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[TA Instruments website] tainstruments.com
Welcome to AERC 2019 in Slovenia

Dear participants of the Annual Rheology Conference (AERC 2019), welcome to Slovenia, and welcome to Portorož, where in 1998 the first European Rheology Conference was organized, after the European Society of Rheology (ESR) was formally established in 1996, and after the first ESR Committee Meeting took place in 1997.

Welcome back, we will do our best to make this event memorable.

Scientific program consist of 12 Symposia, two plenary lectures of Professor Paula Moldenaers and Professor Peter Fisher, and the Weissenberg Awardee lecture of Professor Jan Vermant. Within symposia there are also 9 keynote lectures and, last but not least, a poster session.

We would like to pay a special honor to the Session organized in memorial of our colleague and dear friend Professor Mike Webster for his contributions to the field of Rheology. Mike has unexpectedly passed away last year.

In comparison to the previous conferences, there are two new Symposia addressing solids, Mechanics of Time-Dependent Materials and Granular Materials & Highly filled systems.

At this conference we want to emphasize the importance of societal value of rheology, and the importance of research-based innovation for the well-being of humankind. Rheology can and should play one of the key roles in research-based innovation that will bring our societies to the new level of well-being.

The conference was supported by eleven international and fifteen Slovenian sponsors. We would like to express our gratitude to all of them for helping us to make this conference a memorable event.

Finally, a special thanks go to symposia organizers, and all participants who made this conference a great scientific success!

Welcome, enjoy the Conference and Portorož!

Alexandra Aulova and Igor Emri

for the AERC 2019 Organizing Committee
Dear Members of the European Society of Rheology,

Welcome to Portoroz and to the Annual European Rheology Conference 2019 (AERC 2019). We are looking forward to an exciting scientific and social program, which will certainly keep us busy for the next days. Enough time to listen to something new and exciting, exchange ideas, engulf in stimulating discussions, start new collaborations and projects, and maybe save the world.

All this would not be possible without the enthusiastic commitment of the local organizers, the session chairs, exhibitors, sponsors, and those who are working ‘behind the scene’. Thank you very much!

Wishing you a very successful Annual European Rheology Conference 2019.

Peter Fischer, on behalf of the ESR Executive Board
Members of the Local Organizing Committee:

Igor Emri
Alexandra Aulova
Peter Emri
Edvard Govekar
Slobodan Zumer
Manica Ulcnik Krump

Slovenian Society for Experimental Mechanics
Slovenian Society of Rheology
European Society of Rheology

Members of the Honorary Scientific Committee:

Crispullo Gallegos
Rene Gaudu
Han Meijer
Giuseppe Marrucci;
Evan Mitsoulis
Paula Moldenaers
Jean Michel Piau;
Ivanov Yatchko
Manfred Wagner
Ken Walters

Delegates of the 1st Committee Meeting of ESR, Belgium 1997
Symposia Organizers/Chairmen

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<td>Mechanics of time-dependent materials</td>
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<td>P. Moldenaers (PL2) – Europe I - Towards miniaturization: how does confinement affect the break-up and coalescence of droplets in shear flow</td>
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<td>9:30</td>
<td>CS15 - J. Park - Interaction between latex binder and the secondary phase: The importance of capillary suspension of Li-ion battery anolyte</td>
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<td>9:45</td>
<td>CS15 - J. Godbold - Dynamic of alginate/sericin droplets impacting as bait of calcium</td>
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<td>10:00</td>
<td>CS18 - J. Choi - Coarse-grained particle simulation of capillary bridges in thinning suspension systems</td>
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<tr>
<td>10:30</td>
<td>CS19 - D. Andrade - The solid regime and the solid-liquid transition of layer oil</td>
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<td>Coffee Break</td>
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<tr>
<td>11:20</td>
<td>CS20 - G. Petsalidis - Flow dynamics of concentrated drop-like racetrack: A superposition rheometry investigation</td>
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<tr>
<td>11:30</td>
<td>CS21 - P. Bonacchi - Performance of time-dependent particle interactions in the physical aging of colloidal suspensions</td>
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<td>12:00</td>
<td>CS22 - T. Libert - Controlling the elasticity of colloidal gels by ionic species</td>
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<td>12:30</td>
<td>CS23 - J. Vermant - Yielding in depolymerising aminated 3D colloidal systems</td>
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<td>12:40</td>
<td>CS24 - M. Minala - Viscosity measurements of fluorinatically-purified water</td>
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<td>13:30</td>
<td>CS25 - G. Giusti - Normal stress differences and flow type identification in disperse systems</td>
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<td>13:45</td>
<td>CS26 - V. Trappe - Contributions of viscous dissipation in the flow of concentrated soft glassy gels</td>
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<td>14:00</td>
<td>CS27 - M. Ng - GM - ColdBEAR - Capillary break-up experiments on Graphene Oxide dispersions</td>
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<td>14:30</td>
<td>CS28 - M. Torkel - Rheological behavior of magnetothermoelastic fields under precession magnetic fields: experiments and particle-level simulations</td>
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<td>14:45</td>
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<td>15:15</td>
<td>CS28 - E. A. Valeiato - Buckling and non-bonding elastic yield of anisotropic power-law fluids (amorphous)</td>
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<td>15:30</td>
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<td>16:15</td>
<td>CS29 - B. Sarabji - Sedimentation rate of non Brownian inclinations in networks of rod-like particles</td>
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<td>16:30</td>
<td>CS30 - R. Martone - Constant volume suspensions under oscillatory shear flow: flow dependence on the applied strain and frequency</td>
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<td>CS31 - V. Bolduc - Rheology of rod-shaped nanocellulose (CNCS) particle suspensions in the presence of aqueous polymer solutions and their potential applications</td>
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<td>CS10 - X. Zhou - Rheological tests and methods and data interpretation for metal for reinforcement semi-solid cast materials for metal castings</td>
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<tr>
<td>10:00</td>
<td>CS33 - E. Moghimi - Rheology of soft-patchy particles made of Telechelic Star Polymers</td>
<td>CS34 - V. Labalette - Structure and rheology of a suspension of colloidal particles with shape and charge anisotropy</td>
<td>SM38 - D. Long - Dynamic heterogeneities, yield stress, plastic flow and arch-jamming in glassy polymers</td>
<td>MN1 - D. Podosov - High-throughput microfluidic characterization of erythrocyte shape and mechanical variability</td>
<td>PS4 - O. Philippova - Rheology of double networks composed of polymer and micellar chains</td>
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<td>SW40 - A. Varale-Felipe - Magnetic sensitive nanocomposites by electrospinning: From elaboration to investigation of rheological behaviour under applied magnetic field</td>
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<td>CS35 - S. Makino - Suspensions of granular particles embedded in fumed silica gels</td>
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<td>MN2 - A. Lindner - The dynamics of flexible Brownian fibers in viscous flows</td>
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<td>12:30</td>
<td>FN39 - J. Chen - Characterization of the effective slip in non-Newtonian fluid flows over corrugated surfaces in terms of the energy dissipation rate</td>
<td>EM15 - S. Bindgen - Implementing shear flow in a versatile simulation environment</td>
<td>EM17 - R. Kädär - Percolation and structural fingerprinting of 3D hierarchical polymer nanocomposites from nonlinear osiculatary shear</td>
<td>MN6 - J. Cappello - Controlling particle trajectories in confined flows via particle shape</td>
<td>TM4 - C. Nagraw - Experimental investigation of start-up flows of time-dependent materials</td>
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<td>CS40 - A. Townsend - Simulating flexible frame suspensions and their sedimentation</td>
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<td>EM18 - P. Fischer (PL3) - Closing Ceremony (Europe I)</td>
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<td>14:40</td>
<td>GM14 - M. Sperij - Rheology of granular media on ground and in space</td>
<td>IP18 - S. Dittrich - Rheological behavior of glass ceramic pastes used as sealants for solid oxid fuel cells</td>
<td>PS56 - L. Bravo Anaya - Role of electrostatic interactions on supemolecular organization in calf-thymus DNA solutions under flow</td>
<td>MN8 - M. Malosi - Structure of suspensions of soft microcapsules in confined flow, an experimental study</td>
<td>TM6 - L. Grassia - Resolution of the local segmental mode in amorphous polymers: do the chain relaxation modes affect the structural relaxation?</td>
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<td>IP19 - F. Okkels - New tool for process rheology</td>
<td>PS57 - G. Ducouret - Sol-Gel transitions of modified polysaccharides under temperature and salt control</td>
<td>MN9 - M. Taasier - Microheterogeneity withologous tweezers: peaks &amp; troughs</td>
<td>TM7 - A. Bélugue - Onset of mechanical nonlinearity for amorphous polymers in their glass transition regime: experimental results and model</td>
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<td>MN14 - D. Nicol - Rheology of Cariopol dispersions</td>
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<td>17:35</td>
<td>PS114 - M. Naccache - Rheology of Caribopol dispersions</td>
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<td>PS15 - T. Kimmel - Rheology of Caribopol dispersions</td>
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Tuesday Morning

Symposium PL

Plenary Lectures

*Weissenberg Lecture*

**Tuesday 9:10 Europe I**

**Can (interfacial) rheology save the world?**

*Jan Vermant*

Soft Materials Group, ETH Zurich, Zürich CH-8093, Switzerland

Complex fluid-fluid interfaces arise when surface active species accumulate at interfaces and interact which each other. In addition to changes in the surface energy and the possible occurrence of Marangoni stresses, rheological properties can influence the dynamics of interfaces. The last few years have seen a strong research activity in developing techniques or analyzing better existing techniques to separate to clarify which material functions can be measured (1-3). For shear rheometry, progress in analyzing the flow fields in the measurement devices has been key, combined with advances in control over surface concentration and microstructural evaluation. For dilatation/compressional rheometry much work has been done on separating changes in the surface tension from the extra rheological stresses, and there seems to be clarity on how to now use the rheological interfacial properties to design new materials or investigate the response of biological systems. In the present talk I will focus on applications of interfacial rheology in important issues such as beer foam stability, lung surfactant functioning, the design of very stable foams (5) and emulsions (6) with potential applications in the field of energy or electronics. In the second part of the talk I will turn to minimal model biomembrane mimics, using a microfluidic platform (8). We will try to understand if interfacial rheology can help elucidate if block copolymer architecture can be engineered to dictate a lipid bilayer membrane response. Here, we investigate the influence of the structure of the pluronic on the interaction with artificial biological membrane.


**Symposium CS**

Colloids & Suspensions

**Organizers: Michel Cloitre, Guillaume Ovarlez and Norbert Willenbacher**

**Tuesday 10:00 Europe I**

**Shear-thickening of a non-colloidal suspension with a viscoelastic matrix**

*Adolfo Vazquez-Quesada*¹, *Roger I. Tanner*², and *Marco Ellero*³

¹Department of Theoretical Condensed Matter Physics, Universidad Autonoma Madrid, Madrid, Spain; ²School of Aerospace, Mechanical and Mechatronic Engineering, University of Sydney, Sydney, Australia; ³Basque Center for Applied Mathematics, Bilbao, Spain

In this work we study the rheology of a non-colloidal suspension of rigid spherical particles interacting with a viscoelastic matrix. Three-dimensional numerical simulations under shear flow are performed using the smoothed particle hydrodynamics method and compared with
Discontinuous shear thickening in mixtures of isometric and rod-like particles

Nadia Sidaoui1, Massamba Thiam1, Placido Arenas Fernandez2, Olga Volkova1, Georges Bossis1, and Pavel Kuzhir1

1Institute of Physics of Nice, University Cote d’Azur, Nice 06100, France; 2Department of Applied Physics, University of Granada, Granada, Spain

In this talk, we report experimental data on shear stress-controlled rheology of concentrated aqueous suspensions of isometric (polyhedral shaped) calcium carbonate (CaCO3) microparticles with an adsorbed comb polymer layer (polymethacrylate backbone with side polyethylene oxide chains) with and without addition of uncoated micron-sized polyamide fibers. Independently of the presence of fibers, the suspensions undergo a discontinuous shear thickening (DST) at the CaCO3 particle volume fraction above 64% (the particle size distribution being polydisperse) and exhibit a stick-slip instability above some critical shear stress likely because of periodic collapse and restitution of the adsorbed polymer layer leading to periodic formation and failure of percolated network of frictional interparticle contacts. Addition of long (aspect ratio r=50) and relatively thin fibers (fiber diameter to CaCO3 particle size ratio d/fdp=2) shifts the DST to lower shear rates likely due to localization of the flow blockage within highly sheared regions of the CaCO3 suspension in the gaps between fibers. The homogenization approach of Château et al. (2008) (based on evaluation of local shear rates in suspensions of particles dispersed in a non-Newtonian solvent) ensures a reasonably good prediction of such a shift. On the contrary, addition of short (r=10) and relatively thick (d/fdp=5) fibers shifts the DST to higher shear rates that is tentatively explained by the fact that this thicker fibers may partially break the percolated network of frictional contacts between isometric CaCO3 particles. Apart from its fundamental interest, the results of this work could be useful for new formulations of fiber-reinforced self-consolidating concretes.


Shear-thickening in a dilute suspension of spheres in a weakly viscoelastic fluid: an approach with a direct numerical simulation

Yuki Matsuoka1, Yasuya Nakayama2, and Toshihisa Kajiwara2

1Sumitomo Bakelite Co., Ltd., Shizuoka 426-0041, Japan; 2Department of Chemical Engineering, Kyushu University, Fukuoka 819-0395, Japan

Most recently, the shear thickening of the viscosity in dilute suspensions of spheres in weakly viscoelastic fluids has been investigated theoretically (Koch et al. 2016, Einarsson et al. 2018) and numerically (Yang et al. 2016). These studies suggested that an increase in the particle-induced fluid stress is the main cause of the shear thickening. However, the physical interpretation of the changes in the stress contributions is still unclear. In this work, we study the underlying physics of the shear-thickening in dilute suspensions in viscoelastic fluids. For this purpose, we developed a three-dimensional direct numerical simulation (DNS) for suspensions in viscoelastic fluids based on the Smoothed-Profile method for solid-fluid coupling which allow us to use fixed regular grids for suspensions rather than surface-conforming grids (Nakayama et al. 2005, 2008). Our numerical results with the Oldroyd-B fluid for the suspending medium show the shear viscosity thickens with the Weissenberg number (Wi) consistent with the prior works. Analysis of the changes in the flow pattern and the distribution of the viscoelastic stress with Wi reveals that a fraction of shear-flow-driving energy stored in the conformation stretch increases with Wi inducing two effects; (i) a decrease in the stresslet contribution, which is consistent with the reduction of the rotation speed of the particle (ii) an increase in the region and the magnitude of the elastic stress around the particle. The latter effect overwhelms the former one, resulting in the shear thickening. The increase in the fluid stress contribution turns out to be attributed to the unrelaxed polymer stress caused by the advection and the stretching around the sphere. The DNS based on the Smoothed-profile method for viscoelastic suspensions is found out to be accurate so that it can be applicable to more complex phenomena in dense particle suspensions which are important in many industrial products.
Very concentrated suspensions of iron particles in water or ethylene glycol can be obtained thanks to the use of superplasticizer molecules used in cement industry. At high volume fractions, these suspensions show a discontinuous shear thickening. The numerical simulations of Mari et al (JOR 2014) were successful in reproducing this behavior by introducing frictional forces between the particles. By measuring the electrical resistance of these suspensions of iron particles of micronic size in different rotational geometries, we have obtained an experimental proof of the formation of a percolating network of frictional contacts associated with the discontinuity, both in rate and stress controlled modes. In this last case, the rheological curve, including the yield stress and the stick-slip behavior observed above the critical stress, is modeled with the help of the Wyart-Cates model (PRL 2014) and of a relaxation equation for the frictional contacts. The comparison with the experimental curves shows that the dependence of the frictional contacts on the applied stress and/or their relation with the viscosity used in this kind of model, is not satisfactory and should be revisited. In the presence of an increasing magnetic field, although the critical stress increases, we found that if we subtract the yield stress due to the magnetic field, it remains constant, indicating that the critical stress is more driven by the shear of the polymer layer than by its compression. At last, we will show that the jamming transition is also present in a capillary flow, and that it manifests through the formation of a non-consolidated porous medium at the constriction between the barrel and the capillary. In suspension of iron particles, the dynamics of formation of this porous medium, and so the pressure, can be controlled by a low magnetic field and is reversible for a constant volume flow rate, opening potential new applications in the domain of dampers and force control devices.

Tuesday 11:50 Europe I
Thixotropy and strain hardening of aqueous carbon black suspensions
Elie Ngouamba, Laurent Tocquer, Julie Goyon, and Philippe Coussot
Université Paris Est, Laboratoire Navier, Champs sur Marne 77420, France
Carbon black (CB) suspensions are used as a support of electrolyte solutions in batteries, as the particles form a network potentially enhancing the electrical conductivity of the electrolyte, and leading to a yield stress avoiding the sedimentation of the coarse electrochemical particles. So far most rheological studies focused on suspensions of CB particles in oil, and original behavior trends were observed: shear thickening at high shear rate [1], or some kind of anti-thixotropy [2], associated with the specific morphology and colloidal characteristics of CB particles: fractal submicrometer-sized particles interacting through low Van der Waals forces. Here we focus on aqueous CB suspensions with addition of CaCl2. The poor dispersion of CB in water is by-passed by adding gum Arabic. We obtain a thixotropic yield stress fluid. From creep tests, these materials exhibit a solid-liquid transition in the form of a viscosity bifurcation associated with a fast liquefaction of the material beyond a given critical strain. This implies that no steady state flows are possible below a critical shear rate, whose value increases with the time of rest after preshear. More surprising is the behavior of these suspensions in the solid regime, which appears to strongly depend on the deformation history. We follow this behavior through the elastic modulus (measured under small deformations), which provides a basic information about the strength of the structure. This elastic modulus, measured after different strains applied to the system, appears to increase with the strain previously applied, by a factor up to 5 at the approach of the critical deformation. We suggest that this strain hardening behavior results from the rough aggregates of CB which tend to interpenetrate for large strains and bring the material into a more jammed state.


Tuesday 12:10 Europe I
The history-dependent rheology of suspensions of particles with short-range attractive forces
Julien O. Sindt and Jin Sun
School of Engineering, University of Edinburgh, Edinburgh, United Kingdom
How to increase the solid content of dense suspensions while keeping the suspensions flowing as desired is a billion-dollar question in industries as diverse as paints, drilling, food, etc. Such efforts have, however, been hampered by the rapid increase of viscosity with solid volume fraction (SVF) and/or shear rate/stress, i.e., shear thickening. Recent developments in dense suspension rheology have shown that the viscosity, and jamming, are dictated by how particles interact when in contact: suspensions of smoother, near-frictionless particles can flow, while suspensions of rougher, frictional particles would have jammed at the same SVFs. The transition from frictionless to frictional contacts at a critical onset stress leads to shear thickening. Decreasing the effective particle roughness by e.g., coating them with surfactants, or steric- and charge-stabilisation, enables the suspension to flow at higher shear rates and at higher SVFs. However, it remains unclear how the details of the interaction force affect shear thickening or rheological behaviour in general. We study shear-thickening suspensions of particles interacting with a DLVO-type force, comprising of attraction acting at a range significantly shorter than repulsion, using numerical simulation to resolve particle dynamics. We present the surprising effects that results from the addition of the attraction component, namely we notice increases in the low-stress viscosity plateau and history-dependent results. These effects would not manifest in normal steady-state shear or could go undetected without purposeful tests. Finally, we demonstrate how the rheology, in particular the critical onset stress and the jamming SVF, can be controlled by tuning the attractive/repulsive force profiles.
Liquid migration in shear thickening suspensions flowing through constrictions

Rory E. O'Neill¹, John R. Royer¹, Guillaume Ovarlez², and Wilson Poon³

¹School of Physics and Astronomy, University of Edinburgh, Edinburgh, United Kingdom; ²University of Bordeaux, CNRS, Solvay, LOF, Pessac 3360, France; ³University Of Edinburgh, Edinburgh, United Kingdom

Dense suspensions often become more dilute when forced to flow through a constriction. This phenomenon, commonly referred to as liquid migration (LM), can lead to catastrophic consequences. For example, LM can damage equipment and lead to product loss in extrusion-based manufacturing, and in medical applications, such as the injection of bone cement into a bone fracture, LM can be fatal. Despite these severe potential consequences, the mechanism(s) behind LM are poorly understood, making it difficult to predict and avoid the onset of LM.

We investigate LM during the extrusion of well-characterised shear-thickening dispersions of repulsive particles. We find that above the onset of LM, the extruded material maintains a steady concentration, \( \phi_c \), independent of time or initial concentration. This critical concentration depends on both the flow rate, \( Q \), and the constriction (die) radius, \( r_d \), and at low flow rates collapses onto a universal function of \( Q/r_d^3 \), a characteristic shear rate in the die. Below \( \phi_c \) no LM is observed, so that our collapsed data \( \phi_c(Q/r_d^3) \) defines a phase diagram for the onset of LM. We show that this phase boundary can be captured analytically by coupling the suspension shear rheology to a simplified 'suspension-balance' model describing the relative solid-liquid flow in response to local stress gradients [1].

Using x-ray imaging, we visualise local variations in \( \phi \) near the die entrance throughout the extrusion process. This allows us to spatially map out both the lower-concentration dilution zone near the die, and the material in the barrel continually increasing in concentration. We show that this x-ray imaging can serve as a high-throughput method to efficiently measure \( \phi_c \), and thus obtain the LM phase boundary, for a range of extrusion parameters.


Syposium NF

Non Newtonian Fluid Mechanics & Flow Instabilities (in honor of Prof. Mike Webster)

Organizers: Tim Phillips, Russel Davies, Natalie Germann and Corneliu Balan

Personal and scientific contributions of Mike Webster

Timothy N. Phillips¹ and A Russell Davies²

¹School of Mathematics, Cardiff University, Cardiff, United Kingdom; ²School of Mathematics, Cardiff University, Cardiff, Wales CF24 4AG, United Kingdom

Michael Francis (Mike) Webster was a Professor of Engineering at Swansea University who made extensive contributions to the field of computational rheology. Mike died suddenly, after a short illness, in July 2018, at the age of 65. He graduated in Mathematics from Manchester University in 1976 before moving on to postgraduate work in computational rheology with the rheology research group at Aberystwyth University, gaining a PhD in 1979. This early work was the start of a career dedicated to establishing numerical algorithms to simulate the flow of non-Newtonian materials. After brief appointments at the University of Reading (Mathematics), Sydney University (Engineering) and Aberystwyth University (Mathematics) he took up a lectureship at Swansea University which was to become his academic home for the rest of his career, first in the Computer Science Department before transferring to the School of Engineering.

