregate producing asphalt mixtures in the paving industry. In order to enhance the pavement durability, different modifiers can be added to the asphalt binders. A pavement modified by polymer usually exhibits more resistance to thermal deformation and collapse. The search for materials that have greater resistance to deformation and may extend the life of the pavement, especially the ones that could be associated with polymers, becomes one of the major goals in pavement industry. It is known about the montmorillonite (MMT C and MMT D) compatibility with the polymeric materials, however, the effects of modification in a Nanoscale by montmorillonite, although promising, have not been much studied. The aim of the present work was to investigate the rheological behavior through oscillatory test of modified asphalt binders with montmorillonite and polymer SBR. Four samples of modified asphalt binder were tested: 2% and 4% MMT C/ SBR; and 2% and 4% MMT D. The master curves show that in regions of high and medium modulus ( $G^*$ ) (which means in low service temperatures) the binder aged modified with 4% MMT showed lower values to complex modulus (maintaining the stiffness) and exhibited lower phase angle (more elastic). The addition of 4% of MMT C suggested less aging to short and long term if compared to the asphalt binders without MMT additives.

#### P141-PM

##### **Preparation of HIPS/TiO<sub>2</sub> Nano-Composites and Investigation of Mechanical and Antibacterial Properties**

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In this work, by using of a twin-screw extruder, HIPS with antibacterial properties was produced. For this purpose, TiO<sub>2</sub> was used as filler in micro and nano-scale. The samples for mechanical and anti-bacterial testing were prepared by injection molding process. Titanium dioxide plays role of both toughening and strengthen in all of the composites. At 1 % wt of TiO<sub>2</sub>, impact and tensile strength were maximized. Also, adding of titanium dioxide leading to improved melt flow index and vicat softening point of composites. HIPS/ TiO<sub>2</sub> composites have a satisfactory antibacterial effect on E.Coli and S.Aureus as examples of Gram-positive and Gram-negative bacteria. Due to smaller size and more accessible surface area of nano-TiO<sub>2</sub>, it is recommended for antibacterial purposes.

#### P142-PM

##### **Asphalt/polyethylene blends: Rheological properties, microstructure and viscosity modeling**

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An analysis on chemically-grafted polyethylenes as asphalt modifiers was carried out. Results show that the softening point of asphalt increased, while the penetration degree decreased in blends prepared with grafted polyethylene. The phase distributions of micrographs from fluorescence microscopy show that non-grafted polyethylene polymers were not readily miscible with asphalt. Rheological tests indicate that most of asphalt blends exhibit improved performance at higher temperature with grafted polyethylene such as enhancing rutting resistance, flow activation energy and superior time-temperature-dependent response as compared to the reference polyethylene blends. Zero shear viscosity (ZSV) was calculated using the different models available in literature to determine its suitability in predicting the rutting behavior of asphalt binders.

#### P143-VP

##### **A Lattice Gas Model of Granular Flow Behaviours in a Shear Cell**

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Depending on the degree of excitation, granular materials may be forced to exhibit solid, fluid or gaseous states. When in a solid state granular medium carry applied loads via an inhomogeneous contact network consisting of force chains while the fluid state is marked by particle motion that is determined by collision dynamics. Both Molecular Dynamics and Contact Dynamics have been frequently used to simulate these behaviours. However the efficiency of the former is determined by the efficiency of the computation of inter-particle forces while the latter is more relevant for perfectly rigid particles where dissipation occurs solely by friction. Recently Lattice Gas (LG) models, which have

been predominantly used to simulate liquid flows, have been adapted for granular dynamics due to their computational efficiency. Here we present a further adaptation of the LG model, the Sheared Granular Lattice Gas (SGLG) model, towards the simulation of rigid granular particles subject to external shear [1]. This algorithm differs from previous LG models of granular media in that force chain dynamics are now described for the first time. Using the algorithm we recover experimental non-equilibrium responses such as dilation at the shear plane, velocity profiles and qualitatively granular anisotropy. We also demonstrate the granular jamming transition with our results comparable to previous molecular dynamic simulations. Finally we also calculate the distribution of contact forces and show quantitatively similar changes in its distribution as observed in previous simulations and experiments.

[1]. B.W. Fitzgerald, I. Clancy and D. Corcoran, submitted to Physica A.

#### P144-VP

##### **Damping characteristics of granular polymeric materials exposed to hydrostatic pressure**

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Reduction of noise and vibration coming from the rail transport activities is an important objective of the environmental policy of the European Union, due to its impact on human and animal health. It has been identified that one of the major sources of noise and vibration in rail transport is from the interaction between the wheel and the rail, the so called rolling noise. One way to mitigate this noise is to attach damping elements to the rail. This study investigates the use of new generation damping elements composed of glass fiber textile tubes filled with pressurized granulated polymeric materials. Granular material with properly selected multimodal particle size distribution acts as pressurizing agent, similar as compressed air in tires. At the same time the generated hydrostatic pressure changes frequency dependence of the granular material bulk properties. By modifying material bulk properties we can modify damping characteristics of the new generation damping elements. Applying these damping elements to the rail can substantially reduce vibration amplitudes as well as sound pressure levels, thus reducing exposure of human and animal to noise and vibration.

#### P145-VP

##### **Effect of superplasticizers and particle packing on thixotropy of high performance concrete**

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Fresh properties of high performance concretes like flowability after rest, segregation resistance and formwork pressure are mainly affected by thixotropy. Thus, the control of thixotropic properties is the key for a successful application of these concretes. The rheological properties of concentrated suspensions, like high performance concretes, are affected by the properties of the granular skeleton, the surface properties of the particles and the adsorbed superplasticizer polymers. In particular, the use of superplasticizers to adjust rheological properties of fresh modern high performance concrete has gained in importance during recent years.

To understand the mechanisms, the effect of superplasticizer adsorption and particle packing on thixotropy of self-compacting concretes as well as ultra-high performance concretes has been experimentally investigated. Within the experimental program the solid fraction, the maximum packing density, the superplasticizer dosage, the molecular structure of the superplasticizer and the cement type were varied. For the determination of thixotropy rheological measurements were performed. The results show a strong correlation between solid fraction, polymer adsorption and thixotropy of the suspensions. With increasing superplasticizer adsorption and decreasing solid fraction a decrease in thixotropy was observed. Based on these results a qualitative description of the origin of thixotropic properties of high performance concretes is derived.

#### P146-VP

##### **Rate-dependent contact mechanics of polymer composites**

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Polymers play an increasingly important role in tribological applications. This is a challenging subject because of the

complex contact conditions involving many variables. Therefore, simplification to a well-defined contact situation is needed: the single-asperity sliding friction test. With this test, a wide range of surface mechanical properties are analyzed in a controlled manner. In a previous study a hybrid experimental-numerical approach was employed which revealed the subtle interplay between the constant polymer-indenter adhesion and the velocity/rate-dependent deformation of the polymer during scratching [1]. Understanding the polymers' intrinsic mechanical response proved to be key.