Mike was very much an applied mathematician who wanted to see the theoretical work he developed used in practical application. He worked in a number of rheological problem areas, including injection moulding, wire-coating, roller-coating, dough kneading, cable-coating, thin-film stretching, enhanced oil-recovery, and processing of viscoelastoplastics, micellar & viscoelastic surfactants. This involved interaction with international companies and multidisciplinary research colleagues worldwide, and in particular to the analysis of complex viscoelastic flows, free-surface phenomena, transients, contraction flows, enhanced pressure-drops, micro-fluidics and three-dimensional calculations. He published his work in over 250 articles. He continued in active research, supervising students and postdoctoral researchers, right up until his death.

Apart from his research work, Mike made a significant contribution to the rheological community in a variety of ways. He served as Treasurer of European Society of Rheology from 2005 until 2017, and sat on the Executive Council of British Society of Rheology as both Treasurer and Membership Secretary. He was secretary of the Institute of non-Newtonian Fluid Mechanics and served as Associate Editor on the Board for Journal of non-Newtonian Fluid Mechanics.

This talk will contain personal reminiscences of Mike's life and contributions, and also a more detailed account of some of his most recent research.
On the prediction of drag enhancement for flow of Boger fluids past a sphere using the FENE-P-MP model
Ross M. Kynch, Alexander T. Mackay, and Timothy N. Phillips
School of Mathematics, Cardiff University, Cardiff, United Kingdom

The benchmark problem of viscoelastic flow past a sphere is considered. This problem is of practical interest in the context of flow around obstacles, for example in sedimentation, the settling of suspensions, rheometry and in industrial settings where particles are present (such as mineral and chemical processing or combustion engines). The aim of this paper is to predict computationally the level of drag enhancement observed experimentally for Boger fluids. A variant of the FENE-P model, the FENE-P-MP model, is used to model Boger fluids. The model is derived using the generalized bracket framework. The framework accounts for both reversible and non-reversible dynamics and ensures that the derived models are consistent with the laws of thermodynamics. Garduno et al (2016, 2017) developed modifications to the White-Metzner and FENE-P models and showed that strain hardening is crucial in order to capture the drag enhancement observed experimentally with increasing elasticity. The FENE-P-MP model also possesses the strain-hardening property. The computations are performed using a DEVSS-G-DG stabilised spectral element method. The method was developed by Kynch and Phillips (2016) for Oldroyd B and Giesekus fluids. The drag force on the sphere and important flow features are investigated for a range of Weissenberg numbers and dissipation parameters. The model predicts drag enhancement with increasing values for the Weissenberg number and good agreement is obtained with the predictions of Garduno et al (2017) using the swanNNFM(q)-FENE-CR model.

A numerical scheme for solving transient viscoelastic planar flows
Jonathan D. Evans1 and Cassio M. Oishi2
1Mathematical Sciences, University of Bath, Bath BA2 7AY, United Kingdom; 2Departamento de Matematica e Computacao, UNESP, Presidente Prudente, Brazil

A numerical scheme is presented for computation of unsteady viscoelastic planar flows in which the constitutive equations for the polymer stresses are formulated along the direction of flow. A space-step restriction is derived for the stability of the scheme, which shows its efficiency near stress singularities but which becomes more demanding in stagnation regions. This contrasts with the usual Cartesian stress formulation of the equations. Results are presented for the 4:1 contraction and stick-slip flows of Oldroyd-B, Phan-Thien–Tanner and Giesekus models. The numerical scheme is shown to capture the known theoretical asymptotics at the stress singularities, with improved results over the Cartesian formulation.

The role of the negative wake on the deformation and breakup of droplets rising in viscoelastic fluids
Baltasar Mena

The influence of the negative wake on the deformation and breakup of droplets rising in a viscoelastic fluid is examined experimentally using particle image velocimetry techniques. Results are analyzed for both Newtonian and non-Newtonian droplets and compared to solid bodies. It is concluded that the negative wake is formed when the external fluid is viscoelastic regardless of the droplet material. In the case of Newtonian droplets rising in a viscoelastic medium, the droplets adopt a teardrop shape and breakup leads to the release of volume in smaller droplets. A negative wake appears at the tail of the droplet and apparently has no influence upon the breakup mechanism. In the case of viscoelastic droplets rising through a viscoelastic medium, the negative wake appears almost at the beginning of the droplet tail and continues during all the length of the tail but has very little, if any influence upon the breakup of the droplet. It does however contribute to an elongational flow that extends the tail forming a second droplet.

Enhanced pressure-drop predictions in planar contraction flows with continuous-spectrum models
J. Esteban López-Aguilar1, Michael F. Webster2, Hamid R. Tamaddon-Jahromi2, and David M. Binding3
1Chemical Engineering Department, National Autonomous University of Mexico UNAM, Mexico City, Mexico City 04510, Mexico; 2College of Engineering, INNFm - Swansea University, Swansea, Swansea SA1 8EN, United Kingdom; 3Institute of Mathematics, Physics and Computer Science, University of Aberystwyth, Aberystwyth, Ceredigion SY23 3BZ, United Kingdom

This study addresses a rheological problem that has been outstanding now for the past few decades, raised by the experimental findings of Binding and Walters [JNNFM 30 (1988) 233-250]. There, it was established experimentally that planar contraction flows for some Boger fluids could display enhanced pressure-drops (epd) above Newtonian flows, as was the case for their tubular counterparts. Nevertheless, flow-structures to achieve this result were reported to be markedly different, planar to circular. Here, it is shown how predictive differential-viscoelastic solutions with continuum models can replicate these observations. Key to this success has been the derivation of a new definition for the third-invariant of the rate-of-deformation tensor in planar flows, mimicking that of the circular case [López-Aguilar et al. JNNFM 237 (2016) 39-53 & PoF 29 (2017) 121613]. This provides a mechanism to successfully incorporate dissipation within planar flows, as performed earlier for tubular flows. Still, to reach the necessary large rates to achieve planar epd-levels, and whilst maintaining steady flow-conditions, it has been found crucial to
invoke a continuous-spectrum relaxation-time model [López-Aguilar et al. PoF 29 (2017) 121613]. The rheological power and flexibility of such a model is clearly demonstrated, over its counterpart Maxwellian single-averaged relaxation-time approximation; the latter transcending the boundaries of steady-to-unsteady flow to manifest equivalent levels of epd. Then, the role of extensional viscosity and first normal-stress difference, each play their part to achieve such planar epd-levels. As a by-product, the distinctive planar ‘bulb-flow’ structures discovered by Binding and Walters [JNNFM 30 (1988) 233-250], absent in tubular flows and associated as the main cause for marked epd-observations in planar geometries, are also predicted under the regime of high deformation-rates.

Dedicated to the memory of our dear friend and colleague, late Professor Michael F. Webster.
Shear rheology of marginally entangled ring-linear poly(ethylene oxide) blends through nonequilibrium atomistic molecular dynamics simulations

Alexandros J. Tsamopoulos¹, Dimitrios G. Tsalkis¹, and Vlasis G. Mavrantzas²
1Chemical Engineering, University of Patras & FORTH ICE-HT, Patras, Akhaia 26504, Greece; ²Chemical Engineering & Mechanical and Process Engineering, University of Patras & FORTH ICE-HT & ETH-Z, Patras, Akhaia 26504, Greece

Atomistic simulations of ring polymer melts under equilibrium conditions have been very useful in extracting scaling laws for the conformational and transport properties (chain center-of-mass diffusion coefficient and zero shear rate viscosity) of this unique class of polymers in the crossover regime around the entanglement molecular weight $M_e$ [1]. In combination with a detailed geometric analysis, these atomistic simulations have also helped characterize topological constraints developing in ring melts due to ring-ring but also ring-linear threading (caused by remaining linear impurities) [2] and their connection with the slow relaxation modes.[3]

In the present work, we extend our study to nonequilibrium conditions by investigating the effect of linear contamination on the shear rheology of marginally entangled ring polymer melts using as a model system poly(ethylene oxide) (PEO). We have conducted nonequilibrium molecular dynamics simulations (NEMD) of ring-linear PEO mixtures under shear flow over a wide range of concentrations of the linear component. We have thus calculated the relevant viscometric functions (shear viscosity and first and second normal stress coefficients) as a function of applied shear rate and degree of linear contamination. In addition, selected configurations from the NEMD trajectories have been subjected to a detailed geometric analysis [2-3] to provide information on the effect of flow on the degree of ring-ring and ring-linear threading, and thus on the underlying topological network that forms in such melts under equilibrium conditions as penetrating linear chains tend to form bridges between ring molecules.

[1] Tsalkis, D. G.; Alatas, P. V.; Peristeras, Mavrantzas, V. G., ACS Macro Letters 7, 916, 2018

Extensional rheology of ring polystyrene melt and linear/ring polystyrene blends

Qian Huang¹, Ole Hassager¹, Junyoung Ahn², Taihyun Chang², and Dimitris Vlassopoulos³
¹Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark; ²Department of Chemistry, Pohang University of Science and Technology, POSTECH, Pohang, Republic of Korea; ³Institute of Electronic Structure & Light, Foundation for Research and Technology Hellas, FORTH, Heraklion, Greece

The state-of-the-art understanding of entangled linear polymers is based on the concept of physical network formation from entanglements. The physical network is characterized by a plateau modulus in linear viscoelastic (LVE) measurements. However, linking the two free ends of a linear polymer, thereafter called a ring polymer, has dramatic consequences. For example, non-concatenated rings have much lower zero-shear-rate viscosity compared to their linear entangled counterparts. A plateau modulus is not observed in LVE measurements for ring polymers [1].

Due to the difficulties in synthesis, which leads to very limited amount of samples, well-defined ring polymers have never been studied in extensional flow. In this work, we present the first results of extensional rheology of a ring polystyrene (PS) melt with the molecular weight 185k (Ring-185k). We show that the ring PS is surprisingly strain hardening in extensional flow, and reaches the same extensional steady state viscosity as its linear counterpart (Lin-185k) when the stretch rate is fast enough. We further present the extensional rheology of blends made of Ring-185k and Lin-185k, with weight fraction of 5%, 20%, and 30% of Ring-185k, respectively. We show that in the transient stress-strain responses, stress overshoot is observed for the samples containing 20% and 30% Ring-185k, while the stress overshoot is not observed for the pure Ring-185k and Lin-185k.

The present results shed light into the fascinating flow properties of polymers without free ends, while they also advance the state-of-the-art in polymer physics. At the same time, they open the route for understanding the response of folded proteins and chromosome territories under strong external fields.

[1] Pasquino et al., ACS Macro Lett. 2013, 2, 874-878

Nonlinear elongational rheology of unentangled polystyrene and poly(p-tert-butyl styrene) melts

Yumi Matsumiya¹, Hiroshi Watanabe¹, Yuichi Masubuchi², Qian Huang², and Ole Hassager³
¹Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan; ²Department of Materials Physics, Nagoya University, Nagoya, Aichi 464-8603, Japan; ³Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark

Nonlinear rheology under uniaxial elongation was examined for unentangled melts of polystyrene (PS27; $M_0 = 27k$) and poly(p-tert-butyl styrene) (PtBS53; $M_0 = 53k$) having nearly the same number of Kuhn segments per chain, $N_K$. For both materials, the steady state elongational viscosity $\eta_0$ exhibited strain-rate-hardening and then strain-rate-softening on an increase of the Weissenberg number $Wi = 0.3$ ($Wi = \kappa \tau_i$, with $\tau_i$ and $\kappa$ being the longest relaxation time and the Hencky strain rate). For the unentangled melts, the hardening and softening were free from any entanglement nonlinearity, so that the hardening was unequivocally related to the finite extensible nonlinear elasticity (FENE) of the chain, and the softening,
to suppression of the FENE effect due to reduction of the segment friction $\zeta$ occurring for the highly stretched and oriented chain. Thus, the $\zeta$-reduction was experimentally confirmed with no ambiguity. Quantitatively, the hardening at intermediate Wi was stronger and the softening at higher Wi was weaker for PtBS53 than for PS27 despite the similarity of their $n_k$ values, which suggested that the magnitude of $\zeta$-reduction changes with the chemical structure of the chain and is non-universal. For quantitative estimation of this magnitude, the FENE-PM model was modified for the $\zeta$-reduction with an assumption that $\zeta$ at a given time is fully determined by the tensile stress at that time (that reflects the chain conformation). This modified model was able to mimic the $n_k$ data excellently, and the $\zeta$-reduction utilized in the model was weaker for PtBS53 than for PS27 to confirm the non-universality of $\zeta$-reduction. Nevertheless, the same model failed to mimic the transient stress growth and relaxation data on start-up and cessation of fast flow. This failure is discussed in relation to a possible delay in the transient change of $\zeta$ occurring through the segmental motion.

Tuesday 11:50 Emerald II
Monomeric friction reduction prevails in fast flows of all polymer melts
Giovanni Ianniruberto and Giuseppe Marrucci
Department of Chemical, Materials and Production Engineering, Federico II University, Napoli, NA 80125, Italy

Polymer rheology in fast flows is far from being completely understood. For example, entangled polystyrene (PS) melts behave anomalously in fast elongational flows insofar as the steady-state elongational viscosity keeps decreasing with increasing stretching rate [1], without showing the stretch-induced upturn at Wi’1 (with Wi the Rouse time based Weissenberg number), typically observed in PS solutions. We have suggested that such an anomalous behavior of PS melts is due to a decrease of the monomeric friction coefficient brought about by alignment of the Kuhn segments of the polymer to the stretching direction, as confirmed by nonequilibrium molecular dynamics simulations over a sequence of styrene oligomers [2]. Indeed, in PS solutions, friction reduction effects are expected to be in fact absent since the solvent molecules remain isotropic, though recent data suggest the possible importance of flow-induced polymer-solvent nematic interactions [3].

Very recently, flow-induced friction reduction effects have been invoked to also explain the unexpected rheological behavior of unentangled PS melts in fast extensional flows [4]. Indeed, friction reduction due to chain stretch and orientation is a local phenomenon, irrespective of entanglements. The local nature of friction reduction effects is also confirmed by the fact that in melts with a different chemistry flow-induced friction reduction effects, though still present, appear to be quantitatively different [4].

Here we review the state of the art of the modelling of the fast flow behavior of entangled and unentangled polymers, showing that, in view of the above facts, theories for the nonlinear rheology of all polymer melts must necessarily account for friction reduction effects.


Tuesday 12:10 Emerald II
Concentration dependence of the interchain tube pressure effect in elongational flow of concentrated polystyrene solutions
Manfred H. Wagner1 and Esmaeil Narimissa2
1Polymer Engineering and Physics, TU Berlin, Berlin 10587, Germany; 2Chemical Engineering Program, Guangdong Technion Israel Institute of Technology GTIIT, Shantou, Guangdong 515063, China

Rheological equations of state of polymer melts and solutions are of significant scientific interest and have important impacts on the industrial application of rheology e.g. in the characterization of polymeric materials and the simulation of polymer processes. The elongational viscosity data of Bach et al. (2003) and Huang et al. (2013, 2015) on monodisperse polystyrene melts and concentrated polystyrene solutions in oligomeric styrene represent a unique benchmark for improvement of the tube model of Doi and Edwards (1978) with respect to its predictive capabilities of nonlinear viscoelasticity and especially chain stretch. Tube theories relating stretch to a deformation-dependent tube diameter have been particularly successful in modeling nonlinear rheology of polymer melts. At deformation rates larger than the inverse Rouse time of the chain, the tube diameter is reduced by the topological constraints and chain stretch is inverse proportional to the tube diameter. Tube diameter reduction leads to an interchain pressure in the lateral direction of the tube, which is proportional to the 3rd power of stretch (Marrucci and Ianniruberto, 2004), and an entropic spring force in the longitudinal direction of the tube, which is linear in stretch. While this concept allows parameter-free modeling of the elongational viscosity of monodisperse polystyrene melts (Wagner and Rolón-Garrido, 2009), its extension to polymer solutions has been a challenge. Here we demonstrate that when the dependence of the interchain tube pressure effect on polymer concentration and molar mass of the oligomeric solvent is taken into account, good agreement with the elongational benchmark data in the investigated concentration range from 13% to 100% (melt) can be obtained.

Tuesday 12:30 Emerald II
Rheology of polymer solutions in uniaxial stretching accompanied by phase separation
Ivan Y. Skvortsov, Alexander Malkin, Lydia A. Varfolomeeva, and Valery Kulichikhin
Laboratory of Polymer Rheology, A.V. Topchiev Institute of Petrochemical Synthesis, TIPS RAS, Moscow 119991, Russia

Fiber formation in polymer solutions as a result of high extension rates is a well-known phenomenon described in numerous papers. The mechanisms of this process may be different, and its stability determined by the combination of surface tension forces, viscoelastic properties of
solutions, concentration of a polymer and its properties. A novel technique for fiber spinning from polyacrylonitrile solutions in different solvents based on investigation of their rheological properties under high extensional rates was developed.

At the first stage, the process of stretching solutions to the constant length was visualized and studied in detail by movie shooting coupled with measuring the longitudinal stress during phase separation. We observed appearance of turbidity at some extension ratio and exudation of the solvent on a surface of the spin fiber. Then the process of shrinkage of a fiber was recorded, accompanied by an increase in normal stresses.

The next step was to study fiber spinning in the continuous stretching mode. It was found that the stable spinning process is characterized by the constant normal stresses, which vary as a function of the strain rate. It was shown that for realization a continuous spinning process, the solution should have the sufficiently dense entanglement networks, while the limiting stage of a stable fiber spinning process consists in gelation of a solution.

The result of the research was a new continuous spinning process – mechanotropic spinning. Polyacrylonitrile fibers with strength of 700 MPa and elastic modulus of 7 GPa at an elongation of 30% were obtained.

This work was supported by the Russian Foundation for Basic Research (Grant #18-29-17002)

Detailed results of this study were published in Polymers (DOI: 10.3390/polym10080856).

**Symposium BE**

**Blends, Emulsions, Foams & Interfacial Rheology**

Organizers: Anniina Salonen, Jan Vermant and Jose Munoz

Tuesday 10:00 Europe II

**A novel method for interfacial rheology using an indirect interfacial rheometer**

Iain Muntz and Job H. J. Thijssen

*School of Physics and Astronomy, University of Edinburgh, Edinburgh, United Kingdom*

We have developed a system for performing interfacial rheology without attaching a probe directly to the interface itself. This indirect rheology is motivated by the applications of Pickering type systems, where rather than shear being applied directly to an interface, one of the continuous phases is sheared. The behaviour of the system as a whole is then governed, in part, by the rheology of that interface. We use this setup to measure flow curves in a system of poly(methyl methacrylate) at a water/dodecane interface. The lack of a direct probe ensures two things: 1) we avoid substantial pre-shearing which would normally occur due to the probe attached to the interface and 2) the response measured is due to the interface itself and not the probe [1]. In this indirect setup a shear is applied to the upper oil phase using a standard stress controlled rheometer. The response of the interface is then measured by confocal microscopy. A range of rheological behaviour is observed dependent on surface coverage, shear rate and surface structure. The direct visualisation of the interface allows all of these input parameters to be measured and various flow curves can be produced to observe their effect on the rheology of the interface.


Tuesday 10:20 Europe II

**Limitations of interfacial shear rheometry**

Damian Renggli¹, Randy H. Ewoldt², and Jan Vermant¹

¹Soft Materials Group, ETH Zurich, Zürich CH-8093, Switzerland; ²Mechanical Engineering Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL, United States

The interfacial rheology of liquid interfaces can become complex if surface active species such as surfactants, particles or proteins are present at the interface. The broad interest in these complex interfaces covers topics from foam or emulsion stability to structural design in food or understanding the behavior of phospholipids as lung surfactants and is still an active area of research. Measuring the interfacial rheology can be very challenging. Confining soft matter to a fluid interface leads to very thin layers of material, therefore resulting in a very weak mechanical response which might be insufficient to be measured accurately. This inherently soft response combines with other important challenges, including instrument inertia, sample inertia (momentum diffusion), subphase flow (Boussinesq limits), contact line imperfections, and alignment errors. In this work, we study this list of experimental challenges and derive equations for the operating limits of various macroscopic rheometers including the interfacial needle shear rheometer and the double wall ring. We experimentally investigate the limitations defined intrinsically by the interface as well as the ones emerging from the properties of the interface of interest. The results provide cautionary examples and guidelines for anyone measuring interfacial rheology with these techniques.
In two-phase flow of immiscible Newtonian fluids in a porous medium, the flow rate shows non-linear dependence on the pressure drop as well as on the volumetric saturation due to the interplay between capillary and viscous forces [1,2]. A change in the saturation alters the viscous forces due to the difference in the viscosities of the fluids, as well as the capillary forces due to the surface tension at the interfaces. Here we address the regime of high capillary number, where the capillary forces are negligible and the total flow rate varies linearly with the viscous pressure drop. The flow in this regime should therefore depend only on the viscosities of the two individual fluids while changing the saturation. We demonstrate that, the steady-state two-phase flow in porous media at high capillary number regime may be characterized by an effective viscosity that is well described by the Lichtenecker-Rother equation which connects the effective viscosity with the individual fluid viscosities and their saturations by an exponent α. The value of α characterizes the flow behavior depending on the pore geometry, wettability and viscosity contrast of the fluids. We find α = 1 when two fluids are well mixed with small bubbles, α = 0.6 in two- and α = 0.5 in three-dimensional systems when there is less mixing with the appearance of big bubbles, and α = -0.5 when lubrication layers appear along the pore walls [3]. Our results are based on analytical and numerical methods where we have used the pore-network modelling and lattice Boltzmann simulations.