In practice, however, most polymers are filled. These fillers are added for many different reasons: to improve mechanical properties, to change the appearance through colorants, or even to reduce costs by adding a cheaper material in the polymer matrix. These additives have an effect on both the intrinsic mechanical response, and the adhesive interaction with the indenter tip. Consequently, the frictional response of the polymer changes completely.

To characterize the effect of filler particles experimentally, our model material, i.e. polycarbonate, is filled with either hard ( $\text{TiO}_2$ ) or soft (MBS) particles. An identical experimental-numerical approach is used to investigate the response of these model systems. The effect of adding fillers to the polymer matrix is revealed by scratch tests; the interplay between composite-indenter adhesion and the composites' response to deformation are revealed by finite-element simulations. Adding either soft or hard fillers only results in a change in magnitude for properties like modulus and yield stress. A similar effect is seen for the response in friction. The dependence on scratch velocity does not change, whereas the penetration into the composite changes with filler type and amount.

[1] Van Breemen et al., *Wear* 2012, 274-275, 238-247.

#### P147-VP

##### **Bingham flows in a rectangular channel with wall slip**

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We solve numerically the Poiseuille flow of a Bingham plastic in a tube of rectangular cross section under the assumption that slip occurs along the wall following a slip law involving a non-zero slip yield stress. Hence, in the numerical calculations both the constitutive and slip equations are regularized [Damianou et al., *J. non-Newtonian Fluid Mech.* 204, 24-37 (2014)]. Four different regimes are observed defined by three critical values of the pressure gradient. Initially no slip occurs, in the second regime slip occurs only in the middle of the wider wall, in the third regime slip occurs in the middle of both walls, and eventually variable slip occurs everywhere. The performance of the regularized slip equation in the two intermediate regimes in which wall slip is partial is tested for both Newtonian and Bingham flows. The combined effects of viscoplasticity and slip are then investigated with the emphasis given to the calculation of the yielded and unyielded regions.

#### P148-VP

##### **Predicting the development of permanent deformation in asphalt mixtures from the creep-recovery behavior of bituminous binders**

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In this study, the creep-recovery behavior of three unmodified and five polymer and/or wax modified bituminous binders was investigated to retrieve the rheological parameters for investigation of asphalt mixtures' propensity to permanent deformation. Frequency sweep and Multiple Stress Creep Recovery (MSCR) measurements were conducted on the binders to calculate values of rheological parameters that have been proposed to indicate the binder's susceptibility to plastic deformation. Furthermore, compacted asphalt mixtures, which were prepared from the aforementioned binders, were tested in a wheel tracking test device to characterize the binders' contribution to the mixture permanent deformation susceptibility. All the aforementioned tests were conducted at 50°C. It was found that the non-recoverable creep compliance ( $J_n^r$ ) and accumulated strain ( $\gamma_{acc}$ ) parameters derived from the MSCR test have a superior capability of predicting asphalt mixture permanent deformation in wheel tracking test compared with other proposed rheological parameters. For both of these parameters the relationship was found to be linear with a very high  $R^2$ -value of 0.99 when 3200 Pa creep stress was used in the MSCR test. However, it was observed that specimen preparation method has a significant effect on the rheological response of modified binders, and therefore on their MSCR test results. The observed variability in these test results was deduced to be caused by the variations in the morphology and crystallinity of the binder modifiers during testing, and strain sweep tests were performed to confirm

this assumption. Finally, it was shown that some highly modified binders exhibit significant nonlinearity in creep experiments, especially at medium and high creep stresses and at medium to long loading times. Hence, it was concluded that loading times and creep stresses play a major role particularly in the characterization of the plastic deformation susceptibility of modified binders.

#### P149-VP

##### **Study on the failure of joint rock masses using smooth joint model**

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A comprehensive study has been carried out on the influences of microscopic parameters of the smooth joint model (SJM) on the unconfined compression behavior of synthetic rock masses (SRM) using 3D DEM simulation method. The model was constructed by incorporating a smooth joint plane into a parallel-bonded particle assembly which was used to represent an intact rock mass and validated against the unconfined compression test results of marble samples taken from the site of Jinping II hydropower station in Sichuan, China. Simulation results indicate that for a SRM containing a non-bonded, non-persistent joint, mechanical micro-parameters including joint contact stiffness and friction coefficient, and geometrical micro-parameters including joint radius and dip angle all show significant effects on the unconfined compressive strength behavior. They are reflected in the development of a major shear band along the joint plane or within the intact matrix not involving the joint plane. However, strong coupling effects exist among these mechanical and geometrical micro-parameters so the eventual sample failure is a result of the complicated interaction among these micro-parameters. For a bonded joint, the above competition mechanism remains unchanged but is reflected in the interplay between the bond strength of smooth joint contacts and parallel bond strength of particle contacts.

#### P150-VP

##### **Rheological properties of backfill materials of a nuclear waste repository**

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The long-term performance of tunnel-backfill materials of a nuclear waste repository is vital in controlling the saturated density of the buffer that protects the fuel canisters. According to the current Finnish KBS-3V repository design, the saturated density of the buffer should be maintained within a narrow range of 1950-2050 kg/m<sup>3</sup> at all-time in order to ensure the safe disposal of the canisters. The lower bound of this density criterion prevents microbial activities near the canister surface while the upper bound protects the host rock from cracking due to the excessive pressure created by the swelling of the buffer. Tunnel backfill materials play an important role in controlling the swelling of the buffer by creating sufficient counter pressure to the swelling of the buffer. As the saturation of the buffer and the backfill takes place over a long time period (hundreds of years), the material properties could change with time, especially those of backfill materials and therefore they have to be studied in detail. This paper presents the rheological properties of Friedland clay that has been proposed as the main tunnel backfill material in the Finnish KBS-3V repository design. Viscoelastic behaviour of Friedland clay was studied with varying salt concentration of the ground water. State-of-the-art Modular Compact Rheometer with a parallel-plate measuring head was used to carry out a series of amplitude sweep tests in which the clay samples were subjected to oscillating forces with increasing deflection. It was observed that the resistance of the sample, the 'storage modulus' ( $G'$ ) to the applied deformation ( $\gamma$ ) within the linear viscoelastic range (LVE) was significantly increased with increasing salt concentration. The results from this study can be incorporated in the long-term modelling and analysis of the buffer-backfill interaction of KBS-3V.