Tuesday 10:40 Europe II

**Immiscible two-phase flow in porous media: Rheology at high capillary number**

Santanu Sinha, Magnus Å. Gjennestad, Morten Vassvik, Mathias Winkler, Alex Hansen, and Eirik G. Flekkøy

*1Beijing Computational Science Research Center, Beijing, Haidian District 100193, China; 2Physics Department, PoreLab, Norwegian University of Science and Technology, Trondheim 7491, Norway; 3Department of Physics, PoreLab, University of Oslo, Oslo 0316, Norway*

In two-phase flow of immiscible Newtonian fluids in a porous medium, the flow rate shows non-linear dependence on the pressure drop as well as on the volumetric saturation due to the interplay between capillary and viscous forces [1,2]. A change in the saturation alters the viscous forces due to the difference in the viscosities of the fluids, as well as the capillary forces due to the surface tension at the interfaces. Here we address the regime of high capillary number, where the capillary forces are negligible and the total flow rate varies linearly with the viscous pressure drop. The flow in this regime should therefore depend only on the viscosities of the two individual fluids while changing the saturation. We demonstrate that, the steady-state two-phase flow in porous media at high capillary number regime may be characterized by an effective viscosity that is well described by the Lichtenecker-Rother equation which connects the effective viscosity with the individual fluid viscosities and their saturations by an exponent α. The value of α characterizes the flow behavior depending on the pore geometry, wettability and viscosity contrast of the fluids. We find α = 1 when two fluids are well mixed with small bubbles, α = 0.6 in two- and α = 0.5 in three-dimensional systems when there is less mixing with the appearance of big bubbles, and α = -0.5 when lubrication layers appear along the pore walls [3]. Our results are based on analytical and numerical methods where we have used the pore-network modelling and lattice Boltzmann simulations.


Tuesday 11:30 Europe II

**Experimental and numerical analysis of the pendant drop experiment for complex interfaces**

Nick O. Jaensson, Patrick D. Anderson, and Jan Vermant

*1Department of Materials, ETH Zürich, Zürich, Switzerland; 2Eindhoven University of Technology, Eindhoven, The Netherlands*

Pendant drop experiments are frequently employed to obtain the interfacial or surface tension of liquid-liquid or liquid-gas interfaces. The general approach is to fit the Young-Laplace equation to a droplet suspended from a capillary, which yields the surface tension and capillary pressure inside the droplet. By performing oscillatory measurements, information about the adsorption/desorption of surface-active entities can be obtained. However, a crucial assumption when applying the Young-Laplace approach ceases to be valid, and other approaches for estimating the surface stress become necessary.

Tuesday 11:50 Europe II

**Surface dilatational rheology of interfaces stabilized by poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock-copolymers: a combined computational and experimental study**

Ahmad Moghimikheirabadi, Martin Kröger, Patrick Ilg, and Leonard M. Sagis

*1Polymer Physics, Department of Materials, ETH Zurich, Zurich 8093, Switzerland; 2Department of Mathematics & Statistics, University of Reading, Reading, United Kingdom; 3Food Physics Group, Wageningen University, Wageningen, The Netherlands*

Recent studies show that the surface rheological properties of complex interfaces often dominate the macroscopic dynamics and stability of multiphase materials that contain such interfaces, e.g. foams, emulsions, encapsulation systems[1]. Complex interfaces can be formed by a wide range of surface active components including proteins, lipids, polymers, colloidal particles, or their mixtures. Here we focus on interfaces stabilized by linear triblock-copolymers known as Pluronic types, with a hydrophobic poly(propylene oxide) middle block and two identical hydrophilic poly(ethylene oxide) ending blocks. These copolymers are commercially available in different molecular weights and corresponding degrees of hydrophobicity which potentially allows a targeted design of complex interfaces with tailor-made properties.

We measured the surface dilatational viscoelasticity of Pluronic copolymers at the air-water interface for both spread and adsorbed layers by using the oscillating barrier technique. The effect of block length ratio is investigated via both amplitude and frequency sweeps on two Pluronic types with different degrees of hydrophobicity: F-108 (Mn^*14600 g/mol) and P-123 (Mn^*5800 g/mol). Large amplitude oscillatory dilatation (LAOD) is performed to capture nonlinear behavior of the interfacial films, exhibiting strain hardening during compression and strain softening in extension.
We complement our experimental measurements with nonequilibrium molecular dynamics (NEMD) simulations of a coarse-grained molecular model [2]. This model is optimized to reproduce the surface pressure-area isotherms qualitatively. Simulations are performed in both linear and nonlinear regimes where the structure-rheology relationship is obtained over a wide range of frequencies and amplitudes.


Tuesday 12:10 Europe II BE6

Drainage dynamics of polymer-solution films
Emmanouil Chatzigiannakis and Jan Vermant
Soft Materials Group, ETH Zurich, Zürich CH-8093, Switzerland

Thin liquid film (TLF) dynamics is considered to be an important if not deciding factor when it comes to foam and emulsion stability. When two bubbles/droplets come into close proximity a TLF is usually formed between them, which gradually drains until it ruptures. The role of the interfacial properties on the hydrodynamic drainage process of various systems has received some attention [1,2]. However, to the best of our knowledge, there are no experimental studies regarding how the rheological properties of the bulk liquid (e.g. viscoelasticity, shear thinning) affect the overall drainage process. In this study, the drainage dynamics of liquid-liquid and liquid-air films of polymer solutions were examined using a variation of the thin film balance technique [3]. A standard thin film balance was modified to perform hydrodynamic studies. The effect of three parameters on drainage was studied, namely that of driving force, polymer concentration and molecular weight. All parameters were found to influence non-trivially the drainage of the thin liquid films, giving rise to a multitude of phenomena, both with respect to flow instabilities (symmetric-to-asymmetric drainage transitions, cyclic dimpling and vortices), as well as with respect to confinement effects on structure and possibly rheology (thickness variations comparable to the length-scales of the polymer chains).


Tuesday 12:30 Europe II BE7

Emulsion stability: Dynamics of thin films studied by extensional rheology
Fernando Avino1, Cecile Monteux2, and Paul S. Clegg1
1School of Physics and Astronomy, The University of Edinburgh, Edinburgh, United Kingdom; 2Laboratory of Soft Matter Science and Engineering, ESPCI Paris, Paris, France

Hydrophobic dipeptide molecules are able to form viscoelastic interfacial films, coating bubbles and droplets made from a range of oils. 2NapFF dispersed at high pH form micelles, which transform into a hydrogel of fibers in response to the addition of salt. We use the gels prepared at different salt (MgSO4 and CaCl2) concentrations to stabilize interfaces. In our previous work [1], we revealed that the gel is too weak to prevent ripening of the bubbles at low dipeptide concentrations (0.01 wt%), thus reducing the long-term stability of the foam. By contrast, under the same conditions, we are able to form long lived emulsions using a range of different oils. Foams and emulsions are formed under high shear. This disrupts the hydrogel (although it reforms) and stretches droplet interfaces. To study the latter, we form thin catenoid shaped films from the gel, that are studied whilst stretched at different speeds (5, 50 and 100 mm/s) to mimic the rupture dynamics of thin films between drops in emulsion formation. We then use a high-speed camera to capture the moving images and analyse the data by using image processing techniques. Surprisingly, we find different collapse scenarios for each salt used (MgSO4, CaCl2 and NaCl) and observe a non-monotonic effect dependence of film strength on salt.


Symposium FP

Food, Pharmaceutics & Cosmetics
Organizer: Patricia López Sánchez

Tuesday 10:00 Europe III FP1

Rheology for safe swallowing - the Gothenburg throat
Mats Stading1, Waqas Mohammad Qazi1, and Olle Ekberg2
1Product Design and Perception, RISE Research Institutes of Sweden, Gothenburg 40229, Sweden; 2Diagnostic Centre of Imaging and Functional Medicine, Skåne University Hospital, Lund University, Malmö 20502, Sweden

Swallowing disorders, or dysphagia, is a growing problem especially as the population gets older. In the age group above 70, 40 % suffer due to factors such as degenerative diseases and side effects of medication. These persons must eat texture adjusted foods.
Healthy individuals apply highly unconscious, but very well coordinated strategies for the oral processing producing easy-to-swallow boluses. People who suffer from dysphagia have impaired swallowing mechanisms. Swallowing disorders covers a broad range of problems, from coughing during meals to malnutrition, and 30-60% of the patients in homes for the elderly are estimated to be malnourished. Foods that give a better controlled passage through the opening to the larynx, even with a malfunctional epiglottis, will make a significant contribution to an improved quality of life. Fluid foods are thickened with hydrocolloids which provide increased viscosity, as determined by the shear viscosity at the "standard" 50 l/s. However, the effects of thickening on impaired swallowing are not fully understood and the relations to basic rheology are scarce. Also, clinical studies are difficult to perform due to the general impaired state of the patients.

The Gothenburg Throat is an in vitro model of the upper part of the throat, the pharynx, designed to elucidate the effect of bolus rheology on swallowing and to simulate different types of disorders. A bolus is injected at controlled volume and speed, and the pressure at four different places is monitored together with the velocity profile during the passage through the pharynx. The closing of the epiglottis covering the airways, the closing of the vocal cords as well as the nasopharynx and upper esophageal sphincter is controlled to mimic healthy as well as malfunctioning swallowing. The model has been thoroughly validated and bolus flow determined. Shear rates for commonly used thickeners have been observed in the range 10-200 l/s, and have also been validated by in-vivo studies.

**Tuesday 10:40 Europe III**

**Effects of dispersing conditions on rheological properties of edible fibre suspensions**

Francesca R. Lupi\(^1\), Francesco Puoci\(^2\), Elisabetta Bruno\(^1\), Noemi Baldino\(^1\), Rosamaria Marino\(^3\), and Domenico Gabriele\(^1\)

\(^1\)DIMES, University of Calabria, Rende, Italy 87036, Italy; \(^2\)Department of Pharmacy, Health and Nutritional Sciences, University of Calabria, Rende, CS 87036, Italy; \(^3\)Silvateam Food Ingredients srl, Rende, CS 87036, Italy

The daily consumption of edible fibres is becoming a relevant issue owing to their potential role in reducing the risk of gastrointestinal disorders (e.g. Crohn's disease, appendicitis, colon carcinoma, duodenal ulcer, etc.), coronary heart disease, stroke, hypertension, diabetes and obesity. Aiming at increasing the daily intake (currently lower than values recommended by national and international authorities) food industry is "fortifying" different foods with fibres taking advantage also of their ability of modifying final consistency of foods. Starting from these considerations it seems relevant to understand better the effects of dispersing conditions on ability of fibre to modify rheological properties of materials; in the present work, a commercial edible fibre has been used to prepare aqueous dispersion, with a rotor stator device, at different energy and power of mixing. Samples have been investigated with small amplitude oscillations and obtained rheological properties have been related to mixing conditions. It has been observed that structured systems are obtained and the strength of these weak gels increases with the increasing power up to a plateau obtained at the highest tested powers. Optical microscopy evidenced that when fibre is dispersed in water, the increase in supplied power improves dispersion and interaction of particles that build a three-dimensional network extending through the whole sample. The results obtained can be useful in tuning the process conditions as a function of the specific use in order to obtain the desired consistency.

**Tuesday 11:30 Europe III**

**Rheological characterization of legume protein-stabilized oil/water interfaces and emulsions**

Manuel Felix, Cecilio Carrera, Alberto Romero, and Antonio Guerrero

Department of Chemical Engineering, Universidad de Sevilla, Sevilla, Spain

Emulsion stability is the primary requirement for the industrial applications of many commercial food products. This is a key point for consumer's acceptance of food emulsions, which also require adequate microstructural and rheological properties to achieve and maintain desirable textural and organoleptic properties. Many studies have been carried out to link stability to rheology and microstructure. However, knowledge of the interfacial behaviour on a nanoscale is also essential for the development of optimal properties on the microscale (droplet size distributions and microscopy) and macroscale (rheology and stability). This is a topic of high interest, which has many industrial applications but has been insufficiently studied. This study focuses on the comparison between the rheological properties of complex oil-water interfaces and the properties of the emulsions using legume proteins (chick pea or faba bean) as the only emulsifier, as a function of pH, protein concentration and storage time. Interfacial shear rheology (SAOS, non-linear relaxation and steady state flow tests) was studied by means of a double wall-ring geometry fitted to a DHR3 rheometer (TA Instrumnts). Emulsions were prepared using a high-pressure homogenizer and characterized by laser diffraction, microscopy, light scattering and linear viscoelastic measurements. Wagner-I model, based on SAOS results (LVE) and non-linear relaxation tests, can reproduce fairly well the steady state flow behaviour at the legume protein-adsorbed O/W interfaces. Moreover, a fairly good agreement between interfacial shear rheology, emulsion rheology, microstructural parameters and stability has been found. This can be very useful to tailor interfaces that might develop optimal emulsion microstructure and stability, basically by using interfacial shear rheology.

Financial support for this work, framed within the project CTQ2015-71164-P, is gratefully acknowledged to MINECO/FEDER (UE).

**Tuesday 11:50 Europe III**

**Nanorheological studies using magnetic nanoparticles: towards in vivo textural measurements**

Patricia Lopez-Sanchez\(^1\), Vincent Schaller\(^2\), Thana Sriviriyakul\(^3\), Christer Johansson\(^2\), and Mats Stading\(^1\)

\(^1\)Product Design and Perception, RISE Research Institutes of Sweden, Gothenburg 40229, Sweden; \(^2\)Acero, RISE Research Institutes of Sweden, Gothenburg, Sweden

Oral processing of foods is an intricate combination of voluntary and involuntary actions which involves complex flow geometry as well as a mixture of shear and extensional flow. To study textural changes directly in the mouth involves large experimental equipment, which interferes with the oral mechanisms and the perception of food properties. Instead, the use of magnetic nanoparticles (MNPs) enables remote sensing of...
viscoelastic properties by measuring the dynamic magnetic response from the MNPs. This means that rheological properties, texture and aggregation could be followed remotely. Nanorheological studies using MNPs have been previously performed in PEG, gelatine and polymer melts using AC susceptibility (ACS) measurements [1, 2]. To study the viscoelasticity, the MNPs need to exhibit Brownian relaxation (e.g. particle magnetic moment locked in a specific direction of the MNP). In this study, systems relevant for food applications such as xanthan solutions have been studied [3]. MNP systems consist of multi-core particles (micromod Partikeltechnologie) embedded in either starch or dextran matrix. ACS measurements were performed using the DynoMag system. The ACS response was measured, and the data was modelled using dynamic magnetic models such as the generalized Debye model and Raikher-based model [4], as well as different viscoelastic models. The in-phase and out-of-phase components of the shear moduli were determined at each excitation frequency, showing good agreement with traditional rheological measurements obtained by small amplitude oscillatory shear. The outcome of this work will contribute to the design of foods with customized textures for populations with specific needs.


Tuesday 12:10 Europe III

**FP5**

**Accurate methodology to determine slip velocity, yield stress and the constitutive relation for molten chocolate in steady state**

Emeline Talansier¹ and Denis C. Roux²

¹Laboratoire Rheologie et Procédés, Université Grenoble Alpes, Grenoble, France; ²Laboratoire Rheologie et Procédés, Université Grenoble Alpes, Grenoble, France

The characterization of industrial flow of soft concentrated materials is essential for process design considerations, e.g. during pumping or mixing operations. That can be carried on with simple Newtonian or very complex fluids like foodstuffs. A major difficulty is to know the behavior of the material when it is submitted to an imposed stress or shear. Indeed, concentrated soft material like molten chocolate often has the ambiguity of behaving like a solid or a liquid depending on the applied solicitation. However, the determination of the constitutive relation is often unreliable and consequently the yield stress value too. This difficulty of determining yielding stress, particularly when using a standard protocol, such as the IOCCC for chocolate, is a consequence of the presence of slippage of the material at the wall boundaries.

We propose to tackle this problem by using an easy and reliable methodology applied to a commercial chocolate in a melted state with, as equipment, a plate-plate rotational rheometer. This method [1] allows precise determination of the yield stress value, the constitutive relation and the slip velocity equation. It provides also an explanation to the apparent Newtonian plateau and thickening behavior of the raw flow curve. We highlight that the assessment of the slip velocity using Yoshimura and Prud'homme's method [2] can lead to erroneous results. Finally, data of corrected stress versus shear rate flow curve are used to fit classical Herschel-Bulkley and Casson models that were compared to the ones obtained using the Confectionary Office (IOCCC) and the International Chocolate Award (ICA) current standards. We show that limitation of the studied shear rate range of the standard methods greatly affects the evaluation of the yield stress. The latter can be evaluated more precisely if an unlimited time and shear of measurements is considered.


Tuesday 12:30 Europe III

**FP6**

**In-situ rheological and structural characterization of milk foams in a commercial foam generator**

Annika R. Völp¹, Jan Engmann², Deniz Z. Gunes³, Cécile Gehin-Deval², and Norbert Willenbacher¹

¹Institute of Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany; ²Nestlé Research, Institute of Material Science, Lausanne, Switzerland

Processing, lifetime and sensorial perception of food foams are tightly related to their flow properties. Characterization of the foam structure and yielding behavior are central for product development and quality control. Here, we present an experimental setup, which allows for characterization of foam rheology and structure at different heights of a foam column within a commercial whipper. The cylindrical container with eccentric whipping coil and heating plate at the bottom is built into a rotational rheometer. Yield stresses are measured with a vane rotor of 1 cm height at intervals of 1 cm along the rotational axis of the container. Bubble size distributions are analyzed by endoscopic imaging and automated bubble detection at same heights with temporal resolution on the order of seconds. Gas volume fractions are determined using electrical conductivity measurements. Brass rings at the inner container wall and a height adjustable ring submerged into the foam serve as electrodes to detect the conductivity at intervals of 1 cm along the foam axis. Foams made from UHT milk and reconstituted milk have been investigated for up to 20 min foam age. The gas volume fraction increased linearly with height within the foam column, whereas the mean bubble size and bubble size distribution remained constant. The yield stress increased with height as expected from the change in gas volume fraction. During foam aging, the mean and width of the bubble size distribution increased linearly with time. In contrast, the gas volume fraction saturated over time, and accordingly, the yield stress passed through a maximum. The gradients in gas volume fraction and yield stress along the column axis increased over time depending on milk composition. At higher fat content of the milk the gas volume fraction gradient was reduced and foam lifetime was longer. The developed method offers in-situ characterization of key morphological and rheological parameters of foams.
Symposium LA

Living & Active Matter
Organizers: Nadia Antonova, Anke Lindner and Salima Rafai

Tuesday 10:00 Adria LA1
Wrinkling and folding instabilities of biomimetic cells in flow
Clement de Loubens¹, Kaili Xie², Frederic Dubreuil¹, Marc Jaeger², and Marc Leonetti¹
¹CNRS, Lab. Rheologie et Procedes, GIERES, France; ²AMU, M2P2, Marseille, France; ³UGA, CERMAV, GIERES, France

The dynamics and the stability of biological cells in flow have numerous consequences on the function of the human body. Also, understanding cells dynamics in flow should help us to design new biomedical diagnosis tools. For example, Red Blood Cells in flow present a wealth of dynamics of deformation that is governed by their shear elasticity and their bendability that is strongly impaired by some illnesses. We quantitatively investigated the stability of biological soft particles in simple extensional flow by using biomimetic cells, i.e. microcapsules, with controlled membrane elasticity and thickness. We observed the emergence of well-defined wrinkles driven by loop compression of the membrane when the microcapsule is stretched by the flow. The threshold of wrinkles emergence is given by a single dimensionless number relating the effects of shear stress over shear membrane elasticity whatever the nature of the membrane and its bendability over four orders of magnitude. Our experimental set-up allowed us to observe the profile of the wrinkles by bright field microscopy and to analyse quantitatively the evolution of the wavelength with the membrane thickness. Neare the threshold, the wavelength increases with the square root of the membrane thickness, in accordance with the scaling law developed by Cerda and Mahadevan (Nature, 2002). According to the membrane microstructure and far from this first threshold, wrinkles can merge into folds or interact strongly with the overall deformation of the microcapsule and forms asymmetrical patterns.

Tuesday 10:40 Adria LA2
Statistics of colloidal suspensions stirred by microswimmer
Christian Wagner¹, Thomas John¹, Salima Rafai², Philippe Peyla², and Levke Ortlieb³
¹Saarland University, Saarbruecken 66123, Germany; ²CNRS, University Grenoble Alpes, Saint Martin d'Hères 38400, France; ³University of Bristol, Bristol, United Kingdom

Microparticulate unicellular algae are abundant in the earth's oceans, rivers and lakes. They are crucial for the ecosystem since they have an estimated contribution of 50% to the world's oxygen production. In addition, it is suspected that they play an important role in stirring the top level of the oceans. This so called biogenetic mixing is important for the availability of nutrients for many organisms. In the presence of active microswimmers, a passive fluid is stirred and shows an active spatio-temporal random fluid motion. These fluctuations at the scale of microorganisms can be characterized by tracking suspended tracer particles such as microspheres. We present a statistical analysis of experimental trajectories of micron sized colloids in a dilute suspension of the green algae Chlamydomonas reinhardti. The probability density function of displacements covers seven orders of magnitude and can be described by a convolution of two Gaussian distributions. The central peak results from classical thermal Brownian motion and the non-Gaussian long time tail is caused by single microswimmers. Still, we find that the mean squared displacements of tracer positions is linear over the complete measurement time interval. Experiments are performed for various tracer diameters, swimmer concentrations and mean swimmer velocities. This allows a rigorous comparison with existing theoretical models. We can exclude a description based on an effective temperature and other mean field approaches that describe the irregular motion as a sum of the fluctuating far field of many microswimmers. Our data are in many respects best described by the microscopic model by Thiffeault, PRE 92 023023(2015).

Tuesday 11:30 Adria LA3
Microrheology of dense active suspensions
Thomas Voigtmann
Institute of Materials Physics in Space, German Aerospace Center, Cologne 55170, Germany

We study the dynamics of dense suspensions of active Brownian particles (ABP) as a model system for active matter. Using a nonlinear-response theory framework, the integration-through transients (ITT) approach, combined with the mode-coupling theory of the glass transition (MCT), we calculate transport coefficients such as shear viscosity and self-diffusion coefficients of the dense ABP system. The theory describes the fluidization of the system due to self-propulsion forces, addressing specifically the separate effects of a change in swimming speed and in the persistence of swimming. We discuss the relation between viscosity and self-diffusion in the active system, in order to provide guidance for microrheology experiments on active matter. Microrheology is a convenient tool to probe the viscous response of a system in particular using small samples, and it is commonly used with biological matter. It relies however on establishing a link between the observed diffusion of a colloidal (passive or actively driven) probe particle and the viscosity of the active host system. Our ITT-MCT approach addresses this link. We also discuss the influence of strong flow gradients on the nonlinear rheological response of the active system. The results obtained from MCT are compared with Brownian Dynamics simulations that reveal two separate flow regimes of active suspensions, separated by the MCT glass-transition density.

Annual European Rheology Conference 2019
Bacteria in liquid crystals
Martyna Goral1, Anke Lindner1, Teresa Lopez-Leon2, and Eric Clément1
1PMMH, ESPCI, Sorbonne Université, Paris, Ile-de-France 75005, France; 2Gulliver, ESPCI, Paris, Ile-de-France 75005, France

Bacteria are considered as a model system of active particles for the understanding of collective motion. Interactions each other or with the surrounding medium can lead to non-trivial macroscopic behavior. Bacterial active motion can for example change the viscosity of bacteria suspensions [1], but the suspending medium itself can also trigger the emergence of new collective bacterial dynamics. Interesting spatio-temporal patterns have recently been observed in nematic liquid crystals, where the motion of bacteria is directed by the orientational molecular order of the liquid crystal [2]. In this work, we study bacterial motion in spherical droplets of nematic liquid crystals, where topological constraints enforce the formation of orientational vortices (topological defects) in the liquid crystal. To produce the droplets, we use microfluidic techniques, which allow us to have high control on the size of the droplet, and therefore, on the curvature of the confining space. The droplets are made of a lyotropic chromonic liquid crystal (LCLCs) in which rod-like bacteria are dispersed. We expect to observe the emergence of complex swimming dynamics resulting from the coupling between the bacterial motion and the orientational field: the field guides the bacteria that in turn modify the field.


Effective viscosity of a suspension of flagellar-beating microswimmers: Three-dimensional modeling
Philippe Peyla1, Levan Jibuti2, Walter Zimmermann3, and Salima Rafai3
1Physics, University Grenoble Alpes, Saint Martin d’Hères, France; 2Theoretical Physics I, University of Bayreuth, Bayreuth 95440, Germany; 3Theoretical Physics I, University of Bayreuth, Bayreuth, Germany; 4CNRS, University Grenoble Alpes, Saint Martin d’Hères 38400, France

Micro-organisms usually can swim in their liquid environment by flagellar or ciliary beating. Here, a three-dimensional model is proposed for the micro-alga Chlamydomonas Reinhardtii (CR) swimming with a breaststroke-like beating of two anterior flagella modelled by two counter-rotating fore beads. In order to calculate the effect of the flagellar beating on the rheology of a dilute suspension of CR, we analyse the influence of flagellar beating on the orbits of a swimming cell in a shear flow. Our model reveals unusual angular orbits in a linear shear flow. Namely, the swimmer sustains orientations transiently across the flow. Such behaviour is a result of the interplay between shear flow and the swimmer’s periodic beating motion of flagella, which exert internal torques on the body cell. This peculiar behaviour has some significant consequences on the rheological properties of the suspension. We calculate Einstein’s viscosity of the suspension composed of such isolated modelled micro-swimmers (dilute case) in a shear flow. We use numerical simulations based on a Rotne-Prager-like approximation for hydrodynamic interaction between simplified flagella and the cell body. The results show an increased intrinsic viscosity for active swimmer suspensions in comparison to non-active ones as well as a shear thinning behaviour in accordance with previous experimental measurements.

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Soft microbial tissues in dilute bacterial suspensions
David Stopar1, Simon Sretenovic2, Rok Kostanjevšek1, Biljana Stojkovic3, Igor Poberaj4, Tina Turk5, and Iztok Dogša1
1Biotechnical Faculty, University of Ljubljana, Ljubljana 1000, Slovenia; 2Plant Science and Landscape Architecture, University of Maryland, College Park, MD, United States; 3Impol d.d., Slovenska Bistrica 2310, Slovenia; 4Aressis d.o.o., Ljubljana 1000, Slovenia; 5Marine Biological Station, NIB, Piran 6330, Slovenia

Biofilm is the most prevalent lifestyle of bacteria in the environment. It forms when neighbouring cells interconnect and attach to surfaces. To bond to each other bacteria produce extracellular polymeric material composed of hydrated polysaccharides, proteins and nucleic acids. The extracellular matrix enables structural and functional integrity and enables emergent properties of biofilms. We have applied optical tweezers to probe early mechanical connections between cells in very dilute bacterial suspensions and demonstrated that bacteria in planktonic suspensions regularly form viscoelastic soft tissue-like microbial structures. Mechanical coupling of neighbouring cells enables correlated motion of bacteria on large distances (over 100 m). Based on microrheology measurements we argue that planktonic lifestyle of bacteria is an exception rather than a rule in microbiological world. This breaks with centuries old assumption that bacterial cells in planktonic suspensions are not physically connected. We will propose a new mechanism for biofilm formation based on cell lysis and provide molecular details important in formation of soft microbial tissues.
Tuesday Afternoon

Symposium CS

Colloids & Suspensions

Organizers: Michel Cloitre, Guillaume Ovarlez and Norbert Willenbacher

Tuesday 14:20 Europe I

Repulsion, attraction and contact in dense suspensions
John R. Royer, Joseph French, Vasileios Koutsos, and Wilson Poon
University of Edinburgh, Edinburgh, United Kingdom

Particle contacts, and the constraints induced by these contacts, are key to understanding non-Newtonian flow and jamming in dense suspensions. While numerical simulations and mean-field models based upon stress-induced transitions between lubricated and frictional contacts have had remarkable success reproducing the shear thickening rheology of dense suspensions, in real experimental systems the precise nature of these frictional contacts remains ambiguous. Using charge-stabilized silica spheres, where particle interactions can be easily tuned through the fluid ionic strength, we employ a combination of bulk rheology and single-particle atomic force microscopy (AFM) to probe the nature of these contacts. Directly measuring the forces between a silica sphere and silica surface with AFM, we can access both the finite ranged interactions as well as the force at contact, defined by a constant compliance region in the AFM force-displacement curve. As the fluid ionic strength increases from low to moderate values, both the force at contact from AFM and the onset stress for shear thickening decrease. This agrees with expectations from numerical simulations, though the force at contact from AFM lies slightly below the contact force predicted from the onset stress. As the ionic strength further increases, in the bulk rheology shear thickening becomes obscured by an increasing yield stress, while the particle interactions measured in AFM transition from repulsive to attractive at short distances. Together, these results indicate that the frictional contacts formed in dense, shear thickening suspensions represent true solid-solid contacts.

Tuesday 15:00 Europe I

Velocity traveling bands in shear-thickening dense suspensions
Guillaume Ovarlez¹, Anh Vu Nguyen Le², Wilbert J. Smit³, Abdoulaye Fall³, Guillaume Chatté³, and Annie Colin⁴
¹University of Bordeaux, CNRS, Solvay, LOF, Pessac 33600, France; ²ESPCI, Paris, France; ³Laboratoire Navier, Université Paris-Est, Champs-sur-Marne, France; ⁴CBI-MIE, ESPCI Paris, PARIS 75005, France

Dense suspensions of solid particles immersed in a Newtonian solvent often display shear thickening. Recent works suggest that it stems from the breakdown of lubrication between particles and the onset of hard frictional contacts. However, the description of the dynamics and of the structure of the flow remains elusive.

Here, we make a major advance thanks to a new combination of rheological measurements and X-ray radiography, which allows us to get time- and spatially-resolved concentration fields in flowing suspensions. We report inhomogeneous flows in two shear-thickening dense model suspensions. We observe collective motions which involve axial symmetry breaking. Periodic density waves propagate in the velocity direction at half the rotor velocity. We analyze our results in the framework of traveling bands as inferred from recent model and numerical simulations.

Tuesday 15:20 Europe I

Numerical simulation of particulate suspensions in viscous and viscoelastic medium combining Brownian dynamics and smoothed particle hydrodynamics method
Howon Jin and Kyung Hyun Ahn
Seoul National University, Seoul, Republic of Korea

Brownian dynamics (BD) simulation is one of the simplest methods describing particulate soft matter systems, which has an advantage in calculating collective properties of the matters due to its low computational cost. However, BD itself lacks any rule in momentum exchange between the particle and suspending medium, so that the particle interactions or morphology of particles cannot be instantaneously reflected in the local suspension velocity. Recently, as a part of an effort to resolve such a problem, new simulation method, called hydrodynamically coupled Brownian dynamics (HCBD), is developed, which combines Brownian dynamics and smoothed particle hydrodynamics method [Ahuja et al., J. Chem. Phys., 2018]. In this method, the motion of a colloidal particle is governed by overdamped Langevin equation as in the original Brownian dynamics, except that the prescribed velocity field is replaced to the background SPH particle velocity field. The velocity field of SPH particle is given by solving SPH-formulated Navier-Stokes equation with extra body force term exerted from the colloidal particles to simulate simultaneous momentum exchange between the colloid and solvent. In this work, on the extension of HCBD, the Maxwell type viscoelastic constitutive model is applied to the governing equation of SPH solvent particles instead of Newtonian Navier-Stokes equation. The effect of viscoelasticity on the
microstructure and stress of the particles immersed in the polymeric fluid is investigated. Further details of the formulation and results will be discussed in the presentation.

Tuesday 16:30 Europe I
Computational oscillatory rheometry of rigid particle suspensions at finite inertia
Massimiliano M. Villone, Marco E. Rosti, Outi Tammissola, Luca Brandt, and Pier Luca Maffettone
1Università di Napoli Federico II, Naples, Italy; 2KTH Royal Institute of Technology, Stockholm, Sweden

Oscillatory motions are widely used in rheometry to determine the viscoelastic properties of fluids and multiphase systems, e.g., suspensions, emulsions and foams. The design equations of oscillatory rheometers ideally assume that inertial effects are negligible, yet such approach could lead to misinterpretation of the experimental data, especially for low-viscosity fluids or at high frequency. Therefore, it could be useful to quantify the incidence of inertial effects on the measured “apparent” viscoelastic properties of a sample. In order to understand the importance of inertia on the viscoelastic moduli of suspensions of rigid spheres in a Newtonian matrix subjected to oscillatory shear flow, we perform immersed boundary method numerical simulations at varying the particle volume fraction and the relative weight of inertial and viscous forces.

Tuesday 16:50 Europe I
Direct numerical simulations of shear-induced migration in pipe flows
Stany Gallier and Elisabeth Guazzelli
1ArianeGroup, vert le petit, France; 2Aix-Marseille University, CNRS, IUSTI, Marseille, France

This study intends to understand the migration of particles of a non-Brownian non-inertial suspension in a pipe flow. This phenomenon of shear-induced migration leads to inhomogeneities in the particle concentration and has therefore practical interest in many situations ranging from microfluidics to flows of industrial suspensions (concrete, solid rocket fuels, etc.). In this work, we perform fully-resolved simulations at the particle level by solving Stokes equations including lubrication forces, frictional contact and long-range hydrodynamics. A novelty of this work is to make use of an immersed boundary technique to handle more complex domains, here a cylindrical pipe. Simulations aim at reproducing faithfully the well-documented experimental configuration by Snook et al. [1] so that one-to-one comparisons between simulations and experimental data are possible. Four volume fractions (10, 20, 30 and 40 %) are addressed and we show a very good agreement between simulations and experiments with a marked migration for the 30 and 40 % case, a mild migration for 20 % and an absence of migration for the 10 % case. This contrasts with predictions from a classical Suspension Balance Model (SBM) which anticipate a strong migration even for the most dilute cases. We have also studied the migration dynamics and again, a good correlation with experiments is found while SBM predicts a faster migration than experimentally observed. Because experiments are actually done in an oscillatory shear, we have also simulated such unsteady configurations and have found-like in experiments- that the accumulated strain per oscillation cycle must exceed a threshold value for the migration to appear, in good accordance with Pine's observations [2]. Friction between particles is investigated but is found to have only limited effects. Ongoing efforts intend to understand the noted differences between simulations and SBM model.


Tuesday 17:10 Europe I
Variable friction between particles as an origin of shear thinning in non-Brownian suspensions
Laurent Lobry, Elisabeth Lemaire, Frédéric Blanc, Stany Gallier, and François Peters
1Institut de Physique de Nice, CNRS UCA, Nice, France; 2ArianeGroup, vert le petit, France

Although shear-thinning behaviour has been observed for years in most concentrated non-Brownian suspensions, its origin is still debated. In the past few years, the strong influence of the friction between particles on the suspension viscosity has been evidenced. In particular, introducing finite friction in the contact law of simulated suspensions led to a more than threefold increase of the viscosity of a 50% volume fraction suspension, bringing the computed viscosity to the level of experimental measurements [1]. We propose here to explain shear thinning behavior by variable friction between particles. Considering the low magnitude of the forces experienced by the particles of suspensions under shear flow, it is first argued that rough particles come into solid contact through one or a few asperities. In such a few-asperity elastic-plastic contact, the friction coefficient is expected not to be constant but to decrease with increasing normal load. Simulations based on the Force Coupling Method and including such a load-dependent friction coefficient are performed for various particle volume fractions. The results of the numerical simulations are compared to viscosity measurements carried out on suspensions of polystyrene particles (40 μm in diameter) dispersed in a Newtonian silicon oil. The agreement is shown to be satisfactory. Furthermore, the comparison between the simulations conducted either with a constant or a load-dependent friction coefficient provides a model for the shear-thinning viscosity. In this model the effective friction coefficient μ_eff is specified by the effective normal contact force which is simply proportional to the bulk shear stress. As the shear stress increases, μ_eff decreases and the jamming volume fraction increases, leading to the reduction of the viscosity. At last, using this model, we show that it is possible to evaluate the microscopic friction coefficient for each applied shear stress from the rheometric measurements.

Magnetorheology in the magnetic saturation regime
Jose R. Morillas and Juan de Vicente
Department of Applied Physics, University of Granada, Granada, Granada 18071, Spain

Conventional Magnetorheological (CMR) fluids are non-brownian suspensions based on a magnetic particulate phase (usually carbonyl iron microparticles) dispersed in a non-magnetic Newtonian fluid (usually oils). These suspensions are characterized by a fast, reversible and dramatic change in their rheological properties upon the application of a magnetic field. The appearance of an electromagnetic field-controlled yield stress makes them strong candidates for electromechanical applications. Indeed, numerous dampers, brakes and valves, currently commercialized in automotive and civil engineering industries, are based on CMR fluids.

The maximum attainable yield stress, and therefore the performance of the CMR fluid, is governed by the particle concentration and their saturation magnetization. Several approaches have been followed in the past to study these dependencies from an experimental, theoretical and modeling point of view. However, simulation techniques are typically expensive and hard to compare with experimental data.

In this work, a very simple modeling method is proposed to compute the yield stress of CMR fluids. Under an external field the particles are arranged in a periodic lattice that affinely deforms under shear. Results obtained are validated using Finite Element Method magnetostatic simulations, experiments (for large and small volume fraction) and a theoretical micromechanical model (for small volume fractions).

Acknowledgements
This work was supported by MINECO MAT 2016-78778-R and PCIN-2015-051 projects (Spain) and European Regional Development Fund (ERDF). J. R. Morillas acknowledges FPU14/01576 fellowship.

Symposium NF
Non Newtonian Fluid Mechanics & Flow Instabilities (in honor of Prof. Mike Webster)
Organizers: Tim Phillips, Russel Davies, Natalie Germann and Corneliu Balan

Numerical study of shear banding in pressure-driven channel flow and 4:1 contraction flow
Soroush Hooshyar and Natalie Germann
Fluid Dynamics of Complex Biosystems, Technische Universität München, Freising, Germany

Under high enough shear deformations, many soft materials are known to develop banded velocity and concentration profiles. To study shear banding in semi-dilute entangled polymer solutions, we developed a thermodynamically consistent two-fluid model using the generalized bracket approach of nonequilibrium thermodynamics [1]. Our model assumes that Fickian diffusion and stress-induced migration generate a nontrivial velocity difference between the constituents of the solution, the latter mechanism being responsible for shear banding. Our model takes into account important features including a stress overshoot during the start-up of simple shear flow, a monotonically increasing steady flow curve, as well as smooth and unique steady-state solutions.

We analyzed our model in several benchmark flows including pressure-driven channel flow with and without wall slip [2] and 4:1 planar contraction flow. The velocity profile of the channel flow forms a plug-like form in the shear banding regime, with a spurt in the profile of the flow rate against the pressure gradient. To enter into the shear banding regime in the contraction case, the uniform velocity at the inlet was gradually increased. While the velocity profile in the upstream channel was still parabolic, the corresponding profile changed to plug-like after the contraction. In agreement with experimental data [3], we found that shear banding competes with flow recirculation. Finally, the profile of the polymer concentration shows a peak in the shear banding regime, which is closer to the center of the channel for larger inlet velocities. With the two-fluid implementation of our model in the latest version of rheotool, localized shear bands in industrial applications can be reliably simulated using a today's workstation.


Inertioelastic effects on a spiral vortex flow instability
Noa Burshtein1, Konstantinos Zografos2, Amy Q. Shen1, Rob J. Poole2, and Simon J. Haward1
1Micro-Bio-Nanofluidics, Okinawa Institute of Science and Technology Graduate Univers, Onna-son, Okinawa 904-049, Japan; 2School of Engineering, University of Liverpool, Liverpool, England L69 3GH, United Kingdom

High molecular weight polymer additives can suppress inertial flow instabilities and reduce turbulent drag. Yet exactly how the polymer does this is difficult to study. For Newtonian fluids, beyond a critical Reynolds number (Re.), an inertial instability in the cross-slot geometry results in the formation of a single steady streamwise vortex, providing a good model system to study vortex flow. A novel configuration of cross-slot allows...
Flow velocimetry in the cross-section of the vortex as Re is increased. Using polymeric fluids of incrementally increasing elasticity (El), we are able to precisely quantify the critical conditions for instability and the subsequent intensification of streamwise vorticity. Increasing El at low levels causes dramatic reductions in both Rec and the vorticity growth. For El ≈ 1, vorticity is completely suppressed and a purely-elastic instability emerges beyond a critical Weissnberg number (Wi). Dimensionless phase diagrams in Re-Wi and Re-El phase space delineate regions of stable flow from those of inertia and elasticity-dominated instabilities. Our findings shed valuable insight into the action of polymer on vortices and bridge the gap between inertial and elastic instabilities in intersecting flows.

**Tuesday 15:20 Emerald I**

**Flow of wormlike micellar solutions around microfluidic cylinders with high aspect ratio and low blockage ratio**

Simon J. Haward¹, Naoyuki Kitajima², Kazumi Toda-Peters¹, Tsutomu Takahashi², and Amy Q. Shen¹
¹OIST, Onna-son, Okinawa, Japan; ²Nagaoka University of Technology, Nagaoka, Niigata, Japan

We employ time-resolved flow velocimetry and birefringence imaging methods to study the flow of a well-characterized shear banding wormlike micellar solution around a novel glass-fabricated microfluidic circular cylinder. In contrast with typical microfluidic cylinders, our geometry is characterized by a high aspect ratio $a = H/W = 5$ and a low blockage ratio $b = 2r/W = 0.1$, where $H$ and $W$ are the channel height and width, and the cylinder radius $r = 20$ mm. The small cylinder radius allows access up to very high Weissenberg numbers $1.9 < Wi < 3750$ while inertial effects remain entirely negligible (Reynolds number, $Re < 0.0001$). At low Wi values, the flow remains steady and symmetric and a birefringent region (indicating micellar alignment and tensile stress) develops downstream of the cylinder. Above a critical value $Wi_c = 60$ the flow transitions to a steady asymmetric state, characterized as a supercritical pitchfork bifurcation, in which the fluid takes a preferential path around one side of the cylinder. At a second critical value $Wi_c = 130$, the flow becomes time-dependent, with a characteristic frequency $f_0$ close to the reciprocal of the Maxwell relaxation time. This initial transition to time dependence has characteristics of a subcritical Hopf bifurcation. Power spectra of the measured fluctuations become complex as Wi is increased further, showing a gradual slowing down of the dynamics and emergence of harmonics. A final transition at very high $Wi_c = 3$ corresponds to the re-emergence of a single peak in the power spectrum but at much higher frequency. We discuss this in terms of possible flow-induced breakup of micelles into shorter species with a faster relaxation time.

**Tuesday 15:40 Emerald I**

**Stabilizing effect of a viscoelastic outer medium on a fluid thread**

Claudiu Patrascu, Istvan Magos, and Corneliu Balan
Hydraulics, REOROM, University Politecnica of Bucharest, Bucharest, Romania

The present study is concerned with the stability analysis of a liquid thread (viscous or viscoelastic) in the presence of a viscoelastic outer fluid. Following Tomotika’s approach for the case of two immiscible Newtonian fluids, a dispersion relation is obtained between the temporal growth rate and the wave number of the perturbation. The presence of elastic properties is introduced via the Jeffreys model, which is further reduced to the Newtonian model. The study emphasizes and compares their effect on the dispersion relation, and that of the different combinations between them. We show that an external viscoelastic medium has a stabilizing effect on the fluid thread, decreasing the value of the maximum growth rate of disturbance. Also, the study points out that, in the linear limit, the most stable combination is found to be that of a Newtonian fluid thread with an outer Maxwell type fluid. Furthermore, if both fluids have the same viscoelastic properties then the instability of the thread is similar to its Newtonian correspondent.

**Tuesday 16:30 Emerald I**

**Jet instability of a shear-thickening concentrated suspension**

Maxime Liard¹, Akihiro Sato², Jérémy Sautel², Didier Lootens³, and Pascal Hébraud²
¹Sika Technology AG, Zürich, Switzerland; ²Université de Strasbourg, Strasbourg, France

We investigate the flow of a concentrated suspension of colloidal particles at deformation rates higher than the discontinuous shear-thickening transition shear rate. We show that, under its own weight, a jet of colloidal suspension, when concentrated enough simultaneously flows and exhibits properties typical of a solid state: it sustains tensile stress and transmits transverse waves. This results in a new flow instability: the jet is submitted to rapid transverse oscillations, that we characterize.