#### P151-MR

### **Nano- microfluidics and rheology of around micro-organisms and exopolymeric aggregates in the oceans**

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For over 25 years (Jenkinson, 1986, Nature), it has been known that some micro-organisms, particularly plankton, increase laminar viscosity (mainly shear thinning) and elasticity in the surrounding water. Secreted exopolymeric substances (EPS) seem to be mainly responsible. Recently, Jenkinson & Sun (Deep-Sea Res. II, in press) showed that laminar flow of plankton and bacterial cultures in capillaries (radius 0.25 to 1.5 mm) was either decreased (drag increase) or increased (drag reduction) relative to that of clean medium. While the drag increase can be ascribed to polymeric thickening, the drag reduction could be superhydrophobic drag reduction (SDR) or a similar effect at the sculptured, hydrophobic surfaces of many micro-organisms and EPS aggregates. These findings will be briefly presented.

Measuring and understanding ocean rheology has long been recommended in order to understand and model many ocean processes. These include biogeochemical and sea-level change as well as air-sea CO<sub>2</sub> exchange and the swimming and feeding of organisms, particularly in relation to climate and environmental change. Jenkinson & Sun's (in press) results have now spurred recommendations by ocean research bodies that nano- and microfluidics (NMF) also be included (McManus et al. 2013, Intergovernmental Oceanographic Commission of UNESCO and the United Nations Science Council for Ocean Research (SCOR); Berdalet et al. Deep-Sea Res. II, in press). We are seeking to create an interdisciplinary ocean rheology and nano- microfluidics working group (WG), endorsed by SCOR. Such SCOR WGs have a life of 10 years and make recommendations that are taken into account by funding agencies world-wide. To the recommendations different ocean science bodies, we seek recommendations to SCOR from international and national rheology societies, as well as participation by rheology and fluidics experts.

#### P152-MR

### **First clues to understand red blood cell interactions: numerical studies of vesicle suspensions**

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Some biophysicists raises questions on blood flow for nearly two centuries -I refer to Poiseuille. To progress, we chose to modelize blood by vesicle suspensions. The behaviour of one single vesicle has been understood; the key question of cell interactions remains. We conduct bidimensionnal numerical studies thanks to the boundary integral method. Confinement plays a major role and I am going to explain how it modifies involved Green functions [1]. Furthermore, confinement introduces an interaction length between vesicles. Simulations benefit from that length to model suspensions at fixed concentrations. I will present some results on a rheological study of bidimensionnal vesicle suspensions.

[1] M. Thiébaud & C. Misbah, Rheology of a vesicle suspension with finite concentration: A numerical study, Phys. Rev. E 88, 062707 (2013).

#### P153-MR

### **Slippage properties of Polymer solutions in micro- and nano- channels**

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Managing the flow of polymer solutions at small scales is a key issue for many applications varying from nanotechnologies to enhanced oil recovery. Those fluids are known to exhibit rather high slip lengths, typically ranging from one to several tens of micrometers. Therefore confining flows at the micron scale or even below requests some better comprehension and management of their slippage properties.

We use standard photolithography and glass wet etching techniques to study unidirectional flows in channels with height varying from hundred nanometers to hundred micrometers. The considered surfaces are either flat or corrugated with a controlled wavelength of several micrometers. We use a z-resolved micro particle image velocimetry

technique thanks to confocal microscopy in order to measure velocity profiles in the vicinity of the channel walls with a good precision. Those measurements lead to the characterization of the slip velocity as a function of the wall shear-stress ranging from 0.01 to more than 100 Pa. On this basis, we systematically varied the concentration, the polymer length and focus on two types of aqueous polymers: polyacrylamide and polyethyleneoxide.

Finally, interpreting the slip velocity as a consequence of a depletion layer leads to the results that, for all the solutions tested, in the dilute regime, this layer is much greater than the characteristic size of the polymer chains. Indeed, this indicates that a flow induced migration is responsible for the slippage properties of our solutions. This migration is dependent on the confinement since we observe a reduction of the slippage velocity for channel height smaller than 10 micrometers. Moreover, we have also observed that the depletion layer slightly increases at high velocities for a given shear stress.

#### P154-MR

### Dynamics of Nanohybrid Hydrogels Studied by Dynamic Light Scattering: Effects of Chemical and Physical Cross-links

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One of the successful strategies of mechanical reinforcement of hydrogels is the introduction of scarifying bonds which dissipates fracture energy during large deformation of the network. Introduction of silica nanoparticles in the chemical network of polymers which absorb on the silica surface can increase the elastic modulus and the elongation at rupture simultaneously. Adsorption/desorption of the polymer chain serves as reversible physical crosslinks.

Now we are interested in the local dynamics of the silica particles in the gel in the presence of the adsorption. Dynamic light scattering was used to characterize the dynamics of the nanoparticles and the network simultaneously.

Nanohybrid gels based on poly(acrylamide-co-N,N-dimethylacrylamide), and colloidal silica nanoparticles, synthesized by radical polymerization. The effects of the chemical crosslink by N,N'-methylenebis(acrylamide) and the physical cross-link by dimethylacrylamide (DMA) / silica interactions were investigated.

In ensemble averaged autocorrelation functions we observed two decay modes, a gel mode and a diffusion mode of the silica nanoparticles. And  $q$  dependence of their characteristic time was analyzed. An increase in the chemical cross-linking ratio did not influence the gel mode while the silica nanoparticles diffusion mode was slowed down with decrease in the correlation length of the network calculated from the elastic modulus.

With increase in the DMA fraction, we observed a higher scattered light intensity than the silica suspension and the gel without silica, an increased plateau value of the autocorrelation function, a slowing down of the silica diffusion mode, and no influence on the gel mode. These results indicate that the hybrid gels have a more heterogeneous structure due to the adsorption of the polymer on the silica nanoparticles, and that the silica nanoparticles, trapped in the network due to the adsorption of the polymer, show a cage dynamics ( $\tau \sim q^0$ ).

#### P155-MR

### Microrheology with optical tweezers reveals anomalous high-frequency oscillations of the particle Normalized Position Autocorrelation Function in rod-like Hydroxyethyl Cellulose solutions

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Cellulose and its derivatives are widely used in biomedical applications such as in artificial membranes, drugs' coating materials and blood coagulants. In particular, hydroxyethylcellulose (HEC), is obtained by reacting ethylene oxide with wood-based cellulose. HEC water solutions have been studied by using both rheological and optical techniques. It has been shown that HEC in water solution forms rod-like structures, having characteristic dimensions of few ( $\approx 7$ ) microns in length and hundreds ( $\approx 300$ ) of nanometers in diameter. Rheological studies [1] have shown the existence of a critical mass concentration (0.2 %) at which the transition from dilute to semi-dilute regime is observed. In addition, optical studies have confirmed the existence of different material topologies within different concentrations' regimes [2]. In this work we adopt optical tweezers (OT) as a microrheological tool for exploring the microenvironment structure of HEC solutions as a function of concentration. In particular we analyze the time-dependent trajectories

of an optically trapped microsphere (5 microns) suspended in different HEC solutions at concentrations ranging from 0.05 % to 0.8 %.