**Tuesday 16:50 Emerald I**

**Dynamics of the interface between immiscible fluids in confined geometries**

Eugen Chiriac¹, Titus Sava², Mihnea-Claudiu Stoica², Diana Broboana⁴, and Corneliu Balan³
¹National Institute Microtechnologies, Bucharest, Romania; ²REOROM, University Politehnica of Bucharest, Bucharest 060042, Romania; ³Hydraulics, REOROM, University Politehnica of Bucharest, Bucharest, Romania

The study is dedicated to the experimental investigations of the interface dynamics between a pure viscous liquid and a viscoelastic fluid. The process is characterized by the measurements of the interface velocity and the vorticity distribution in its vicinity. A special attention if given to the visualization of the flow field in the neighborhood of the wall, following the dynamics of contact angle of the interface with the solid walls. The interface is studied in two confined geometries: (i) a Hele-Shaw cell, and (ii) a microchannel with a contraction flow. The visualizations and measurements of the velocity distributions are performed with a stereo microPIV from DANTEC. Numerical simulations of the interface evolution will be also presented for the case of two generalized Newtonian immiscible fluids in contact.
Tuesday 17:10 Emerald I

Elastic instabilities in pressure-driven channel flow of thixotropic-viscoelasto-plastic fluids with and without shear-banding
Hugo A. Castillo and Helen J. Wilson
Department of Mathematics, University College London, London, United Kingdom

Several recent experiments have shown that channel-flow of highly shear-thinning viscoelastic fluids can be linearly unstable even at very low Reynolds numbers. We use the Bautista-Manero-Puig (BMP) model to attempt to capture the physics of these instabilities. For a thixotropic-viscoelasto-plastic fluid, we obtain an analytic solution for the steady-state velocity profile dependent on our fluid parameters that is able to predict a large variety of base states. We derive dimensionless groups to compare the effects of the viscoelasticity, plasticity, and thixotropy on the flow stability. We find that sinusuous perturbations are slightly more unstable than varicose modes, and dominant thixotropy can stabilise the flow, but instability occurs when the viscoelastic timescale is much longer than both those of thixotropy and plasticity. Additionally, given an unstable flow, the thixotropic structure recovery rate determines the growth rate of instability. Our results are in agreement with experiments. Lastly, we extend our analysis to thixotropic-viscoelasto-plastic fluids with shear-banding. Although both interfacial and bulk modes are present, we show that the latter ones are dominant and have similar characteristics to the instabilities seen for the case without shear-banding.

Tuesday 17:30 Emerald I

Stabilisation of the purely-elastic instabilities in cross-slot geometries using surface tension
Mahdi Davoodi, David Dennis, and Rob J. Poole
School of Engineering, University of Liverpool, Liverpool, England L69 3GH, United Kingdom

The cross-slot geometry consists of mutually bisecting rectangular channels with two opposing inlets and two opposing outlets. In such geometries, due to presence of a free stagnation point at the centre of the geometry, a significant strain rate may develop that is of particular interest in the design of extensional rheometers for example. In the current work, we simulate two phase viscoelastic fluid flows in this geometry using a volume of fluid method. The stress components of the viscoelastic material are simulated using a simplified Phan-Thien and Tanner model with a log-conformation approach. The combined effects of the capillary number (the ratio of the surface tension force to the viscous force), the Weissenberg number (the ratio of the elastic forces to viscous forces), extensibility parameter (ε) and the solvent-to-total viscosity ratio (β) of each of two phases and the ratio of the total viscosities of two fluids (the K parameter) are investigated in 2D geometry. It is shown that the surface tension force plays an important role in the shape of the interface of the two fluids near the stagnation point. By reducing the surface tension force the interface of the two fluids becomes curved and this can consequently change the curvature of stream lines in this region. In this scenario, for fixed values of β, Wi, ε and K parameters the surface tension is shown to have a stabilising effect on the associated steady symmetry-breaking instability. The K parameter is shown to change the location of the stagnation point and the interface position of the two fluids. By increasing the K parameter, the local value of the Weissenberg number near the corners of the geometry is significantly increased and this can consequently lead to a time-dependent purely-elastic instability in 2D geometries. Finally, the Weissenberg number and ε parameter have a destabilising and stabilising effect, respectively.
to the breaking of polymer chains underflow. More precisely, at the second passage, the flow rate at which mobility reduction is maximum depends on the flow rate during the first pass. We propose a universal relation between the flow rate at which the maximum occurs for the second injection and one of the first injection. This relation is independent of molecular weight, concentration, solvent quality, and viscosity. This relation allows predicting the degradation under successive passes.

Tuesday 14:40 Emerald II

**Nonlinear shear rheology of entangled polymers diluted in oligomer matrix**

Hamid Taghipour¹, Dimitris Vlassopoulos², and Evelyne van Ruymbekè³

¹The Division of Bio- and Soft Matter, IMCN, Université catholique de Louvain, Louvain-la-Neuve 1348, Belgium; ²Institute of Electronic Structure & Laser, Foundation for Research and Technology Hellas, FORTH, Heraklion, Greece; ³The Division of Bio- and Soft Matter, IMCN, Université catholique de Louvain, Louvain-la-Neuve 1348, Belgium

The relaxation dynamics of molten monodisperse polymers are well described by tube-based theories in the linear viscoelastic regime. However, predicting their behavior under large shear rates is still a challenge today and many questions still need to be addressed. The objective of the present work is to investigate the role played by the molecular environment on the stretch and orientation state of linear polymer chains under strong shear flow. To this end, we diluted a long linear polystyrene (PS) of molar mass of 820 kg/mol into PS oligomers, at different concentrations varying from 5wt% to 50wt%. The transient shear behavior of these samples was then measured for a large range of shear rates (corresponding to Rouse-Weissenberg numbers from 0.09 to 90), using a strain controlled rotational rheometer equipped with a cone-partitioned plate geometry. From the comparison between the data and their analysis by means of the TMA tube-based model, we attempt at understanding and rationalizing the different scaling laws observed in the shear thinning regime, as well as the transient stress response and in particular the importance of the stress overshoot as function of the long chains concentration. We examine how shear flow affects the capability of the chains to create new entanglements and how this property depends on concentration. Our results provide a framework for developing a rigorous understanding of the nonlinear shear rheology of entangled polymers.

Tuesday 15:00 Emerald II

**Nonlinear rheology of semiflexible polymer solutions**

Tadashi Inoue, Yuka Goto, Yuki Okada, and Osamu Urakawa

Osaka University, Toyonaka, Japan

Nonlinear rheology of a model semiflexible polymer, cellulose tris(phenyl carbamate), CTC, in TCP solution was examined. In a previous study, we demonstrated that linear viscoelasticity of the CTC / TCP solutions can be separated into three modes, link-orientation, bending, and tension modes with the aid of rheo-optical measurements. Steady state viscosity measurements on the CTC solutions indicated that they show shear thinning behavior similar to flexible polymer solutions, which may be characterized with the Cox-Merz rule. Nonlinearity of the link-orientation mode could be described with FENE-P model. The nonlinearity of the bending mode is slightly weaker than that of the rotational mode, although a theory predicts stronger nonlinearity. The tension mode also showed a similar shear thinning behavior. At higher shear rates, startup flow measurements indicated the strain hardening behavior due to the finite extensibility of chain.

Tuesday 15:20 Emerald II

**λ-DNA solutions at high shear rates**

Haider Dakhil¹, Silvia Steiner¹, Sharadwata Pan², Natalie Germann², Barbara Kappes³, and Andreas Wierschem¹

¹Lehrstuhl für Strömungsmechanik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany; ²Fluid Dynamics of Complex Biosystems, Technische Universität München, Freising, Germany; ³Lehrstuhl für Medizinische Biotechnologie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

DNA solutions are paradigmatic systems for studying the rheology of polymer solutions. We study buffered aqueous solutions of λ-DNA at shear rates up to about $10^3$ s⁻¹. At low shear rates, our data nicely merges with literature values [1]. At high shear rates, the viscosity function of the solutions levels off into an infinite-shear viscosity plateau. Hence, DNA viscosity functions are now available for the entire shear-rate range from the first Newtonian plateau to that of infinite-shear viscosity. The shear rates are accessed with a narrow-gap rheometer at gap widths down to 20 µm [2]. Apart from the viscosity function, we study the normal-stress differences and discuss their implications at the high shear rates and particularly in the infinite-shear viscosity plateau. To see whether the DNA is degraded at high shear rates, we also study our samples with agarose gel electrophoresis.

We study polystyrene (PS) stars in melt and in blend with linear PS chains by means of atomistic molecular dynamics simulations. By using a particularly designed protocol for the equilibration of the melts, we prepare star melts with a range of functionalities, tuning their mutual penetration. The atomistic approach together with the used protocol for the preparation allow us to obtain information about the structural and dynamical properties of the PS star-like polymer melts, not easily accessible by experiments or coarse-grained simulation models.

We analyze the intramolecular structure as well as the morphology of the material as a function of the star functionality. A comparison of the properties of stars in two external environments, i.e., in melt and in a blend with linear chains of a length of the star arm, is also made. We quantify the actual slowing down of the dynamics close to the star core, which is believed to be responsible for the extraordinary viscoelastic properties of the stars. We show that the dynamical heterogeneities related to the star-like architecture are more pronounced in the translational motion in comparison to the rotational dynamics of the star arms. We compare our data with experimentally measured quantities, such as segmental relaxation times and glass transition temperature.

To our knowledge, our study provides for the first time an insight into the morphology and dynamics of polystyrene stars at nanoscale, with the aim to shed light on origin of experimentally measured phenomena.
The inverse ed, which may be explained by the Haward and Thackray model. The relaxation of polymers into the liquid state has been a topic in recent years due to its appealing features such as extremely low vapor pressure, excellent thermal and chemical stability, tunable solvation, non-flammability, and high ionic conductivity. The combination of polymers with ILs and their versatile tunable phase transition behaviors have been proposed for preparing novel soft materials with broad possible applications e.g., polymer electrolytes, nano-encapsulations and actuators. Up to date, most research work is mainly focused on the phase separation, crystallization and sol-gel transition in different polymer/IL systems driven by the specific interactions. However, on the smaller scale, the chain entanglement, conformation, and even the structural relaxation of polymers in ILs still remain unclear. The changes of IL structure could result in significant variation of the specific interaction between ILs and polymer, especially the hydrogen bonding. In this study, the influence of IL structure (alkyl chain length on the imidazolium ring, dualcation, and anions) on the segment motion and polymer chain entanglement was investigated by rheology, DSC and FTIR measurements in detail. With the increase of alkyl chain length, the relaxation of entanglement becomes faster, which is dominated by the competition between the hydrophobic interactions and potential new material applications.

Symposium BE
Blends, Emulsions, Foams & Interfacial Rheology
Organizers: Anniina Salonen, Jan Vermant and Jose Munoz

Tuesday 17:30 Emerald II
Rheological and mechanical properties of polystyrene with hydrogen bonding
Wendi Wang, Jeppe Madsen, Anne L. Skov, Ole Hassager, and Qian Huang
Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark

Recent work [1] shows that polystyrene can become flexible at room temperature by stretching the melt at a rate faster than the inverse Rouse time, followed by rapid quenching below the glass transition temperature (Tg). Long-lasting flexibility and good humidity resistance, combined with other advantages such as light weight and interference immunity, make this flexible polystyrene a good candidate for plastic optical fibers (POFs). However, improvements are required to prevent cracks during filament bending.

In the present work, we investigate if crack prevention can be achieved by introducing hydrogen bonding (carboxylic acid groups) into the backbone. The rheological and mechanical properties of polystyrenes with different acid group contents are studied and compared to the corresponding pure polystyrene sample. Linear viscoelastic (LVE) measurements have experimentally confirmed that all the tested samples have a similar number of entanglements per chain (Z), suggesting that the acid groups do not form (or weakly form) hydrogen bonds at temperatures above Tg. This is further confirmed by non-linear extensional behavior measured by stretching the samples in uniaxial extensional flow. However, different mechanical properties at room temperature have been observed, which may be explained by the Haward and Thackray model.[2] The polystyrene fibers are also compared with poly(methyl methacrylate) (PMMA, the most used core material for POFs) to show the potential of polystyrene as plastic optical fibers.


Tuesday 17:50 Emerald II
Segmental motion and chain entanglement of PMMA with the addition of ionic liquids
Yanhua Niu, Xi He, and Guangxian Li
College of Polymer Science and Engineering, Sichuan University, Chengdu, China

Ionic liquids (ILs), known as a kind of low temperature molten salts consisting of anions and cations, have been becoming a hot topic in recent years due to its appealing features such as extremely low vapor pressure, excellent thermal and chemical stability, tunable solvation, non-flammability, and high ionic conductivity. The combination of polymers with ILs and their versatile tunable phase transition behaviors have been proposed for preparing novel soft materials with broad possible applications e.g., polymer electrolytes, nano-encapsulations and actuators. Up to date, most research work is mainly focused on the phase separation, crystallization and sol-gel transition in different polymer/IL systems driven by the specific interactions. However, on the smaller scale, the chain entanglement, conformation, and even the structural relaxation of polymers in ILs still remain unclear. The changes of IL structure could result in significant variation of the specific interaction between ILs and polymer, especially the hydrogen bonding. In this study, the influence of IL structure (alkyl chain length on the imidazolium ring, dual-cation, and anions) on the segment motion and polymer chain entanglement was investigated by rheology, DSC and FTIR measurements in detail. With the increase of alkyl chain length, the relaxation of entanglement becomes faster, which is dominated by the competition between the hydrogen bonds and free volume. Longer alkyl chain length of ILs leads to lower Tg. By changing the type of anions from [PF6] - to [TFSI] -, Tg also shows decrease trend at higher IL content. These results will shed new light on both the theoretical research of polymer dynamics in blends or solutions with specific interactions and potential new material applications.

Symposium BE
Blends, Emulsions, Foams & Interfacial Rheology
Organizers: Anniina Salonen, Jan Vermant and Jose Munoz

Tuesday 14:20 Europe II
Interfacial behavior of asphaltene subfractions and their role in emulsion coalescence
Alexandra Aliche and Jan Vermant
Soft Materials Group, ETH Zurich, Zürich CH-8093, Switzerland

To lower the ecological impact of oil production, the efficient and effective separation of water-in-crude oil emulsions is a generic problem in the oil industry. These emulsions are formed during production and transportation of crude oils and are often observed to be highly stable, which has been attributed to the presence of asphaltenes and resins. Since asphaltenes are classified based on solubility class rather than on chemical composition, different functionalities can be present depending on the origin of the crude oil or on how they are extracted. As a consequence, the interfacial behavior of asphaltenes has been studied for decades but still remains not well understood. Specifically, the mechanisms for emulsion stabilization are not clear. One approach that seems promising is the use of subfractions in order to limit the functionalities present and thus gain a better insight into their individual role on emulsion stability. Our goal is to relate the rheological properties measured in state-of-the-art interfacial rheology devices with microscopic phenomena related to stability. To this end, first we perform a thorough rheological characterization of different asphaltene subfractions[1] at fluid-fluid interfaces. Interfacial shear rheology experiments are carried out using a double wall-ring geometry
mounted on a stress-controlled DHR-3 rheometer. Dilatational rheological properties are investigated using a home-built radial trough device[2], which enables isotropic deformations of the interface and direct surface pressure measurements as opposed to the commonly used oscillating pendant drop technique. Then, the thin-film balance technique is employed to study the thinning behavior and rupture of a liquid film, which mimics the dynamics of drainage of the intervening continuous phase between two coalescing droplets.


Tuesday 14:40 Europe II

High-frequency dynamics and interfacial rheology of a crude-oil droplet in water

Nicolas Abi Chebel¹, Antoine Piedfert¹, Benjamin Lalanne², Christine Dalmazzone³, Christine Noik³, Olivier Masbernat³, and Frédéric Risso⁴
¹LGC-IMFT, Université de Toulouse & CNRS, Toulouse 31432, France; ²LGC-FERMaT, Université de Toulouse & CNRS, Toulouse 31432, France; ³IFPEN, Rueil-Malmaison 92852, France; ⁴IMFT-FERMaT, Université de Toulouse & CNRS, Toulouse 31400, France

Low and high frequency oscillations of a crude-oil pendant drop in water have been investigated. At low frequency, fluid viscosity and inertia are negligible (quasi-static regime), which allows a direct determination of the dilatational interface rheology. At high frequency, eigenmodes of inertial shape oscillations are excited, which allows us to determine their frequency and damping rate from resonance curves. Identification of these parameters is relevant for the prediction of the deformation and breakup of drops in any unsteady flow, without any prior knowledge of either the chemical composition or the precise rheological properties of the interface. Then, interfacial rheology is related to interface dynamics by solving the coupled linearized Navier-Stokes equations for the two liquid phases and the interface. It turns out that the rheology of an oil/water interface is of intrinsic nature rather than of compositional origin. It is found that the crude oil/water interface behaves as a two-dimensional viscoelastic material, with dilatational and shear properties of same order of magnitude. For moderately aged interfaces (< 5,000 s), low frequency (0.1-1 Hz) and high frequency (10-100 Hz) experiments lead to similar results that are well described by the Soft-Glassy Rheological model (SGR), as already reported in the literature for low-frequency experiments. In particular, the surface elasticity and viscosity at high frequency can be extrapolated from low-frequency measurements by means of a simple power law of the frequency. In return, for older interfaces (> 5,000 s), elasticity becomes predominant compared to viscosity, and the SGR type model does no longer apply. This approach opens the way to the modeling of fragmentation of oil/water droplet flows with complex interfaces in turbulent flows, an important issue regarding flow assurance in oil recovery processes as well as in many other industrial sectors involving the processing of emulsions.

Tuesday 15:00 Europe II

Investigation of interfacial characteristics of vegetable proteins in O/W emulsion formulations

Noemi Baldino¹, Olga Mileti², Francesca R. Lupi¹, and Domenico Gabriele³
¹DIMES, University of Calabria, Rende, CS 87036, Italy; ²University of Calabria, Rende, Italy

Proteins are widely used in the food industry due to their nutritive value and potential functional properties. Nowadays, it is increasing the vegetable proteins usage, because of their low cost in comparison to the animal proteins and because they are a good alternative for people suffering of some type of allergy and intolerance or simply for the new trend in lifestyle and environmental sensitivity. Many vegetable proteins can be used as emulsifiers due to their potential surface activity. They can also improve the stability of emulsions, foams and can be used as a basis for soft foods due to their amphiphilic nature. Consequently, the aim of this work is to study the vegetable proteins ability to stabilize multiphase food products, without sedimentation. The objective was prosecuted by investigating the interfacial rheological properties of three vegetable protein systems at O/W interface: soy, as a benchmark, hemp and brown rice proteins. The importance of investigating simple systems is due to the specific effect that each ingredient confers to a final product in the processed food. In fact, the final quality and the design of these materials require a deep rheological understanding of individual ingredients and their relation to food processing. The surface characterization on these three systems was performed using a pendant drop tensiometer and an interfacial shear rheometer (ISR). Static measurements of surface tension versus time, relaxation experiments and dilation properties in asymptotic kinematic were performed at O/W interface. Data were interpreted with appropriated models to obtain information about protein diffusion, film structure, stability and elasticity of the layer at the interface. Then interfacial shear properties were also obtained to investigate the long-term phenomena. Finally, model emulsions were obtained using the investigated proteins and their stability was studied by contrast phase microscope analysis and bulk rheological tests.

Tuesday 15:20 Europe II

Influence of bulk and interfacial viscosity on bubble coarsening

Maxime Schneider¹, Douglas Alves¹, Emmanuelle Rio¹, Cyprien Gay², and Anniina Salonen¹
¹Laboratoire de Physique des Solides, Orsay, France; ²Matière et Systèmes Complexes, Paris, France

Foams coarsen as gas transfers from small bubbles to bigger ones. The rate of coarsening depends on how easily gas can transfer, and how easily the bubbles can dilate, contract and rearrange to relax the stresses that build up in the evolving structure. Therefore, both the viscosity of the surfaces and the bulk solution can influence the rate of coarsening.

We use a model system of two connected bubbles where the rate of coarsening is not limited by diffusion [1] to explore how the bulk and interfacial viscosity change the dynamics of the coarsening process. We model our bubbles as two connected dashpots and thus combine experiments and
modelling in the analysis of the evolution of two bubbles. Our model captures the rate of coarsening well as viscous stresses act to slow down the process. The model can therefore be used to estimate when coarsening will be limited by gas diffusion or by viscous stresses.


Tuesday 15:40 Europe II  BE12

**Effect of bulk and interfacial rheology on the stability of bubbles in oleogels upon changes in temperature**

Saikat Saha¹, Bernard P. Binks², and Valeria Garbin¹

¹Department of Chemical Engineering, Imperial College London, London, United Kingdom; ²Department of Chemistry and Biochemistry, University of Hull, Hull HU6 7RX, United Kingdom

Oil foams, or oleofoams, which are dispersions of gas bubbles in a continuous oil phase, are common in the food industry as well as the oil and gas industry. Recently, crystals of fatty acids/alcohols or edible waxes have been found to provide stability and extend the applicability of oleofoams in aerated food formulations. There is evidence that the stabilisation is due to the adsorption of crystals onto the interface of the bubbles by the so-called Pickering mechanism. Because the excess crystals remaining in the continuous oil phase form an oleogel, an effect of the bulk rheological properties of the continuous phase is also expected. In addition, these systems are extremely sensitive to temperature, because heating can melt the crystals, while cooling at different rates results in the formation of crystals with different size and shapes. Here, we evaluate the contributions of bulk and interfacial rheology below and above the melting point of a wax forming an oleogel in sunflower oil. We study the dissolution behaviour of single bubbles using video microscopy on a temperature-controlled stage. To assess the different rheological contributions, we compare the behaviour of a bubble embedded in an oleogel foam and a bubble extracted from the oleogel foam and re-suspended in oil. In the first case, the bubble owes its stability to both bulk and interfacial rheology, while in the second case the contribution of the interfacial dilational rheology alone can be observed. We find that below the melting point of the wax, bubbles in the oleofoam are stable whereas bubbles that are only coated with wax crystals dissolve. Both systems are unstable against dissolution when heated above the melting point of the wax. These findings are rationalised through independent bulk rheological measurements of the oleofoam and oleogel at different temperatures, as well as interfacial rheological measurements of the wax-coated interface using a pendant drop method.

Tuesday 16:30 Europe II  BE13

**Linear viscoelastic properties of cellulose nanocrystals – lauroyl ethyl arginate**

Agnieszka Czakaj, Marcel Krzan, and Piotr Warszynski

Nanostructures of Soft Matter, Institute of Catalysis and Surface Chemistry PAS, Kraków 30-239, Poland

Lauroyl ethyl arginate (LAE), arginine-based edible surfactant has gained researchers' interest due to its antibacterial properties. It has also the potential to be used as surfactant in cosmetics. There is special interest in society nowadays in foam-based cosmetics with attractive type of application on skin. From manufacturers' side, economic use of ingredients and application through one-press release of the appropriate amount is desirable. Such application prevents much overse or spillage and is environmentally-friendly. Surfactant-based foams have limited stability due to drainage, coalescence and coarsening. Cellulose nanocrystals (CNC) of high aspect ratio are excellent rheology modifier for potential products. They can boost the existence of foam from submilimolar surfactant solution whereas without them the foam brakes immediately. It was shown that they form viscoelastic interfacial network after salt addition due to aggregation of nanoparticles.[1]

Foam shear rheology was studied in bulk in cone-plate geometry in linear viscoelastic region. Bulk elasticity of foams with 0.3 weight percent of CNC was higher than for sodium dodecyl sulphate in mixture with 2 weight percent disc-shaped laponite nanoparticles [2]. In our study we also show foam viscoelastic behaviour in relation to pH changes.