We observe the presence of anomalous high frequency oscillations of the particle Normalized Position Autocorrelation Function (NPAF) [3] in the semi dilute regime only ( $c > 0.2$  %). We speculate that such observation may be linked to the presence of some local ordering in the rod solution at (relatively) high concentration, possibly giving rise to different thermal motions of the test microsphere along and transversally to the local preferred direction. Moreover, we have found good agreement between the solutions' linear viscoelastic properties derived from microrheological measurement with OT and those measured with conventional bulk rheology.

[1] Kastner et al., Colloids and Surface A, 1994

[2] N. Arfin, B. Bohidar, Int. J. Bio. Macromolecules, 2012

[3] Tassieri et al., New J. of Physics, 2012

#### P156-MR

##### **Newtonian Couette flows with wall slip and non-zero slip yield stress**

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We solve analytically the cessation flows of a Newtonian fluid in both plane and circular Couette geometries assuming that slip occurs along the wall provided that the wall shear stress exceeds a critical value, the slip yield stress. In steady-state, it turns out that slip occurs only beyond a critical value of the speed (angular velocity) of the moving (rotating) wall. Hence, in cessation, the standard no-slip solution holds if the wall velocity is below the critical value. Otherwise, slip occurs only initially along both walls. Beyond a first critical time, slip along the fixed wall ceases, and beyond a second critical time slip ceases also along the moving wall. Beyond this second critical time no slip is observed and the volumetric flow rate decays exponentially. The effects of slip and the slip yield stress are discussed.

#### P157-MR

##### **Effect of extensional flow on micellar microstructure**

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The microstructure of wormlike micelles changes under shearing and extensional flows due to self-assembling, growth and alignment of the chains, generating different bulk rheological behaviors. Two concentrations of equimolar CTAB/NaSal micellar solutions belonging to dilute (2.5 mM) and semi-dilute (10 mM) regimes are investigated, because of their different viscoelasticities and chain flexibilities. The effects of extensional flow on the self-structuring of viscoelastic micelles are explored based on the investigation of inertial effects, elasticity, vortex formation and flow-induced microstructural transitions. The use of planar contraction-expansion microcells allow in-situ determination of micellar alignment by polarized light microscopy, under the influence of both shear and extensional flows. The anisotropy factor calculation generates a gray scale mapping of the flow cell, being a simple way to demonstrate the micellar ordering within this geometry. The comparison with particle image velocimetry data allows the estimation of phase transitions and rheological behavior of the moving fluid. The influences of concentration and flow cell confinement on the entry flow of wormlike micelles are also explored. The combination of extensional flow with the viscoelasticity of micellar solutions influences the formation and extension of vortices. Thickening of these solutions under extensional flow instead of thinning behavior, which is measured for the same solutions under simple shear flows, is also reported.

#### P158-MR

##### **Chain flexibility and dynamics of polysaccharide hyaluronan in entangled solutions: a high frequency rheology and diffusing wave spectroscopy study**

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We have investigated the linear viscoelastic properties and the flexibility of water-soluble polysaccharides composed of high molecular weight hyaluronan (NaHA). The flexibility is characterized by the persistence length  $l_p$  and this

parameter has been determined for the first time in the entangled semi-dilute regime using a recently established experimental approach combining mechanical high frequency rheology and Diffusing Wave Spectroscopy (DWS) based tracer microrheology. The frequency-dependent shear modulus has been measured over a broad frequency range from  $10^{-1}$  to  $10^7$  rad/s and an  $l_p$  value of about 10 nm has been determined from the relationship based on a statistical mechanical treatment of a single filament stress response. In a NaHA concentration range varying from 15 g/l to 50 g/l,  $l_p$  is almost independent of increasing NaHA, temperature and ionic strength. This latter result is consistent with the Odijk-Skolnick-Fixman (OSF) theoretical predictions. The scaling exponent describing the concentration dependence of the plateau modulus  $G_0$  agrees well with predictions for polymers in good solvents. The scaling exponents for the specific viscosity  $\eta_{sp}$  and relaxation time  $\tau_r$  are slightly higher than theoretically predicted for polyelectrolytes in the high salt limit, indicating, that molecular aggregation occurs at higher polymer concentrations.

#### P159-MR

### Micro-particle image velocimetry to firstly quantify the flow behaviour for viscoelastic fluids at the entry to the downstream narrow channel

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It is well known that Newtonian fluid experiences from a developing boundary layer to fully developed region with symmetric flow structures. However, the flow behaviour for viscoelastic fluids at the entry to the downstream narrow channel is still rarely reported, and both the observation and physical information are scarce. In this paper, we used micro-particle image velocimetry ( $\mu$ -PIV) to firstly quantify the entrance length functioned with  $Re$  of water flow in a microfabricated 8:1:8 contraction-expansion geometry. Then, the semi-dilute, shear-thinning, polydisperse PEO solution ( $c/c^* = 15$ ) flow through this geometry was carried out. We found the flow structure in the downstream varies from quasi-Poiseuille flow to 'plug' flow with Reynolds number and Weissenberg number. Both the asymmetry and symmetry phenomena were experimentally evidenced in the fully developed flow region. By correlated to the upstream flow streamlines, we tentatively concluded that the sense of the above observations depended on the upstream flow conditions. The microscale dimension leads to quite low Reynolds number ( $\leq 5.2$ ), which is beneficial for understanding how the elasticity component disturbs the flow behaviour in the downstream region. This could be important for well controlling the industrial process, such as extrusion of molten polymers. Also, these quantitative results are expected to be useful in optimizing the lab-on-a-chip design involved with viscoelastic fluids.

#### P160-MR

### Studying the viscoelastic properties thanks to passive microrheology based upon Multi-Speckle Diffusing Wave Spectroscopy

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This work presents a new technique of passive microrheology for the study of the viscoelastic properties of soft materials like emulsions, polymers. Passive microrheology consists of using micron sized particles to measure the local deformation of a sample resulting from thermal energy ( $\sim k_b T$ ).

Our technique is based on Diffusing Wave Spectroscopy [1], an optical technique to determine the scatterers (droplets, fibers) mobility in terms of speed and displacement which are directly related to the samples viscoelastic properties. The determination of a master curve called Mean Square Displacement (MSD) enables to characterize completely the viscoelastic properties of a sample.

In the case of a purely viscous material, the MSD grows linearly with decorrelation time as the particles are completely free to move in the sample (cf. Fick's law).

In the case of a viscoelastic material, the typical shape for the MSD is not linear as the particles are not free to move due to interaction with the polymer network, or neighbouring particles (concentrated system). At the beginning the particles are free to move in the continuous phase. They are then blocked by their neighbours, or by polymer networks, which form a "cage", and the MSD function reaches a plateau. This is characteristic of the elasticity in the product. The lower the plateau, the tighter the network, and the stronger the elasticity. Then, at longer time scales, the particles are able to find a way to escape from the "cages" and the MSD grows again as it would for a viscous fluid. This is characteristic of the macroscopic viscosity, as it corresponds to the speed of the particles in the sample,

over long displacements.

This paper will present different recent application examples of the characterization of soft matter (polymer, gels, emulsions) with this technology.

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## P161-MR

### **Gel point determination thanks to microrheology**

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This work presents a new technique of passive microrheology for the study of the microstructure viscoelastic properties and the gel point transition for polymers and hydrogels. Passive microrheology consists of using micron sized particles to measure the local deformation of a sample resulting from the thermal energy, that is to say the Brownian motion.

Our technique is based on Diffusing Wave Spectroscopy. It consists of Dynamic Light Scattering (DLS) extended to an opaque media. In a DWS experiment (more precisely Multi Speckle-DWS in our case), a coherent laser beam is applied to the sample containing scatterers (particles, droplets, fibers... ). The light is multi-scattered by these scatterers, which leads to interfering backscattering waves. An interference image is detected by a multi-pixel detector. In dynamic mode, the scatterers motion (resulting from thermal energy) induces spot movements of the speckle image. A patented algorithm enables the treatment of this speckle image in order to determine the scatterers mobility in terms of speed and displacement which are directly related to the samples viscoelastic properties. The determination of the Mean Square Displacement (MSD) curve enables to characterize completely the viscoelastic properties of a sample. The technique allows to measure particles displacement in a spatial range between 0.1 and 100 nm and a time scale between  $10^{-3}$  and  $10^5$  seconds.

This work presents a rescaling data processing known in rheology as time cure superposition [1], [2] to determine the gel point transition and gel strength parameters. Results will show the automatic determination of the gel point versus time for gelling systems, gel point versus concentration for xanthan polymer, cross-linker concentration effect on the gel point.

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## P162-FM

### **Numerical optimisation of the flow behaviour of non-Newtonian tear substitutes**

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The dry eye syndrome is due to the appearance of dry spots on the cornea. One possible treatment of this syndrome consists in the instillation of tear substitutes on the surface of the eye. These products are equally divided in newtonian, shear-thinning and yield-stress fluids. In the three cases, the spreading of the tear film during blinking can be modeled with an advection-diffusion equation resulting from the lubrication theory. Numerical tools have been developed and coded to solve this equation in the different cases. Coupling these tools with a multi-objective optimisation software allows to obtain the optimal rheological properties of tear substitutes that simultaneously ensure a sufficient thickness of the film and a good vision quality i.e. a sufficient flatness of the film. The optimisation cost was kept low thanks to a numerical solution of the physical problem based on an implicit dual time-step approach, allowing an efficient progress in physical time. In the case of shear-thinning substitutes, the Ellis model, which takes into account the Newtonian plateau at low shear rate, was chosen. The optimisation process was applied to determine the ranges of the three non-dimensional numbers governing this flow that provide thickness and flatness properties superior to that of natural tears. This method is now extended to viscoplastic substitutes using the Bingham constitutive equation. The developed numerical tool has first been validated on some well documented reference cases such as dam-break flows. Its accuracy and efficiency have been demonstrated. The initial and boundary conditions have then been modified in order to analyse, with the same numerical tool, the main features of the spreading of thin viscoplastic fluids. Finally, the optimisation process will allow to determine the optimal rheological properties of viscoplastic tear substitutes, such as the yield stress, to reach the targeted performance criteria.

## P163-FM

**Combined Pulsating and Oscillating Flow of a Non-Newtonian Biological Liquid**

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In this work, analytical predictions of the rectilinear flow of a non-Newtonian liquid under a combined pulsating, time-dependent pressure gradient and a random longitudinal vibration flow is analyzed. The fluctuating component of the combined pressure gradient and oscillating flow is assumed to be of small amplitude and can be adequately represented by a weakly stochastic process, for which a quasi-static perturbation solution scheme is suggested, in terms of a small parameter. This flow is analyzed with the Tanner constitutive equation model and the viscosity function is represented by the Ellis model. According to the Tanner-Ellis model, the flow enhancement can be separated in two contributions (pulsatile and oscillating mechanism), which depends on the square of the amplitude of the oscillations, the Reynolds and Weissenberg numbers and the characteristic dimensional numbers relationship to the Ellis material properties.

Keywords: (i) Pulsating and Oscillating pipes, (ii) Stochastic Noise, (iii) Tanner and Ellis constitutive equations, (iv) Perturbation and analytical solutions.

## P164-FM

**Theoretical approach of the mean hydrodynamic field in the Conical Taylor-Couette flow**

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The present work is focused to determine the distribution law of the mean velocity field in the laminar steady state regime. The flow system considered is defined by two truncated concentric conical cylinders which the inner cone is rotating and the outer one being maintained fix.

For that purpose, we choose an adequate coordinates system for addressing the analysis of the mean hydrodynamic field in the conical flow configuration. The evolutions of the components mean hydrodynamic field show that the flow is tangential and focused primarily by the tangential velocity component.

## P165-FM

**Rheology of suspensions of vesicles and red blood cells under combined steady and oscillating shear flows**

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Blood is composed primarily of red blood cells suspended in the carrier fluid called plasma. Oscillating shear flow is used traditionally to probe the viscoelastic properties of such complex fluids, while constant shear flow is known to excite several types of non-trivial dynamic motions in red blood cells, such as tumbling or tank-treading. By combining a constant shear flow and a small oscillatory excitation, we are able to extract the viscoelastic properties of red blood cells during different dynamic motions.

We analyse the problem theoretically by using vesicles as a simplified model for the red blood cells. We show that the resulting complex viscosity carries an insightful information about the dynamics of the vesicle and it also depends qualitatively on the type of the motion adopted by the vesicle due to the constant part of the shear rate: First, it is found that the complex viscosity exhibits a resonance for tank-treading vesicles as a function of the frequency of oscillation. This resonance is linked to the fact that vesicles, while being in the stable tank-treading regime (with their longest axis having a steady orientation with respect to the flow direction), possess damped oscillatory modes. Second, in the region of parameter space where the vesicle exhibits either vacillating-breathing (permanent oscillations of the longest axis about the flow direction and breathing of the shape) or tumbling modes, the complex viscosity has an

infinite number of resonances as a function of the frequency. It is shown that these behaviors markedly differ from that obtained when the oscillatory shear flow is applied.