Support from National Science Centre of Poland (grant no. 2016/21/B/ST8/02107) is gratefully acknowledged. AC has been partly supported by the EU Project POWR.03.02.00-00-I004/16.


Tuesday 16:50 Europe II  BE14

**Wall slip of direct and inverse emulsions under various conditions**

Xiao Zhang¹, Elise Lorenceau², and Philippe Coussot¹

¹Université Paris Est, Laboratoire Navier, Champs sur Marne 77420, France; ²LiPhy, Université Grenoble Alpes, Grenoble 38000, France

Foams, emulsions, concentrated suspensions and colloids, may glide along smooth solid surfaces, in the sense that the bulk material apparently moves as a rigid block for a stress lower than the yield stress. This effect may be used to facilitate the transport of products such as in food digestion, cosmetic sensory perception, coal water slurry in pipes, fresh concrete pumping over long-distance, removal of food debris and microbial films. So far wall slip has been mainly studied in “ideal” conditions, i.e. simple shear, and with a limited set of well controlled systems. Here we use model materials (direct and inverse emulsions) and determine the variations of wall slip properties depending on material parameters (droplet size, concentration) and boundary conditions of the flow. The wall slip characteristics are determined from long creep tests at different levels and from internal measurements of the velocity profile in capillary or Couette flow as determined by MRI. First we show that the “slip yield stress” is due either to edge effects in relation with evaporation then pinning around the line of contact, or to a kind of adhesion of the suspended elements to the wall [1]. Then we show that for all our systems, below the yield stress, the slip velocity vs shear stress (from which the slip yield stress,
determined precisely, has been removed) relationship is linear [2]. Moreover, the corresponding value for the apparent slip layer (a few tens of nanometers) appears to be almost independent of the concentration, the droplet size and the surface state and roughness. Also, it is independent of an additional normal force, and it is the same for free surface flows. Nevertheless, we show that for elongational flow conditions (i.e. traction test), wall slip can still occur, with now a much larger apparent wall slip layer (around 10 microns) [3].


Tuesday 17:10 Europe II

Enhanced bubble removal from yield-stress fluids using acoustic waves

Brice Saint-Michel1, Marco De Corato2, and Valeria Garbin1
1Department of Chemical Engineering, Imperial College London, London, United Kingdom; 2University of Barcelona, Barcelona, Spain

Toothpaste, mascara, inkjet ink, concrete and ice cream are examples of yield stress fluids present in our daily lives. Processing of such materials introduces gas bubbles, the smallest of which remain trapped after processing since buoyancy effects may not suffice to yield the fluid [1]. While some yield-stress products --in food and concrete industries-- require a controlled amount of bubbles, most applications look for complete bubble removal, motivating the development of controlled, non-destructive bubble removal techniques.

We explore the use of acoustic waves to promote the removal of small bubbles from simple yield-stress fluids. Acoustic waves induce rapid periodic dilation and compression of the bubble, which in turn exert extensional deformation of the fluid matrix. When the bubble vibration is sufficiently large, local yielding of the fluid occurs and bubbles of any size may rise in the fluidized corona surrounding them. For instance, ultrasound at 20-30 kHz excites the deformation of small bubbles (100-200 µm) that are otherwise difficult to remove.

We developed a model combining the Rayleigh-Plesset equation governing bubble dynamics with the Saramito model which accounts for the fluid rheology both above and below the yield stress. We use extensional yielding criteria [2] to deduce the amount of yield stress and predict optimal conditions for bubble removal.

We compare these theoretical results to experiments performed in Carbopol and a water-in-oil, transparent dense emulsion. Close to resonance, a subharmonic instability in the bubble shape has been evidenced. We investigate the instability threshold and its impact on bubble net motion. We finally discuss the relevance of this process in terms of potential applications for non-ideal [3].


Tuesday 17:30 Europe II

Changing foam elasticity with a colloidal gel

Alesya Mikhailovskaya1, Veronique Trappe2, and Anniina Salonen1
1Laboratoire de Physique des Solides, Université Paris Sud, Orsay 91405, France; 2Department of Physics, University of Fribourg, Fribourg 1700, Switzerland

Many commonly used foamed materials have continuous phases that are complex fluids. Despite of this, a complete description of the mechanical properties of such foams is still missing. We study foams with a colloidal gel as the continuous phase. The gel starts to form inside the foam as the measurement starts. This allows us to probe the elastic response of foams with a continuous phase elastic modulus ranging continuously from 0 to 2000 Pa in a single experiment. The elastic modulus of the foam is initially controlled by the elastic modulus of the bubbles, and as the gel forms its contribution becomes dominant. An additive model, as commonly used for solid foams, can describe the mechanical properties of the resulting material. However, we need to take into account a change in the gel time because of confinement. We show that gelled foams are an interesting model system to probe soft foam elasticity, once the change in the gel formation due to confinement is taken into account. The results can help towards a more rational basis for the design of foam based materials as the interplay between the bulk and the foam elasticity is clarified.

Tuesday 17:50 Europe II

Thermo-rheology: A new tool to understand liquids & melts?

Laurence Noiret1, Patrick Baroni1, Ursula Windberger2, and Kostya Trachenko3
1CEA-Saclay, Laboratoire Léon Brillouin, Gif-sur-Yvette Cédex 91191, France; 2Center for Biomedical Research, Medical University Vienna, Vienna, Vienna 1090, Austria; 3School of Physics and Astronomy, Queen Mary University of London, London E1 4NS, United Kingdom

Based on the Frenkel assumption, viscoelastic fluids and liquids are supposed to exhibit elastic shear waves at high frequency only (GHz). This model is conventionally adopted indicating that liquids contrast with solids by a lack of low frequency shear elasticity (Maxwell-type VE behavior). However a nearly "static" elasticity (0.1-10Hz) has recently been identified at sub-millimeter scale implying that fluids flow above an elastic threshold[1]. The "static" shear elasticity concerns both simple liquids, complex fluids (polymer melts, molecular glass formers, Van der Waals liquids, ionic liquids, H-bond liquids including liquid water) including physiologic fluids. Low frequency shear elasticity has profound implications on fluidic transport mechanisms and thermodynamics. We will detail the identification of static elasticity in physiological fluids in

Tuesday Afternoon
the case of blood and blood plasma. We will emphasize the importance of integrating sample dimensions and boundary conditions as fluidic parameters. Novel properties as flow induced cooling and thermal shear banding will be presented. Low frequency shear elasticity challenges molecular approaches, while flow induced cooling challenges interpretations in terms of viscous friction heating. It opens the route to alternative theoretical models predicting a length-scale dependence of viscoelastic parameters [2-4], revisiting the Frenkel zero-frequency shear elasticity assumption by introducing solid-like gap-based approach [4].


Symposium FP

Food, Pharmaceutics & Cosmetics

Organizer: Patricia López Sánchez

Tuesday 14:20 Europe III

Rheological and microstructural characteristics of organogels: the role of solvent
Francesca R. Lupi¹, Maria P. De Santo², Federica Ciuchi³, Noemi Baldino², and Domenico Gabriele¹
¹DIMES, University of Calabria, Rende, CS 87036, Italy; ²Department of Physics, University of Calabria, Rende, CS 87036, Italy; ³CNR-NANOTEC Department of Physics, University of Calabria, Rende, CS 87036, Italy

The production of hard fats with a reduced saturated fat content is a recommended goal for increasing the health aspects of fat-based foods. Therefore, rheology is a strong tool to design, with predictive models, new fats with high nutritional content, low in saturated fat, free of trans fatty acids, and characterised by textural properties comparable to those of commercial fats. Organogels are widely studied as potential healthy replacers of traditional saturated fats. Their mechanical properties are affected by different factors, such as the organogelator concentration, the preparation conditions and the solvent characteristics. In this work, the role of solvent on the rheological properties of organogels was investigated. Vegetable oils, (rice, sunflower and castor oil) were used as solvents, for producing organogels with monoglycerides of fatty acids or fatty alcohols (policosanol) as gelators. Moreover, two non-edible oils were also used for analysing the properties of solvents completely different in nature with respect to the edible ones, for a better comparison of the results. The rheological investigation of organogels was deepened with a microscopic analysis, given by polarised light and atomic force microscopy, and X-rays to study the crystallinity of the system. Infrared spectroscopy was also used to analyse the intermolecular interactions of gelators, resulting in interesting information about the effect of oil polarity on the driving forces promoting structuration. This investigation showed that when solvents of a similar chemical nature are used, their physical properties, such as polarity, are related to the properties of organogels, such as the onset of crystallisation temperature and the stiffness of the material. Anyway, so far these physical parameters seem insufficient to describe the role of solvents when oils of a different chemical nature are compared.

Tuesday 14:40 Europe III

Millet flour as a partial and total replacement of wheat flour: Rheological properties of sweet batters
Pawel Ptaszek, Anna Ptaszek, Joanna Kruk, and Katarzyna Latkowska
¹Faculty of Food Technology, University of Agriculture in Cracow, Kraków 30-149, Poland

A new approach for producing batter from millet flour as gluten-free components and mixed with wheat flour, was explored. This work focused on tests of rheological properties of the batters, planning the experiments in such way as to be able to compare the obtained results with a reference batter using only wheat flour. The experiment plan involved the partial replacement of the wheat flour part with new starch raw materials: millet flour. Large Amplitude Oscillatory Shear (LAOS) was used to study the nonlinear viscoelastic properties of raw batters. It was demonstrated that all tested systems exhibited viscoelastic properties, but the area of linear dependency was limited to deformation value of 0.01. After passing that value, a transition into nonlinear viscosity range was observed. The systems containing millet flour exhibited the intersection of G' and G
Food 3D printing: Interplay of printing conditions, heat transfer and rheology
Pietro Rando\textsuperscript{1}, Gareth O. Coffin\textsuperscript{1}, Sadie Fleetwood\textsuperscript{1}, Joseph L. Keddie\textsuperscript{2}, and Marco Ramaoli\textsuperscript{1}
\textsuperscript{1}Department of Chemical and Process Engineering, University of Surrey, Guildford GU2 7XH, United Kingdom; \textsuperscript{2}Department of Physics, University of Surrey, Guildford GU2 7XH, United Kingdom

3D printing is a bottom-up fabrication process in which materials are fused and/or sintered and deposited layer-by-layer to form a three-dimensional object that is customised in shape and/or composition. 3D printing is used for several sectors, including prosthetics, automotive, aeronautics and more recently pharmaceuticals and food. This fabrication process is currently being investigated to produce personalised food, targeting the specific nutrition and texture requirements of each age group.

Food 3D printers often use a paste extrusion technology, whereby a non-Newtonian material is extruded in a thin filament through a nozzle and is deposited in a thin layer. This layer should fuse with the layer below and undergo a rapid change in rheological properties to maintain the desired print geometry.

In this research, a set of elementary 3D printing operations was identified and used to understand quantitatively the impact of the rheological properties on the geometrical accuracy of the prints.

In particular, the effect of the formulation on chocolate rheological properties and its impact on printing were considered for different nozzle temperatures and printing velocities. The yield stress of the printed material after deposition has an important effect on the stability of the 3D printed products. The cooling dynamics of the printed chocolate was characterised in-situ, during printing, using a thermal camera and interpreted using a heat transfer model. The experimental temperature profiles and the rheological properties explained the differences in structural stability. The printing strategy significantly affects the cooling dynamics, which in turn affects the rheological properties and the resulting geometrical accuracy.

The understanding provided by this work can help to optimise food 3D printing conditions and product formulation.

Structural and rheological properties of a gluten-free bread with Tetraselmis chuii microalgae incorporation
Cristiana Nunes, Isabel Fernandes, Isabel Sousa, and Anabela Raymundo
LEAF Research Center, Instituto Superior de Agronomia, University of Lisbon, Lisboa 1349-017, Portugal

This work is part of Algae2Future project, that intends to explore the microalgae potential to be a low-carbon-footprint healthy food ingredient. One of the objectives is to increase nutritional quality of gluten-free (GF) bread by addition of microalgae biomass, maintaining its high sensory quality. Bread is a staple food with specific characteristics in terms of development of cohesive and elastic dough structure. Since gluten confers unique rheological properties to yeast-leavened baked products, the replacement of gluten is a technological challenge. The use of alternative ingredients, including starches, GF flours, hydrocolloids, proteins and additives, allows an improvement in doughs structure. Tetraselmis chuii (Tc) is approved by EFSA and has a high protein content, which is an important requirement to be used in bread with specific nutritional profile.

Introducing microalgae in food systems can also impart changes in structure, which can be availed for the development of GF bread. However, consumers are very sensitive to the physical and sensory characteristics, which induces limitations on the total level of microalgae incorporation. A formulation based on buckwheat flour, rice flour and potato starch, with Tc biomass, was studied with technological and nutritional advantages. HPMC was used as a thickening agent, binding water and increasing dough’s viscosity. The impact of different levels of Tc biomass incorporation on GF doughs and breads was studied by means of empirical and fundamental rheology methods. Microdough-Lab Perten instrument was used to determine the water absorption of the GF flours mixture with different Tc content and to study their mixing and pasting properties. Fundamental SAOS rheology (frequency sweeps after fermentation) and texture profile analysis (TPA) were also used to evaluate dough’s structure. In the loaves, volume, moisture, aW, colour and TPA during the aging process were evaluated.

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The role of Psyllium gels on the structuring of gluten-free fresh pasta – a rheological approach
Patricia Fradinho, Isabel Sousa, and Anabela Raymundo
LEAF Research Center, Instituto Superior de Agronomia, University of Lisbon, Lisboa 1349-017, Portugal

The development of gluten-free (GF) food products constitutes a challenge. Over the last years several strategies for GF pasta development have been adopted, focusing mainly on the use of hydrocolloids and proteins, unconventional flours and thermally pre-gelatinized flour. The authors have already successfully developed GF pasta with pre-gelatinized rice flour. However, the rheological and texture characteristics of this formulation could be improved by reinforcing its structure and conferring extensibility. Psyllium husk is a functional ingredient with a health claim approved by FDA for reducing the risk of coronary heart disease. Underlying this approval is Psyllium’s high soluble fibre content, that translates in high water absorption and gelling ability, making it possible to use Psyllium as a structure builder that mimics the gluten matrix. Rheology is a crucial tool for assessing the optimal processing conditions of Psyllium gels prior to dough incorporation. The following variables were studied: size particle, gel processing temperature, psyllium gel concentration and ratio in the fresh pasta. A detailed characterization of the rheology behaviour of Psyllium gels and pasta dough was performed by SAOS measurements (temperature, time and frequency sweeps) in a MARS III controlled-stress rheometer coupled to a UTC-Peltier system for temperature control. A parallel plate sensor system with 35 mm diameter was used. The pasta quality was assessed by determining its cooking quality parameters, texture characteristics (stickiness and cutting)
Sol-gel transition of aqueous chitosan-ßglycerophosphate solutions

Michela Abrami1, Gabriele Grassi2, Domenico Larobina3, and Mario Grassi1
1Engineering and Architecture Department, University of Trieste, Trieste, Italy; 2Department of Life Sciences, University of Trieste, Trieste, Italy; 3Istituto per i Polimeri i Compositi ed i Biomateriali, CNR, Napoli I-80055, Italy

Hydrogels represent reliable systems for the delivery of drugs, including those based on nucleic acids. Indeed, hydrogel nature, structure, and response to physiological or external stimuli strongly influence the delivery mechanisms of entrapped active molecules, making hydrogel very attractive for many pharmacological and biomedical applications. In this study, the attention was focused on a thermo-gelling hydrogel, composed of chitosan/ß-glycerophosphate, which can be injected in situ and induced to gelify at physiological pH and temperature. Particular care was devoted to study the effect of temperature on the gelation kinetics and on the gel final properties, two very important aspects in the light of clinical applications. The rheological characterization (temperature and frequency sweep test) evidenced the important effect of temperature (15°C = T = 47°C), on both the gelation kinetics and the gel final properties. In particular, we found that similar slow gelation kinetics and weak gels occurred below 30°C while similar faster gelation kinetics and stronger gels took place for T = 30°C. This result was confirmed by means of a Low Field NMR (LF-NMR) characterization. Interestingly, it was possible evaluating, by means of rheology and LF-NMR, the time evolution of the polymeric network mesh size upon gelation. Thus, the importance of rheology in a socially relevant field (drug delivery) is evident.

Keywords: Chitosan, thermal gelation, Low Field NMR

Can rheology be useful in the cystic fibrosis frame?

Michela Abrami1, Massimo Maschio2, Marco Confalonieri3, Fabio Gerin1, Barbara Dapas4, Rossella Farra1, Romano Lapasin1, Mario Grassi1, and Gabriele Grassi2
1Department of Engineering and Architecture, University of Trieste, Trieste I-34127, Italy; 2IRCSS Child Hospital Burlo Garofolo, Trieste, Trieste, Italy; 3Cattinara University Hospital, Pulmonology Dept., Trieste, Italy; 4Department of Life Sciences, University of Trieste, Trieste, Italy

Lung functionality assessment in cystic fibrosis (CF) patients is extremely relevant as most patients succumb to respiratory failure. Inflammatory markers (IMs) and respiratory functional tests, i.e. forced expiratory volume in the first second (FEV1), are used to test pulmonary functions/inflammation and to guide therapy. However, FEV1 has suboptimal reproducibility, and IMs detection is costly. Thus, aim of this work is to use rheology to assess lung functionality/inflammation recurring to the characterization CF patients sputum. Despite some known problems connected with the rheological characterization of inhomogeneous biological fluids, we found that there is a statistical linear correlation among the sputum elastic properties (G’ evaluated at different frequencies) and FEV1, while no correlation exists between the sputum viscous properties (G’’ evaluated at different frequency, and zero shear viscosity) and FEV1. In addition, we found a not linear correlation between sputum elastic properties and the average magnetic relaxation time of water hydrogens entrapped in the sputum. We believe that the potential impact of these rheological findings on health is considerable.

Dynamic rheological comparison of silicones for podiatry applications

Carlos Alberto Gracia Fernández1, Díaz-Díaz Ana-Maria2, Sánchez Silva Barbara1, Tarrío Saavedra Javier4, Janeiro Arocas Julia5, López Becerro Jorge6, and Artiaga Díaz Ramón1
1TA Instruments, Madrid, Madrid 28049, Spain; 2Department of Mathematics, University A coruña Higher Polytechnic University Col, A Coruña, A Coruña 15010, Spain; 3Department of Naval and Industrial Engineering, University of A Coruña Higher Polytechnic University College, A Coruña, A Coruña 15010, Spain; 4Department of Mathematics, Higher Polytechnic University College, Universidade da Coruña, A Coruña, A Coruña 15010, Spain, 5Department of Health Science, Faculty of Nursing and Podiatry, Universidade da Coruña, A Coruña, A Coruña 15010, Spain; 6Department of Naval and Industrial Engineering, Higher Polytechnic University College, Universidade da Coruña, A Coruña, A Coruña 15010, Spain; 7Department of Naval and Industrial Engineering, Higher Polytechnic University College, Universidade da Coruña, A Coruña, A Coruña 15010, Spain

This work shows an effective methodology to evaluate the dynamic viscoelastic behavior of silicones for application in podiatry. The aim is to characterize, compare their viscoelastic properties according to the dynamic stresses they can be presumably subjected when used in podiatry orthotic applications. These results provide a deeper insight which extends the previous creep-recovery results to the world of dynamic stresses developed in physical activity. In this context, it should be taken into account that an orthoses can subjected to a set of static and dynamic shear and compressive forces.
The mechanical properties of cells are crucial to their dynamic behaviors, including migration, differentiation, and tissue formation. However, a comprehensive description of the rheological properties of cell monolayers is still lacking due to the technological challenges at both applying and measuring small perturbations from cell monolayers. Previously, we have reported on use of a customized sliding plate rheometer, referred to as the live cell monolayer rheometer (LCMR), to measure the stress relaxation behaviors of cell monolayers, and found that cell monolayers exhibit a viscoelastic solid behavior. Here we will report on the recent developments of a step-stress experiment set-up. In step stress experiments, a pair of anti-Helmholtz coils generates a constant magnetic field gradient parallel to the sample plate, which applies a constant shear stress onto the cell monolayer through a magnet glued on the top plate. The deformation is quantified through an inverted microscope. In step stress experiments, we observed a viscoelastic solid behavior of cell monolayers similar to that observed in step strain experiments. LCMR has proven powerful at studying collective behaviors of cell monolayers. To address the industrial need of minimizing the contact lens/cornea adhesion, we investigated the muco-adhesive strength of corneal epithelial cells against a series of silicone hydrogel materials with varying crosslinking densities. The residual modulus, indicative of the adhesive strength of corneal epithelial cell monolayers, showed an interesting minimum against the crosslinking density of hydrogel materials. We proposed a competitive mechanism between a morphology-dominated adhesion mechanics and a stiffness-induce cell response to explain the observed nonmonotonic relationship between the crosslinking density and the adhesive strength. The results showed that the rheological behaviors obtained from LCMR can potentially probe the molecular interactions between cell monolayers and substrates of various properties.

Blood clots are complex fiber networks that shear stiffen. The network structure and the integration of red blood cells (RBC) into the fibrin network are different in regard to underlying diseases and to the vasculature in which the clots are formed. Clot architecture determines its compliance, and in the future the thrombo-embolic risk of individuals might be predicted through the nonlinear behavior of blood clots. To simulate blood hypercoagulability, native whole blood and plasma from a laboratory rat strain was used and data were compared to blood and plasma from healthy human volunteers. Clots were generated in cone-plate symmetry at 37°C. After gaining a final modulus they were exposed to increasing sinusoidal stress amplitudes at constant frequency (1rad/s). Human whole blood (WB) shows the typical shear stiffening behavior, whereas rat WB clots break before they can relevantly shear stiffen. Rat WB clots show a higher linear G', and the nonlinear behavior starts at higher stresses (indicated by Lissajous) and is short. Clots show a denser network compared to human and appear "brittle". In blood plasma, shear stiffening starts at lower stresses and its degree increases with the decrement of platelets in both species. RBCs stabilize clots against deformation, but also hinder the detection of pure network effects that might be indicative of the thromboembolic risk of patients.
Effect of fibrinogen, dextrans and PEG on the blood coagulation kinetics

Nadia Antonova, Vasilka Paskova, and Ivan Ivanov

Department of Biomechanics, Institute of Mechanics to the Bulgaria Academy of Sciences, Sofia 1113, Bulgaria

A comparative study of effect of fibrinogen, dextrans with different molecular weight and PEG on the mechanical properties of the in vitro induced blood clot is evaluated by means of rheological and electrorheological methods. Blood clotting mechanism was investigated by means of the rheological and electrorheological methods at different flow conditions and under electric field. The kinetics of clot formation was measured and analysed in parallel with changes of the conductivity of the forming clot, estimated by electrorheological method.