The dynamics and rheology of red blood cells under a combination of a constant and an oscillatory shear flows is investigated by numerical simulations and is compared with the recent experimental observations.

#### P166-FM

##### **Effect of rheological properties on cement plugs**

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Oil well cement plugging is largely used in oil industry. In this process, a cement plug (higher density fluid) is placed over the drilling fluid (lower density) to seal and abandon the well. The unstable flow behavior is the result from the heavy weight of an unset cement plug resting on top of a lightweight drilling mud. This is the one of main causes of plug failure. The success of plug placement depends on several aspects, such as the density ratio and the rheological properties of the fluids. In this work, a numerical analysis of the transient flow just after the cement placement in vertical wells is performed using ANSYS FLUENT. The conservation equations of mass and momentum are solved using the finite volume technique. The volume of fluid method is used to deal with multiphase flow - cement/drilling fluid. Both the drilling and the cement paste are viscoplastic liquids, modeled by the Herschel-Bulkley equation. The effects of rheological properties and density ratio on the plug stability are investigated.

#### P167-FM

##### **Role of elasticity of low viscosity Boger fluids in mixing**

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Despite the extensive literature available on the topic, liquid-liquid mixing is still one of the most difficult and least understood mixing problems, especially when one of the two phases shows a non-Newtonian behavior. Non-Newtonian fluid flows at the microscale are complex to describe mathematically due to their shear rate dependent viscosity and their elastic behavior, which are greatly enhanced given the typically small residence times. Since non-Newtonian fluids can have elastic behavior and at the same time exhibit nonlinear viscous effects like shear-thinning of the viscosity, it is particularly difficult to study viscoelastic flows in isolation from other effects. However, there's a class of viscoelastic fluids, known as Boger fluids, in which the viscosity is nearly constant with the shear rate. Boger fluids are particularly important because they enable elastic effects to be probed separately from shear thinning effects; by comparing the results of Boger fluid flow with those of Newtonian fluid flow at the same Reynolds number allows one to assess the influence of elasticity. The present study is focused on the influence of elasticity of the matrix phase on liquid-liquid mixing efficiency. The drop phase was silicon oil, as continuous phase we considered two Boger fluids, made of water solutions of PAA75, showing different elasticity, and a Newtonian fluid having the same viscosity. In the experimental investigation the flow of the three emulsion in a single capillary have been investigated by using flow visualization technique based on an high speed camera. Differences in the fluid dynamic were investigated analyzing, velocity profiles, drop size distribution. As expected, the influence of elasticity is to delay break-up phenomena, thus resulting in a lower mixing efficiency. The fluid dynamic in a convergent channel was also investigated.

#### P168-FM

##### **Coarse-grain Tunable Dissipative Particle Dynamics: Droplet Dynamics under confinement**

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Using complex fluids such as colloids and polymeric liquids and/or melts in confined region has become ubiquitous by steady growth in microfluidic technology and novel processing techniques. In this presentation we would like to capture the effect of confinement on kinetics and dynamic of multiphase fluids. Due to the multiscale phenomena involved in multiphase flows e.g. droplet dynamics, instabilities and interfacial phenomena, on one hand and difficulty of performing experimental studies under confined situation on the other hand, there are steadily growing interests to tackle this problem through computational studies. In this presentation we used Dissipative Particle Dynamics (DPD)

as a mesoscale computational technique to study droplet dynamics under confinement. DPD is capable of capturing microscopic phenomena and provide comparison to macroscopic simulations and experiments much faster compare to common microscale computational techniques e.g. Molecular Dynamics (MD).

In this presentation, we focus on interplay between droplet size and stress level in shear flows in bulk and confined geometries. For this purpose, Newtonian droplet in Newtonian matrix is modeled to ignore any complexity of materials and solely study effect of geometry. Droplet dynamics in these cases will be compared to macroscopic models and experimental results to confirm validity of this mesoscopic simulation method. In addition, dependency of surface tension on droplet size will be addressed and the effect of this term on nanoscopic droplets' dynamics will be discussed.

#### P169-FM

### **Analysis of Grid/Sub-Grid Scale Interactions in Viscoelastic Turbulent Channel Flow by Means of Direct Numerical Simulations**

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It has been known for quite over 60 years that the addition of small amount of polymers to turbulent flows of Newtonian fluids can dramatically reduce the turbulent friction drag (drag reduction, DR) up to 80 %, which makes it attractive for industrial applications. Direct numerical simulations (DNS) of turbulent viscoelastic flow is significantly more expensive than Newtonian DNS because of the larger number of primary variables involved, and the need for longer simulation boxes, especially at high DR since near wall streaks become progressively stabilized and elongated as DR increases. Hence, the need to use large eddy simulation (LES), or other numerically cheap model for dilute polymer solutions in engineering applications have to be developed for modeling turbulent flows of dilute polymer solutions in engineering applications. However, presently virtually no powerful LES exists for viscoelastic turbulence. The difficulty in developing a subgrid-scale closure for turbulent viscoelastic flows can be explained in part by the present poor understanding of the complex non-linear large/small scale interactions in these flows.

In this work DNS of turbulent channel flow with polymer solutions represented by the Finitely Extensible Nonlinear Elastic-Peterlin (FENE-P) constitutive model is carried out for various sets of model parameters in order to identify and quantify the relevant terms for LES. Equations for the evolution of the grid scale (GS) kinetic energy and subgrid-scale (SGS) kinetic energy are derived including the effects of polymer additives. The energy transfer between GS and SGS induced by the polymer is compared with the other existing sources and sinks in the GS and SGS energy balance in order to identify the influence of polymer additives on energy exchange. In this work we concentrate on three particular terms: the classical kinetic energy transfer between GS and SGS, the GS/SGS interactions induced by the polymer stresses, and finally, SGS/polymer interactions.

#### P170-FM

### **Turbulent structures development in drag reducing flows from the start-up of a rotating double gap cylindrical device**

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Polymer-induced drag reducing flow has been investigated for over 60 years. One reason for this is that the drag reducers in flow systems have been successfully applied and represent a great potential benefit to many industrial processes. However, the phenomenon is not completely understood and many aspects of the problem remain unclear. Some important issues are related to the development of turbulent structures and to the breaking of the polymer molecules. These two phenomena impose a transient behavior on the polymer efficiency and the drag reduction, DR, can be clearly divided into three periods of time. Over time, at the very beginning of the test, DR assumes a minimum value (sometimes negative) before reaching its maximum efficiency. When degradation becomes important, DR starts to decrease until it achieves its asymptotic value, a time in which the polymer scission stops and the molecular weight distribution reaches a steady state. In the present paper, we study the drag reduction development from the very beginning of a turbulent flow into a rotating cylindrical double gap device. DR is induced by three different polymers: Poly (ethylene oxide) (PEO), Polyacrylamide (PAM), and Xanthan Gum (XG). The first two are known as flexible molecules while the last one is considered rigid. The goal here is to analyze the problem from its very start

until the maximum efficiency is achieved.

#### P171-FM

### Numerical and experimental in-vitro analysis of blood flow through middle cerebral aneurysms

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Cerebral aneurysms are one of the most common cerebrovascular accidents and are the cause of one-third of deaths worldwide [1]. This kind of accidents starts with a dilatation of an artery usually occurring near arterial bifurcations in the Circle of Willis [2,3]. Despite growing progress, the initiation, growth and rupture of aneurysms are still not well understood. Computational Fluid Dynamics (CFD) has been progressively used for modelling the flow in diseased arteries and it is a tool of great potential for the diagnostic, prediction and treatment of cerebral aneurysms [4].

In this work we numerically and experimentally investigate the hemodynamics in simplified geometries representative of middle cerebral aneurysms. Three geometries are considered consisting of different bifurcations with an aneurysm located at the end of the parent vessel, between two daughter vessels, in which the neck of the aneurysm and the shape of the daughter branches are varied, but all vessel walls are flat to allow easy optical assess in the experiments. For the computations, two different viscoelastic models, namely the Giesekus and sPTT models were used based on fitting the rheology of real human blood to these models [5]. The numerical results were compared with velocity profiles obtained experimentally by means of micro-Particle Image Velocimetry measurements carried out in the different aneurysm configurations using blood analogue solutions recently developed by the group [5].

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#### P172-FM

### Experimental study on contact line motion in a glass capillary

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Contact line motion is important in many areas of physics, chemistry, biology and engineering. Industrially, the contact line motion is important in inkjet printing, coating, film formation and so on. In this research, the contact line motion of polymer solutions is investigated experimentally.

The contact line motion was observed by using a flow inside a capillary. The contact line speed was controlled by a syringe pump. Due to the curved surface of capillary, refraction of light problems occurred. To minimize the effect, the refractive indices were matched. So, glycerol was chosen as the base solvent and experiments were conducted inside a decalin bath. As the polymer, polyacrylamide (PAAm) with molecular weight of 5 M and 0.1 M were used. Capillaries were washed by the Piranha etching method. Contact angle was calculated by using an image processing technique. Images were analyzed to a sub-pixel level for accurate measurements. The interface shape was fitted to the sphere surface to obtain the contact angle.

In case of glycerol, the relation between  $Ca$  and  $\Theta^3$  is linear following the Tanner-Voinov-Hoffman (TVH) relation. However, for polymer solutions with molecular weight of 5 M, the relation becomes no more valid as the concentration increases and the relation becomes curved with concentration. However, the relation is linear in the case of polymers of molecular weight of 0.1M. Experimental results show that the contact line motion of polymer solutions cannot be expressed by the conventional TVH relation. It appears that the polymer migration effects should be considered.

**P173-FM****Spreading of suspension inkjet drop on wettable surfaces and pattern formation**Hansol Yoo, Chongyoup Kim\*

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The spreading dynamics of suspension inkjet droplet on wettable surfaces was investigated from side and bottom of the droplet. As inks, two kinds of polystyrene spheres with diameters of 2 and  $3.5\mu\text{m}$  were dispersed in 1-octanol to 22 vol% extents without any surfactants. The nozzle size was chosen to 80 micrometer considering negligible wall effects on suspended particles. Single, stable drops with Weber number ranging from 3 to 20 were generated and spread on three different transparent surfaces of glass, aldehyde coated glass or mica surface. The result shows that the spreading dynamics of suspensions was the same as the Newtonian fluid with the increased viscosities. In other words, the increased viscosity of suspension did not affect the dynamics since it is impact driven spreading. While spreading on the transparent surface, it was possible to take the images of droplet from the bottom of the surfaces and hence the contact line motion and the particle movement were captured at the same time. Near the contact line, a particle-free fluid zone was observed and the length of the zone is closely related with particle size. Through this work, it was found that drying pattern on wettable surfaces is not determined during evaporation of fluid but during the spreading. It is demonstrated that a monolayer of particles can be obtained by inkjetting.

**P174-FM****Qualifying dispersion and distribution of carbon nanotubes in PA6 matrix during melt-mixing by flow simulation**Cyril Loux\*, Kalappa Prashantha, Marie-France Lacrampe, Patricia Krawczak

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This work aims at numerically simulating the flow of nanocomposites in a twin-screw mixer so as to develop a prediction tool of nanofillers dispersion and distribution in a polymer matrix during processing. Polyamide-based nanocomposites containing 1 to 5 wt% of multi-walled carbon nanotubes were prepared by melt mixing in a twin-screw mixer equipped with temperature and torque sensors. The rheological behavior of the materials was characterized in dynamic mode using a plate/plate rheometer operating from 0.1 to  $100\text{ s}^{-1}$  at different temperatures. Viscosities as function of shear rate and temperature were modeled by appropriate power laws. A finite element numerical simulation was then developed using a commercial software package (COMSOL Multiphysics) and implementing these rheological laws to calculate the velocity profiles during melt-mixing. The Astarita parameter - whose values vary from 0 (pure rotation) to 1 (pure elongation), 0.5 corresponding to pure shear - was computed in order to qualify the dispersion capacity of the mixing device. Trajectories of massless points were also calculated as function of time to determine the stretch length and Lyapunov exponents. These two parameters allow qualifying the distributive capacity of the flow. The flow model was finally validated by comparison of measured and calculated torque evolutions with time. Dispersion and distribution of nanotubes were experimentally qualified by oscillating rheometry and scanning electron microscopy, showing a good agreement with Astarita, stretch length and Lyapunov exponents evolutions.

**P175-FM****Elastic turbulence and heat transfer**Waleed M. Abed\*, David J. C. Dennis, Richard D. Whalley, Robert J. Poole

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As is well known, see Groisman and Steinberg [1] for example, highly-elastic viscoelastic fluids, usually semi-dilute polymer solutions, can undergo a series of flow transitions from viscometric laminar flow, to apparently periodic flow, to chaotic flow and then to fully "elastic turbulence" in conditions of negligible inertia (where the Reynolds number  $Re$  is much less than 1) in a range of flows (i.e. conditions far from the inertially-driven turbulence observed for Newtonian fluids). In the current experimental study we investigate this phenomenon to study enhancement of internal convection heat transfer in a square cross-section (1mm by 1mm) serpentine channel with dimensionless radius  $R/W = 1$ , where  $R$  is the inner radius of curvature of the serpentine channel and  $W$  is the width of the channel [2]. An adiabatic top wall, which is made of (1.2cm-thick) polyvinyl chloride (PVC), and the other three copper walls are held at isothermal conditions. Different concentrations of a high molecular weight ( $\approx 20 \times 10^6$  g/mole) flexible

polyacrylamide polymer in a (10% water/ 90% glycerine) solvent are utilised. Pressure drops across the channel are used to determine if elastic turbulence conditions are reached: in this regime we find the non-dimensional pressure drop is at least twice of the equivalent Newtonian pressure drop (same  $Re$ ).