The study aims to evaluate the effect of Fibrinogen, Dextrans and PEG on the blood coagulation kinetics through the rate of coagulation of the forming clot by means of the rheological and electrical blood properties.

Whole human normal blood conserved with CPD-A1 solution was used for experiments. The process of clotting was initiated in vitro and the kinetics of clot formation, viscous properties of blood clot was evaluated at a steady flow conditions. Fibrinogen solutions, dextrans of different molecular weight (70,000, 250,000 and 500,000 daltons, respectively) as well as PEG of 3,000 Da in saline were added to the whole human conserved blood and a coagulation process was initiated adding 0.1% CaCl2 aqueous solution to the samples. Their effect was assessed by comparing the results for full coagulation times as well as the meanings of the dynamic viscosity and conductivity of the coagulated whole human conserved blood. The results show that fibrinogen, dextran 250 and PEG solutions accelerate the coagulation process while solutions of dextran 70 and dextran 500 delay it in comparison of the whole human conserved blood.

The results can be used to understand coagulation processes.

Keywords: thrombus formation in vitro; kinetics of clot formation; viscosity of blood clot, conductivity, fibrinogen, dextrans, PEG

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Linking fibrin clot structure, rheology and embolisms

Mohamad Alajami1, Landry Seyye2, Denis C. Roux1, Benoit Polack2, and Francois Caton1

1Laboratoire Rheologie et Procedes, University Grenoble Alpes, Grenoble, France; 2TIMC TheREx, Centre Hospitalier Universitaire, University Grenoble Alpes, Grenoble, France

The main step of blood clot formation is the polymerisation of fibrinogen into fibrin. Fibrin is a biopolymer gel which provides most of the blood clot mechanical properties. Those properties are thought to be crucial in many cardiovascular diseases where clots are known to develop anomalously and detach or fail, thus provoking embolisms which can be fatal. While environmental factors (pH, ionic strength,...) are known to influence the polymerization and mechanical properties of fibrin, the possible influence of pathophysiological variations of fibrin structure (under physiological conditions) on the mechanical properties of the clot are unexplored.

To test this possibility, we first characterized in detail the multi-scale structure of two fibrin gels prepared under identical physiological conditions which mimic healthy and pathological plasma clots. The fibrin fibers obtained from healthy-like fibrinogen are straight and almost crystalline while those made from pathological-like fibrinogen are basically amorphous, showing also a much denser micronic network.

Surprisingly, the linear viscoelastic properties of those two fibrin gels show non-significant differences. Conversely, differences appear in the rupture behaviour of those clots, the healthy-like clot showing a progressive rupture, while the other shows an abrupt rupture.

Those results open very interesting perspectives for the understanding of the relationship between abnormal clots rheology and structure, embolisms and cardiovascular diseases.

Mechanics of dense actin networks

Olivia du Roure1, Julien Heuvingh1, Pierre Bauër1, and Joe W. Tavacoli2

1PMMH-ESPCI, Paris, France; 2Department of Energy of Conversion and Storage, Present address: Technical University of Denmark, Roskilde, Denmark

Actin is a protein which self-assembles into highly dynamic filaments organized within the cells in different kind of meshworks. The combination of mechanics and dynamics of these network enables the cell to achieve essential processes like migration, deformation or integration of external mechanical cues. Rheology of actin suspensions has been extensively studied at low concentrations at which the elastic response of filaments within the network is entropic, in agreement with their semi-flexible nature. Here we focus on more concentrated actin networks whose density and microscopic architecture is closer to the one found in cells as their assembly is based on a cellular biochemical machinery relying on a complex of protein called Arp2/3. The Arp2/3-assembled actin networks are dense and dendritic; the typical distance between filaments is small compared to their persistence length implicating that actin filaments behave as rigid rod. We probed the elastic responses of these particular actin networks by a new technique based on magnetic particles. In particular, we have shown that the elasticity is strongly non linear with a non linear modulus that decreases linearly towards low values when applied stress decreases.
Biomaterial with tailored rheological properties to protect cells in additive manufacturing

Edwin-Joffrey Courtial and Christophe A. Marquette

The use of biomaterial including living cells in additive manufacturing, is one of the most advance technology in tissue engineering and regenerative medicine. 3D bioprinting presents the capacity to produce efficiently and in a cost-effective way, tissues with cell density and shape recapitulating human tissue behaviours. Nevertheless, the use of LDM (liquid deposition modelling) technic presents limitations such as cells mortality, due to a high shear stress value inside the dispensing system. In this study, we evaluated the biomaterial capacities to protect cells in our additive manufacturing process. The method is based on the relation between bioink viscoelastic properties, sizing of deposition system and cells viability. To access the shear stress map inside the bioprinting system, a specific algorithm was developed based on Poiseuille tube flow of a pseudoplastic power law fluid. Different kind of cells were used to understand the capacity of them to withstand stress. Living and labelled necrotic cells were counted before and post-printing process to evaluated cell viability and total cell recovery in various conditions. In view of results, the shear stress gradient can be controlled through bioink rheological behaviour and sizing of dispensing system. Cells viability seems to be depend on shear stress value but also duration. In any case, it was shown that using adequate bioink rheological properties, cells viability can be optimal whatever the dispensing system and the applied flow value; protecting cells during the 3D bioprinting process. In future, the recording of data in a library will allow biomaterial engineers to use algorithm in reverse engineering mode, to tailored 3D bioprinting system and/or biomaterials properties in function of the kind of cells. A disruptive innovation could be applied in autograft technique to ensure the success of surgical intervention.

Prediction of the brain tissue viscoelastic response based on the measured relaxation modulus

Barbara Zupancic
University of Novo mesto Faculty of mechanical engineering, Novo mesto 8000, Slovenia

Brain tissue exhibits a complex mechanical behaviour. This is an important reason for the difficulties when modelling mechanics of brain and/or when establishing experimental protocol to capture its mechanical response. Knowing the real material properties of brain tissue and utilizing the adequate analytical and numerical tools is important, for example, to get an insight into the biomechanics of traumatic brain injury, or to more precisely evaluate the difference between the mechanical response of the healthy tissue, and the sick or injured tissue, or when developing advanced surgical simulation systems for modern surgical planning and training. Literature reports that the brain tissue behaves nonlinearly viscoelastic. In order to capture the main features of the nonlinear behaviour, the existing models used require experimental data from several different experiments in order to provide necessary modelling parameters. The methodology we propose enables prediction of the frequency-dependent moduli and the constant strain rate response of brain tissue based only on the known stress relaxation data. Developed approach utilizes the time-strain superposition to construct the master curve from the stress relaxation segments. The obtained master curve then serves as an input for prediction of the frequency-dependent behaviour by applying constitutive viscoelastic laws, and an input for prediction of the constant shear rate response by utilizing the nonlinear internal-clock viscoelastic model. Based on the results, we may justifiably speculate that the proposed approach serves well for prediction of the investigated brain mechanical responses. Since the methodology is evidently supported by the physical background, we believe that the presented outcomes contribute to a better understanding of the phenomenology of brain mechanics and its constitutive modelling, and may have and important influence on dealing with the challenging tasks exposed at the beginning of this paper.

Constitutive modeling of human skin

Jibbe Soetens1, Gerrit Peters2, and Cees Oomens1
1Biomedical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands; 2Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands

Skin mechanics is important for research fields like pressure ulcer etiology and the interaction between skin and devices or materials such as shaving appliances. Prediction of the mechanical response of skin is essential. From a mechanical point of view, skin should be considered as a highly dynamic and complex composite that has non-linear viscoelastic, anisotropic and heterogeneous properties. The aim of this work was to develop a constitutive material model that is based on experimental evidence and capable of capturing the complex mechanical behaviour of skin. We implemented the constitutive model in a finite element code as a fibre-reinforced matrix with an elastic fibrous component and an isotropic, non-linear viscoelastic matrix. The fibres only contribute in extension and provide anisotropic properties. Heterogeneity was included by gradually varying the stiffness over skin thickness. Parameter optimization with respect to the experimental results was performed using an iterative parameter estimation method. Three intrinsically different experiments were performed on ex-vivo human skin. Large amplitude oscillatory shear (LAOS) combined with digital image correlation (DIC) on the cross-sectional area to assess heterogeneity resulting in the non-linear viscoelastic properties of the matrix. Secondly, biaxial tensile tests to determine the fibre contribution, again combined with DIC to determine local deformations and assess anisotropy. Finally, micro indentation experiments to determine the contribution of volume change. The model showed to be able to describe the non-linear viscoelastic response to LAOS. The anisotropic response of human skin to biaxial tensile loading was described more accurate than the well-established Ogden model. Overall our constitutive model is capable of describing the complex mechanical behaviour of human skin under shear, biaxial tension and indentation with a single parameter set.
2D and 3D rheology of organic matter in the surface microlayer of the ocean and other natural waters. Implications for modulating cross-surface substance and energy exchange and the control of climate

Ian R. Jenkinson\(^1\), Elisa Berdalet\(^2\), Wei-Chun Chin\(^3\), Haibing Ding\(^4\), Florence Elias\(^5\), Zhuo Li\(^6\), Alenka Malej\(^7\), Xavier Mari\(^8\), Laurent Seuront\(^9\), Jun Sun\(^10\), Tim Wyatt\(^11\), Oliver Wurl\(^12\), and Igor Emri\(^13\)

\(^1\)Inst. Oceanol, CAS Key Lab of Mar. Ecol. Env. Sci., Chinese Academy of Sciences, Qingdao, Shandong 266071, China; \(^2\)Institute of Marine Sciences CSIC, Barcelona, Spain; \(^3\)Department of Bioengineering, University of California, Merced, CA, United States; \(^4\)Key Laboratory of Marine Chemistry Theory and Technology, Ocean University of China, Qingdao, Shandong, China; \(^5\)Laboratoire Systèmes et Matières complexes, CNRS UMR 7075, Université Paris Diderot, Paris, France; \(^6\)State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai, Shanghai 200092, China; \(^7\)Institut za Biologijo Ljubljana, Piran 6330, Slovenia; \(^8\)CNRS IRD Mediterranean Institute of Oceanography, Aix-Marseille Université, Marseille 13288, France; \(^9\)UMR 8187 Laboratoire d’Océanologie et de Géosciences, Centre National de Recherche Scientifique, Wimereux 62, France; \(^10\)Tianjin Key Laboratory of Marine Resources and Chemistry, Tianjin University of Science and Technology, Tianjin, Tianjin 300457, China; \(^11\)Wyatt Laboratory, Gondomar, Pontevedra 36378, Spain; \(^12\)Institute of Chemistry and Biology of the Marine Environment, Carl von Ossietzky Universität Oldenburg, Wilhelmshaven 26382, Germany; \(^13\)Dep Mech. Polymers and Composites, Cent. Experimental. Mech., University of Ljubljana, Ljubljana 1125, Slovenia

The surface microlayer (SML) of natural waters including the ocean is about 60-80 µm thick. It contains strong chemical and physical gradients. Organic matter (OM) originating mainly from phytoplankton production fuelled by sunlight accumulates in the SML. It consists of carbohydrates (mainly hydrophilic), proteins (mainly amphiphilic), lipids (hydrophobic), polymeric molecules bearing mixed radicals, as well as living organisms and dead detrital particles. Gas bubbles are sometimes abundant both below the SML and in foam (including whitecaps) above the SML. At windspeeds <=13 m s\(^{-1}\), OM in the SML reduces fluxes of heat and momentum energy, as well as water and greenhouse gases. At higher windspeeds, control of fluxes is more complex, involving and including flying foam, spray, aerosols, microalgal spores, bacteria and viruses. Foam coverage varies as a function both of windspeed and OM types and amount. It thus also depends on abundance, taxonomic composition and physiological state of ambient microalgae and probably bacteria. Foam reflects solar energy back into space, thus reducing solar heating and penetration of photosynthetically active radiation. Satellite-measured mean coverage of the ocean surface by foam ranges from <1% to >6%. In this presentation we will review published 2D and 3D rheological measurements made in the SML compared to underlying water, wave and ripple damping, and measurements of OM-modulation of evaporation and exchange of both gases and energy. The SML is the gateway through which all substances and energy exchange between the ocean and the atmosphere. OM in the SML is thus studied in large international research programmes sponsored by the United Nations bodies in order to understand and predict climate change in relation to human activity. Despite the largely physical nature of trans-SML exchange, little understanding of OM rheology or surface science is present in these programmes. Here we bring this opportunity to the attention of the AERC.
Towards miniaturization: how does confinement affect the break-up and coalescence of droplets in shear flow
Paula Moldenaers
Chemical Engineering, KU Leuven, Leuven 3001, Belgium

For many years, polymer blending has been recognized as a method to generate materials with improved properties. When recycling polymers, the resulting morphology is also often multiphasic. The properties of these polymer blends are highly dependent on the flow-induced phase morphology. The bulk dynamics of immiscible blends during flow is relatively well understood, especially when the system consists of Newtonian components. Stimulated by the trend towards miniaturization, studies have recently focused on flow of immiscible blends in confined geometries. In that case, the morphology development is not only affected by the material properties and the flow type, but also by the degree of confinement.

Here, we present an overview of the morphological changes in dilute, immiscible two-phase blends in confined shear flow. Droplet break-up and droplet coalescence are investigated systematically for a range of viscosity ratios, where the droplets are visualized in a counter rotating shear flow cell equipped with a microscope. It was observed that geometrical confinement promotes droplet break-up when the viscosity ratio is above 1, which implies that the critical capillary number for break-up decreases. At viscosity ratios around one, confinement does not affect the conditions for droplet break-up whereas the critical capillary number increases with increasing confinement at viscosity ratios below 1, indicating that confined droplets are stabilized by the presence of the walls. Numerical simulations, using a boundary-integral method, in collaboration with TUE, reproduce and elucidate these findings.

For coalescence, on the other hand, the effects of confinement are qualitatively similar for all viscosity ratios; confinement decreases the coalescence angles and renders coalescence feasible at higher capillary numbers and initial offsets. Moreover, confinement induces a lower initial offset boundary, below which the approaching droplets reverse flow direction without coalescence. However, the range of conditions for which coalescence occurs decreases with increasing viscosity ratio. The results are supplemented with finite element numerical simulations in 2D to explain the observations.

Interaction between latex binder and the secondary fluid in the capillary suspension of Li-ion battery slurry
Jieun Park1, Norbert Willenbacher2, and Kyung Hyun Ahn3
1Seoul National University, Seoul, Republic of Korea; 2Karlsruhe Institute of Technology, Karlsruhe, Germany; 3Seoul National University, Seoul, Republic of Korea

Capillary suspension is getting more attention due to its facile applicability for modifying flow behavior of industrial slurries. Capillary suspension is a ternary system which employs capillary force by adding a small amount of the secondary fluid and completely changes the flow behavior of the suspension. Exploiting the concept of capillary suspension to industrial slurry system brings about several problems since industrial slurries contain more components such as binders. Previous works have mainly focused on the ternary system without any other component. Therefore, the interaction between the components of capillary suspension and the binder has not yet been thoroughly investigated. The effect of this interaction needs to be examined since binder is a key controlling factor for mechanical properties of industrial materials. In this study, Li-ion battery system is selected as a model slurry. The interaction between styrene-butadiene rubber (SBR) binder of Li-ion anode slurry and the secondary fluid, octanol, is determined by rheological measurement and optical microscopic images. The binder concentration and mixing condition affect the flow behavior and network structure when capillary suspension includes a binder. Mixing condition such as mixing time and mixing rpm is a key factor for adjusting the degree of network structure. Based on experimental data, it can be inferred that mixing condition alters the distribution of SBR binder in the capillary suspension. Interfacial tension measurement supports this finding. An enhanced understanding of this interaction in this study allows us to easily distribute binders to a specific location and precisely design the microstructure of industrial slurries using the concept of capillary suspension.
**Wednesday 9:50 Europe I**

**Dynamics of alginate/ceramic suspension droplets impacting a bath of calcium ions**

Julie Godefroid¹, David Bouttes², Etienne Barthel², and Cecile Monteux¹

¹Laboratoire de Soft Matter Science and Engineering, ESPCI Paris, Paris, France; ²Saint-Gobain, Cavaillon, France

Dripping alginate solutions into a bath of calcium ions is a robust process to obtain gelled capsules which can be used in various applications [1,2]. This process relies on the fact that calcium ions bridge the alginate chains of the droplets to form a rigid gel. The Reynolds and Weber numbers, defining the competition between inertia, viscous dissipation and surface tension forces are known to influence the final shape of the droplets[1]. Indeed inertia tends to drive the spreading of droplets upon impact with the bath while high droplet viscosity and surface tension tend to limit their extension upon impact.

However, very little is known about the time evolution of the droplets shape during impact and how they relax during their fall into the calcium bath. Using a high speed camera, we study the shape of alginate/ceramic suspensions as they impact and penetrate a bath of calcium ions. We observe that droplets extend as they impact the surface and that they relax to a more spherical shape inside the bath.

As expected, the drops maximum elongation increases with increasing impact velocity and decreasing droplet viscosity. The effect of the calcium concentration in the bath is less intuitive. As it increases, the maximum extension of the droplets tends to decrease and the droplets tend to relax faster to a spherical shape. This relaxation is related to a syneresis phenomenon which instantaneously occurs as the droplets hit the bath: the gelled membrane tends to shrink by expelling water. This phenomenon puts the outer membrane under tensile stress and therefore is the driving force of the bead relaxation. However, the droplet's relaxation in the bath stops before reaching a perfect sphere. We perform mechanical simulations to understand the evolution of the stress in the gelled membrane as the droplet relaxes and gells.


**Wednesday 10:10 Europe I**

**Coarse-grained particle simulation of capillary bridges in ternary suspension systems**

Jin Hwan Choi, Howon Jin, and Kyung Hyun Ahn

Seoul National University, Seoul, Republic of Korea

In a capillary suspension, two immiscible liquids and solid particles interact to form a sample-spanning network. One of the liquids are added in a small amount and results in forming capillary bridges between the particles, inducing an attractive force that is several magnitudes higher than that of Van der Waals force [1]. The resulting sample-spanning network conveys increased rheological properties that can aid improvements in edge shape, pore distribution, and heat resistance [2-4]. Although the capillary suspension has much potential for industrial purposes, the relatively short amount of time since its first observation has limited its research on experiment basis. In this study, we attempted to bring particle simulation and coarse-grained capillary interaction together to describe capillary suspension systems in simulation. To avoid the complexity of describing complicated behaviors such as droplet deformation and contact angle, a coarse-grained interaction is developed. Also, the secondary fluid droplet is described as a part of sphere with constant volume in the simulation. By doing so, the aforementioned complexity is reduced to just one variable, the contact angle. The results indicate that the low shear viscosity versus volume fraction does follow the tendency shown in experimental results, and further details will be discussed in the presentation.


**Wednesday 10:30 Europe I**

**The solid regime and the solid-liquid transition of waxy oil**

Diogo V. Andrade and Philippe Coussot

Laboratoire Navier, IFSTTAR, Université Paris-Est, Champ-sur-Marne, Île-de-France 77420, France

During the production and transportation of crude oils the materials can reach temperatures as low as 4°C, i.e., the seabed temperature. At low temperatures the solubility of high molecular weight components in the oil decreases, precipitating mainly the n-paraffins as crystal structures, so that these materials now exhibit a yield stress due to the concentration of wax crystals [1]. These suspensions were shown to exhibit reversible or irreversible viscosity evolution in the liquid regime [2-3]. Here we focus on the mechanisms of the solid-liquid transition from the material state obtained after static cooling. First we show that under these conditions the material exhibits a very high elastic modulus (in the order of 10⁶ Pa) for low deformation. We then study its behavior through a series of creep tests imposed at different stress levels to the material in the same initial state, which requires following a careful procedure to prepare again the material between each stress level. We show that the solid-liquid transition occurs in the form of a viscosity bifurcation, i.e. below some critical stress the material deforms in a very limited way, beyond some critical stress it collapses and starts to flow at a very shear rate. Moreover, by this means we can identify properly the critical deformation at which such transition occurs, which appears to be very low (say, around 0.005%). This behavior strongly contrasts with that observed after breakage: now the material presents a much lower elastic modulus and larger critical strain. We deduce that such material exhibits a brittle structure after static cooling, due to strong but fragile links between crystals, and a soft structure after breakage of this initial structure, which can only be recovered after a thermal cycle.
Flow dynamics of concentrated star-like micelles: A superposition rheometry investigation into the relaxation mechanisms

George Petekidis1, Alan Jacob1, Andreas Poulos2, Alexander Semenov3, and Jan Vermant4
1Institute of Electronic Structure & Laser, Foundation for Research and Technology Hellas, Heraklion, Greece; 2Forschungszentrum Jülich GmbH, Jülich, Germany; 3Institut Charles Sadron, Strasbourg, France; 4Soft Materials Group, ETH Zurich, Zürich CH-8093, Switzerland

The steady state flow of a concentrated dispersion of star-like micelles above the colloidal glass transition concentration is interrogated by superimposing a small amplitude straining motion orthogonal to the main flow direction. Strain amplitude sweeps reveal that the linear response region of the orthogonal perturbation increases with increasing flow rate, consistent with a fluidization of the materials. Orthogonal dynamic frequency sweeps (ODFS) are obtained for a wide range of shear rates probing the full flow curve. The shear-induced fluidization of the initially glassy suspension is more clearly evidenced by the appearance of a crossover frequency \( \omega_c \) in ODFS, which steadily increases reflecting a faster structural relaxation under shear. The dependence of \( \omega_c \) on the shear rate is sub-linear and follows a power law with exponent of 0.8. We show that the shape of the orthogonal viscoelastic spectrum changes at a critical shear rate, indicative of a structural relaxation modulus that changes from exponential at lower shear rates to multi-step with alternating exponential and power law response at higher shear rates. We finally provide a theoretical framework which explains the observed sub-linear power law dependence of the crossover frequency and relates it with the shear rate dependence of the viscosity measured by the flow curve.