The experimental results for the Newtonian fluid show a good agreement with previous numerical data [3] whilst, the results for viscoelastic fluid exhibit an enhancement in the heat transfer as evidenced through the Nusselt number.

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#### P176-FM

### On creeping drag flow of a Bingham plastic fluid over a solid cone: effects of blockage ratio

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This work is concerned with the creeping drag flow of Bingham plastic fluids past a cone situated on the axis of a cylindrical tube. The apex of the cone is oriented towards the upcoming flow. The effect of blockage ratio (tube diameter to cone diameter) has been studied by systematically varying it from 2:1 to 8:1. The governing equations (continuity and momentum) and boundary conditions together with the Papanastasiou regularization for the Bingham equation have been solved numerically using the finite element method. New extensive results on the distribution of shear rate and velocity in the proximity of the submerged cone, morphology of the yielded/unyielded regions and drag coefficient are presented and discussed to delineate the influence of the fluid yield stress on the structure of the flow field for different values of the blockage ratio. Also, the present numerical drag results have been correlated with the Bingham number ( $0 < Bn < 1000$ ) via a simple expression thereby enabling their interpolation for the intermediate values of the Bingham numbers in the limit of zero Reynolds number. Broadly, the extent of yielded regions diminishes with the increasing value of the Bingham number.

#### P177-FM

### Red Blood Cells Behaviour in Microcirculation

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Blood performs multiple functions in the body, like oxygen, carbon dioxide and nutrients transfer or body temperature control by heat transfer. The flow properties of blood are complex, in opposite to simple fluids such as water or air. This complexity arises from its inhomogeneous composition: a little less than half of the blood is made up of cellular compartment suspended in an aqueous fluid (plasma). The solid part of the blood is mainly formed by erythrocytes, or red blood cells (98% of the blood cells), and the rest is composed by white cells and platelets. The plasma itself, is a complex solution of solutes: ions, metabolic molecules (e.g. glucose and amino acids) and proteins, suspended in water. In the healthy adult human, the red cells have a tendency to aggregate and form, under certain conditions, large aggregates called rouleaux. This phenomenon is a consequence of the presence of some kinds of macromolecules in the plasma such as fibrinogen (a plasma protein known to induce aggregation). According to the literature, the aggregates are supposed to disaggregate under the effect of shear forces. Under microcapillaries flow conditions, red cells are known to form small train of cells called clusters due to hydrodynamical interactions. The role of plasma proteins was marginalized due to the high shear rate in microcapillaries. Using a combined experimental and numerical approach, we show that, despite the large shear rate in microcapillaries, either fibrinogen or the synthetic polymer dextran leads to an enhanced formation of robust and stable clusters of red cells, even at haematocrits as low as 1%. To achieve this numerically, we consider the red cell in 2D as a closed deformable and non permeable membrane encapsulating an inner fluid and suspended in an outer fluid. The reduced area of the cell as well as the viscosity contrast between the inner and outer fluid are taken to be that of a human red cell. The membrane total force is composed from a bending force, a tension force to fulfill the area conservation constraint, and a cell-cell interaction force to reproduce the depletion forces due to the effect of the plasma macromolecules [3,4]. The cells are placed in a confined geometry (two parallel walls) and subjected to a Poiseuille flow. The boundary conditions could be resumed into: i) no slip condition, ii) stress balance, and iii) membrane inextensibility. The inner and outer fluids obey to Stokes equations. This equations are solved using the boundary integral formulation.

P178-FM

**Mesoscopic theory of polymeric media flows**Darina Merzlikina, Mikhail Tolstykh, Grigory Pyshnograï\*

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The work found a connection flow rate of the pressure gradient at different values of the channel width on the basis of the solution of the problem of a steady flow of nonlinear viscoelastic fluids with a tensor internal parameter between parallel planes under a constant pressure drop. This allows for a known coordinate values of flow pressure gradient, and the profile of the velocity and of the stress tensor components and the inlet and outlet sections of the channel by changing its width. Also found numerically the dependence of the longitudinal velocity of the pressure gradient and the distance to the wall and compared with available experimental data and the approximate analytical solution.

Also in practice during polymer processing, we meet quite often branched polymeric materials with significant polydispersity. This results in a necessity to take into account multiple relaxation processes for a description of the rheological equations of state. The aim of this contribution is to generalize the modified Pokrovskii-Vinogradov model for the case of multiple non-interacting modes. Each mode corresponds to a particular contribution of an individual polymer fraction to the stress tensor and is characterized by its corresponding relaxation time and viscosity. Simultaneously a determination of an internal friction is expressed by means of the parameters depending on the first invariant of the anisotropy tensor. This enables an application of the generalized model at wider range of frequencies acting externally on the studied polymeric materials. Consequently, it implies a possibility to describe sufficiently slow flows of polydisperse polymers (both linear and branched) in a unique theoretical approach. Theoretical modelling is compared with rheological characteristics measured for PE materials and there is a good agreement between the experiments and derived theoretical curves.

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# Overview Urban Park & Zoological Garden Karlsruhe

Take a walk through the main park of Karlsruhe or visit the zoological garden.  
**Every participant of the AERC 2014 has free entrance with his badge.**

**● AERC 2014**

## Special Gardens / Places

- Bodenspiele
- Spielplatz
- Rosengarten
- Seebühne
- Blindengarten
- Japangarten
- Staudengarten
- Gondoletta Anlegestelle
- Lauterberg Aussichtspunkt
- Botanische Besonderheiten
- Sonnenuhr

## Different Animals

- Flamingowiese
- Schwanen- u. Stadtgartensee
- Kropfgazellen
- Eulen
- Schneeleoparden
- Afrika-Savanne
- Strauße & Zebras
- Giraffenhaus
- Pinguine
- Eisbären
- Bennettkängurus
- Seelöwen/Seehunde
- Südamerikahaus
- Dickhäuterhaus
- Kaninchen
- Raubtierhaus
- Affenhaus
- Kraniche
- Zier-Ententeich/Affeninsel
- Trampeltiere
- Haustiere und Streichelgehege (ab 2011)
- Rosa-Pelikane (Sommer)



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