Relevance of time-dependent particle interactions in the physical aging of colloidal suspensions

Francesco Bonacci1, Xavier Chateau2, Julie Goyon3, Eric M. Furst2, and Anaël Lemaître1
1Université Paris Est, Laboratoire Navier, Champs sur Marne 77420, France; 2Department of Chemical & Biomolecular Engineering, University of Delaware, Newark, DE, United States

Aging is a widespread phenomenon found in the soft glassy state. Understanding its origin and its impact on the mechanical properties is thus of critical importance, both from a physical and a technological point of view. Through advanced scattering techniques, rheological experiments and confocal microscopy, aging has been extensively studied in dilute colloidal gels and repulsive hard-sphere glasses, while its characterization in dense colloidal suspensions remains elusive, especially for strong attractions between particles which prevent structural reorganization. In this work, we focused on the mechanical aging of model colloidal suspensions in the dense gel state (volume fractions of 0.3-0.4). Through complementary rheology, confocal microscopy and optical tweezers experiments, we studied the behavior of silica suspensions flocculated with addition of calcium chloride. We performed bulk elasticity measurements for different particle sizes, volume fractions and ionic strengths and we found that, whatever the formulation, the shear modulus is a monotonically increasing function of time for all the duration of the measurement. At the same time, using a confocal microscope, we investigated the sample microstructure and we found no significant changes in the network occurring over the same time interval. Here we show that the evolution of the storage modulus is nearly perfectly correlated to the time evolution of the interaction between particles. To do so, we used optical tweezers to form linear aggregates of particles. We followed in time their response to three-point bending tests and clearly found the presence of an effective time-dependent flexural rigidity. Finally, a very simple model has been used to relate the growth in time of the flexural rigidity to the strengthening of the macroscopic suspensions. Our findings unambiguously demonstrate that bond aging can significantly affect the rheological response without invoking changes in the network structure.

Controlling the elasticity of calcite suspensions by ionic species

Teresa Liberto1, Jean Colombani2, Catherine Barentin2, and Marie Le Merrer3
1Faculty of civil engineering, Vienna University of Technology, Vienna A-1030, Austria; 2Institut Lumière Matière, Université Claude Bernard Lyon 1, Villeurbanne 69622, France

Calcite is an extremely widespread material that can be found naturally in rocks and is employed in many industrial fields such as paper filling, pharmaceutical, art or construction. Understanding the mechanical properties of calcite suspensions is a first step to improve the workability of the paste as well as the final properties of solid mineral materials. Here, we show how a macroscopic quantity of the calcite suspensions, namely the elasticity, measured by rheological measurements can be linked to microscopic interactions, via DLVO analysis. Our pure calcite pastes are weakly attractive systems, showing a typical colloidal gel behavior, and characterized by an elastic shear modulus and a critical strain (Liberto et al. 2017). We have tuned the interaction forces between particles by addition of simple ionic species (Ca\(^{2+}\) and OH\(^{-}\)). Rheological measurements are compared to DLVO calculations, obtained by chemical speciations and \( \zeta \) potential measurements on dense suspensions. Addition of calcium hydroxide improves the initial workability of the paste by lowering the elastic modulus of the paste, which is further recovered upon carbonation in contact with atmospheric carbon dioxide. The degree of carbonation is monitored through pH measurements. Besides, we observe a minimum in the initial elastic response for a pH close to 12, correlated to a maximum in the electrostatic repulsion in the DLVO potential. Below this pH,
the main effect is a change in surface potential with calcium concentrations, while at high pH, modifications of the ionic strength and Debye lengths are dominant.

Wednesday 12:20 Europe I

Yielding in depletion gels: a time resolved 3D confocal study
Gabriele Colombo and Jan Vermant
Soft Materials Group, ETH Zurich, Zürich CH-8093, Switzerland

Colloidal gels are a class of soft materials finding widespread use in consumer products and industrial formulations, as well as in emerging technological applications. The microstructural details of the yielding transition in colloidal gels have so far escaped experimental visualization. Pronounced changes in mechanical properties result from subtle, highly localized microstructural rearrangements in a heterogeneous, disordered network, which are difficult to resolve using ensemble averaged techniques as e.g. light scattering. In this work, we evaluate the microstructural basis of thixotropy and yielding by directly imaging colloidal gels during simple shear deformations. The experimental approach relies on the quantitative study of the gel microstructure using high-speed, structured illumination confocal microscopy. Experiments are performed using a rheometer with a home-made shear cell for counter-rotation of the lower glass plate, allowing single particles to be imaged for long times at the stagnation plane. Fast axial scanning is implemented using an electric focus tunable lens, circumventing issues of immersion oil squeeze flow typical of mechanical focus repositioning. The unprecedented combination of temporal and 3D spatial resolution of our setup allows the study of intermediate volume fraction gels at high shear rates and with larger than usual fields of view. First the events at the yield stress are visualized and analyzed, subsequently at low shear rates just past the yielding point, a transient network develops with an increasingly heterogeneous and anisotropic structure, due to local compaction and the formation of large voids. As shear is increased, structural breakdown takes place and the sample is progressively fluidized. For a model depletion gel, such shear-induced transitions are demonstrated to be more crucial in determining the final gel microstructure than variations in the attraction strength itself, showing that flow history (and rheology) matters.

Wednesday 12:40 Europe I

Viscosity measurements of iteratively-perturbed-water
Liana P. Paduanu, Claudia Carotenuto, and Mario Minale
Department of Engineering, University of Campania Luigi Vanvitelli, Aversa, CE 81031, Italy

In recent years, the research group of prof. Elia observed unexpected and intriguing properties of water. In particular, Elia et al. [1] measured several modifications of the properties of ultra-distilled water when it is simply put iteratively in contact with hydrophilic surfaces. The iteratively-perturbed-water presents different properties respect to the original pure-water in terms of electrical conductivity (which can vary of orders of magnitude), pH, heat of mixing with acids, ultraviolet absorption spectra, etc. The authors, also following the pioneering idea of prof. Pollak [2], attributed the change of the water properties to the formation, at the interface with the hydrophilic surfaces, of water-macromolecules solved in “classic” water. A vivid debate is under way in literature among supporters and opponents of this interpretation. The experimental procedure to induce a chemical-physical modification of the water is, in principle, very simple and consists into an iterative process of successive drying and wetting of hydrophilic polymers; more iterations imply stronger water modification. We contribute to the discussion performing, for the first time on this kind of samples, viscosity measurements. We considered samples iteratively perturbed, at different degrees, with Nafion, Cellulose and Craboy polymers. Tests are performed with a rolling ball viscometer (LOVIS-DMA, Anton Paar) suitable to measure very low viscous samples and to detect even very small viscosity changes among them. Density is simultaneously measured. Intrinsic viscosity tests are also run to try to measure the hydrodynamic volume of a possible microstructure dissolved in the iteratively-perturbed-water.


Symposium NF

Non Newtonian Fluid Mechanics & Flow Instabilities (in honor of Prof. Mike Webster)
Organizers: Tim Phillips, Russel Davies, Natalie Germann and Corneliu Balan

Wednesday 9:30 Emerald I

A new finite element formulation for viscoelastic flows: circumventing simultaneously the LBB condition and the high-Weissenberg number problem
Stylianos Varchanis, Alexandros Syrakos, Yannis Dimakopoulos, and John Tsamopoulos
Chemical Engineering, University of Patras, Patras, Greece

In this paper, we propose a new, fully consistent and highly stable finite element formulation for the simulation of viscoelastic flows. In our method, we have implemented equal order interpolants for all variables and a combination of classical finite element stabilization techniques (PSPG/DEVSS-TG/SUPG) with the log-conformation representation of the constitutive equation that has allowed us to obtain numerically stable solutions at high Weissenberg numbers. The validity of the presented FEM framework is testified by comparing the numerical results of our method to those of the literature in three benchmark tests: the 2-dimensional flows of a viscoelastic fluid in a square lid-driven cavity and past a
cylinder in a channel, and the 3-dimensional flow in a cubic lid-driven cavity. We consider both direct steady-state and transient calculations using the Oldroyd-B and linear PTT models. In all cases, we can reach, and in some cases surpass, the maximum Weissenberg number values attainable by mixed finite element methods, but at a considerably lower computational cost and programming effort. In addition, we perform mesh-convergence tests illustrating that the proposed method is convergent and features almost 2nd order accuracy in space.

Wednesday 9:50 Emerald I
**A novel active mixer for yield stress fluids**

Eliane Younes¹, Kamal El Omari², Yann Moguen², Yves Le Guer², Cathy Castelain¹, and Teodor Burghelia¹
¹Laboratoire de thermique et énergie de Nantes, Nantes 44306, France; ²SIAME, Pau 64000, France

Mixing of pasty materials in the absence of inertial contributions (i.e. at low Reynolds numbers) is of a paramount importance to many industrial applications related to food processing, cosmetics, biotechnology and oil field industry. The central aim of the paper is to introduce a novel inline mixing concept able to efficiently mix yield stress fluids by laminar chaotic advection. By simple scaling arguments we demonstrate in the first part of the talk that, in principle, by a judicious choice of the axial inflow rate Q, the amplitude of the rotation of the drums and its frequency, a good mixing could be obtained corresponding to an optimum value of the Strouhal number (St) that depends solely on the mean flow rate via the Péclet number (Pe). We show in the second part of the talk that this phenomenological conclusion is corroborated by the results of direct numerical simulation using a finite volume method. The latter approach allows a parametric study of the domain of mixing efficiency by investigating the role of additional parameters such as the Reynolds number and the ratio of angular to axial velocity. The third part of the talk concerns with an experimental study of the mixing of two yield stress fluids. The mixing efficiency is characterised by a statistical analysis of fluorescent mixing patterns and the inner topology of the chaotic flow is systematically characterised by measurements of the Lagrangian particle trajectories and statistics of the fields of the Finite Time Lyapunov Exponents. The first results obtained have shown that this new inline mixer will be efficient for fluid mixing under some conditions.

Wednesday 10:10 Emerald I
**Yield-stress analysis of elasto-visco-plastic materials in strong extension**

Stylianos Varchanis, Georgia Ioannou, Athanasios Kordalis, Yannis Dimakopoulos, and John Tsamopoulos

Chemical Engineering, University of Patras, Patras, Greece

While much attention has been paid in the rheological response of elasto-visco-plastic materials in shear flows, surprisingly few studies have been focused on pure extensional flows of such materials. This fact is probably associated with the practical difficulties related with the generation of a purely extensional flow field. In addition, recent experiments by Zhang et al. [1] have revealed noticeable differences with respect to the extensional behavior of complex yield-stress materials (e.g. the ratio of the extension yield-stress to the shear yield-stress is larger, by a factor of 1.5, than expected from the standard theory). Such findings indicate the importance of the investigation of yield-stress materials in elongational flows. We propose the standard and optimized [2] cross-slot devices to measure the extensional properties of complex yield-stress fluids. More specifically, we fit the Saramito/Herschel-Bulkley [3] model to a 0.08% Carbopol solution and carry out simulations of elasto-visco-plastic flows in both cross-slot geometries. Performing a wide-range parametric analysis of the dynamics of this stagnation flow, we show that due to the low elasticity of these materials, it is possible to obtain a steady state vorticity-free flow around the stagnation point even for high extension rates. However, in certain cases we find a critical value of the extension rate, above which either steady or transient elastic instabilities take place. The impact of the interplay of plasticity and elasticity on the nonlinear dynamics of these two cross-slot flows are examined in detail. Finally, we examine certain simple ways to extract the material functions from these planar extensional flows.


Wednesday 10:30 Emerald I
**Stability analysis of Taylor-Couette flow of shear-thinning fluids**

Sultan Topayev¹ and Cherif Nouar²
¹SIMPPE, LEMTA, CNRS & University de Lorraine, Vandoeuvre-les-Nancy, Meurthe-et-Moselle 54500, France; ²LEMTA, CNRS & Universite de Lorraine, Nancy, France

In the present communication, we discuss the stability of a circular Couette flow of shear-thinning fluids between two coaxial cylinders with a large gap. The inner cylinder is rotating and the outer one is at rest. The rheological behaviour of the fluid is described by the Carreau model. First, the critical Reynolds number for the onset of Taylor vortices are determined for a large range of rheological parameters. It is shown that the critical Reynolds number defined with the zero shear-rate viscosity decreases with increasing shear-thinning effects. The vortices are smaller than in the Newtonian case and are squeezed against the inner wall. It is also worthy to note that with increasing shear-thinning effects, the characteristic time for the instability to grow increases and the coherence length decreases. Departing from the onset, the weakly nonlinear analysis is carried out up to seventh-order in the amplitude equation. The influence of shear-thinning effects on the flow structure, the torque applied on the inner cylinder and the modification of the viscosity field is characterized. The results are in good agreement with numerical simulations using Freefem++ solver. To complete this study an experimental investigation was performed. The radius ratio of the experimental setup is R1/R2 = 0.4 and the aspect ratio is 30. The flow structure is determined using Particle Image Velocimetry (PIV) and visualizations. New results dealing with the secondary instability are found.
Wednesday 11:20 Emerald I  
**Dean flow of a Bingham plastic through a curved rectangular duct**  
Ian A. Frigaard$^1$ and Miguel Moyers-Gonzalez$^2$  
$^1$University of British Columbia, Vancouver, British Columbia V6T1Z4, Canada; $^2$Mathematics, University of Canterbury Christchurch, Christchurch, New Zealand

Dean flow of a shear-thinning fluid shares many of the same stability characteristics of Newtonian fluids, but with the secondary flow vortices contributing to drag reduction. In considering a yield stress fluid in similar geometries the picture is less clear. Unfortunately the analytical solution in [1] is incorrect, so the flow has been barely studied. Firstly, we expect there to be a critical pressure gradient required for flow onset. Secondly, there is the question of whether or not the secondary flow even exists and in what parameter ranges? Thirdly, does the secondary flow result in breaking of the plug that exists in the leading-order azimuthal velocity? Lastly, there is the question of flow stability. We present new results from our analysis of these questions.


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Wednesday 11:40 Emerald I  
**Pressure- and capillarity-driven flow of Carbopol aqueous solutions in microfluidics geometries: Effect of yield stress and wall slip**  
Raffaele Graziano$^1$, Valentina Preziosi$^2$, Giovanna Tomaiuolo$^2$, Behzad Mohebbi$^3$, Ian Claussen$^3$, and Stefano Guido$^2$  
$^1$DICMAPI, University of Napoli Federico II, Napoli, Italy; $^2$Department of Chemical, Materials and Production Engineering, University of Napoli Federico II, Napoli, Italy; $^3$Procter and Gamble, Schwalbach am Taunus, Germany

There is an increasing interest in the literature about the flow behaviour of yield-stress fluids in confined geometries. Here, we use Carbopol, a high molecular weight, cross-linked polyacrylic acid polymer, in water as a model yield-stress fluid. Carbopol finds application in a broad range of fields, from food and pharmaceutical to drug-delivery and petrochemical thanks to its versatility, biocompatibility and mucoadhesive properties. Both pressure- and capillarity-driven flow of Carbopol aqueous solutions at different concentrations has been investigated by using a microfluidic approach. In particular, glass circular capillaries of different diameters have been used to look at the impact on Carbopol yielding properties. The yield stress estimated from flow velocimetry was compared to values obtained by rotational rheometry and some discrepancy was found. The filling time of the capillaries was also measured as a function of Carbopol concentration and capillary diameter. The data were compared with a simplified model based on the interplay between surface tension and yield stress. The results are discussed in terms of the general problem of yield-stress fluid flow behaviour in complex materials, such as porous media.

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Wednesday 12:00 Emerald I  
**Application of the Liu procedure of thermodynamics to rheology**  
Kwang Soo Cho  
Kyungpook National University, Daegu, Republic of Korea

The Liu procedure [1] is a Lagrange multiplier method to determine entropy flux and entropy production rate. We extended the procedure to extended thermodynamic space spanned by classical and internal variables [2] in order to find a general constitutive equation of stress. The constitutive equation covers viscous fluid, elastic solid and viscoelastic body. Here, classical variables are the ones whose evolution equations can be obtained from conservation laws and kinematic analysis while internal variables are thermodynamic state variables representing microstructure of rheological material. We suggest a systematic method to relate the evolution equations of thermodynamic state variables and entropy. Although the original Liu procedure is based on differential forms of entropy evolution equation and balance equations, we consider integral forms of evolution equations of entropy and thermodynamic state variables. We assume that the evolution equations of internal variables consist of objective time derivative, thermal flux and source. The source could be decomposed to mechanical and relaxational one. We will exploit the arbitrariness of the time derivatives of internal variables, velocity gradient and the thermal fluxes of internal variables in order to describe arbitrary path in the thermodynamic space. Stress constitutive equation is resulted from the non-negativity of entropy production rate for arbitrary thermodynamic path.


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Wednesday 12:20 Emerald I  
**Buckling and coiling instabilities of yield-stress and power-law fluids filaments**  
Rudy Valette, Anselmo Pereira, Romain Castellani, and Elie Hachem  
CEMEF, MINES ParisTech, PSL - Research University,, Sophia-Antipolis, Sophia-Antipolis 06904, France

Fluid buckling instabilities represent a major source of irregularities for several industrial and natural processes such as container filling, glass plate fabrication and folding of geological structures. Despite some recent and significant works regarding such instabilities in Newtonian fluids, the buckling of non-Newtonian materials remains scarcely explored in the literature. In the present work, we analyse through scaling laws and
direct numerical simulations the buckling and coiling of filaments of power-law and viscoplastic Bingham fluids. Two types of flows are considered. First, filaments generated by a fluid falling freely from a hole onto a plate, for large fall heights. In the Newtonian case, this « inertial » [1] coiling regime is characterized by a balance between inertia and viscous forces that resist bending [2], and the wavelength of the instability is controlled by the inverse Reynolds number. We demonstrate that power-law fluids obey a similar behaviour and propose a formal general description of the instability that depends on the power-law exponent. Secondly, we investigate Bingham fluid filaments compressed at constant velocity by two parallel plates, where one would expect the wavelength of the instability to be controlled by the distance between the plates as shown in the Newtonian case of slender filaments [3]. We actually observed three regimes: a first one driven by the capillary force and during which there is no deflection and a folding regime that is dominated by the compressive viscous force and for which the inertia is negligible and a twist/coil regime appearing at larger Reynolds number. Introducing a yield stress induces localization that restricts the buckled flow dimensions. Our main results are summarized in a four-dimensional phase diagram whose axes are a slenderness parameter, capillary number, Reynolds number and Bingham number.


Symposium SM

Polymer Solutions, Melts & Composites

Organizers: Giovanni Ianniruberto and Evelyne van Ruymbeke

Wednesday 9:30 Emerald II SM17

Viscoelastic and dielectric relaxation of reptating type-A chains affected by reversible head-to-head association and dissociation

Hiroshi Watanabe1, Yumi Matsumiya1, and Youngdon Kwon2
1Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan; 2School of Chemical Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do 16419, Republic of Korea

For entangled linear polymer having type-A dipoles and undergoing head-to-head association and dissociation reaction, viscoelastic and dielectric behavior is theoretically analyzed on the basis of the reptation dynamics combined with the reaction kinetics. Specifically, for the dissociated unimer and associated dimer (indexed with j = 1 and 2, respectively), the normalized complex modulus g1* and the normalized complex dielectric permittivity ej* are analytically calculated via eigenfunction expansion of the orientational anisotropy and orientational memory defined in terms of the bond vectors u of entanglement segments. The reaction activates mutual conformational transfer between the unimer and dimer. Multiple coupling occurs for the anisotropy decay modes of the unimer and dimer due to this transfer, and g1* and g2* of the unimer and dimer, respectively, exhibit considerably retarded and accelerated relaxation compared to the pure reptation case. In contrast, the memory decay modes of the unimer and dimer are only pair-wisely coupled, so that the reaction-induced acceleration and retardation for e1* and e2* are much milder than those seen for g1* and g2*. The orientational anisotropy is the tensorial, second-moment average of u associated with no cancellation in the conformational transfer, whereas the orientational memory is the vectorial, first-moment average accompanied by partial cancellation, which results in the difference between g1* and ej*. This difference is noted also for the associating/dissociating Rouse chains. Nevertheless, the reaction-induced retardation of the viscoelastic relaxation is stronger for the reptating unimer than for the Rouse unimer, whereas the reaction-induced acceleration is similar for the reptating dimer and Rouse dimer. These features are discussed in relation to the motional coherence along the chain backbone being present and absent in the reptation and Rouse dynamics.

Wednesday 9:50 Emerald II SM18

Linear and non-linear rheology of associative polymers. Effect of the number of interactions on the viscosity

Leire Sangroniz1, Ainara Sangroniz1, Mercedes Fernández1, Alejandro J. Müller2, Agustin Etxeberria1, and Antxon Santamaria1
1Polymer Science and Technology Department, POLYMAT, University of the Basque Country, San Sebastian, Gipuzkoa 20018, Spain; 2Polymer Science and Technology Department, POLYMAT, IKERBASQUE, University of the Basque Country, San Sebastian, Gipuzkoa, Spain

Polymers containing secondary interactions, such as hydrogen bonds, ionic bonds or metal ligand coordination, have attracted great interest in the last decades. These interactions modify significantly chains dynamics and, therefore, the rheological properties. Practically all the published works deal with rheological properties under shear flow, employing SAOS measurements to analyse the linear viscoelastic regime. Studies on the properties in the non linear regime are scarce, although they have a paramount relevance during processing and some practical applications. Indeed, a systematic study of the effect of these interactions under different flow types is still needed. In this work the reliability of different rheological techniques to detect the effect of hydrogen bonds in linear and non linear shear and extensional flows is investigated, to scope a unified view of the role of hydrogen bonds. For this purpose, a phenoxy resin which contains hydroxyl groups that form hydrogen bonds, has been selected. The level of hydrogen bonds is controlled modifying the phenoxy resin.
Based on the viscosity values obtained from SAOS, a model accounting for the combined effect of entanglements and secondary interactions on viscosity is proposed. The generalization and consequent adequacy of this model to other associative polymers is presented. LAOS measurements show that this rheological technique is a useful tool to investigate associative polymers. As an example, it is demonstrated that the non-linear parameter Q0 decreases as the number of secondary interactions is reduced.

Strain hardening behaviour, noticed in extensional flow measurements, is observed only in samples which contain a determined amount of hydrogen bonds. The liaison between extensional flow results and the relaxation time spectra obtained from SAOS data is shown.


Wednesday 10:10 Emerald II

Transition from viscoelastic liquid-like to solid-like behaviour of amine functionalized polynorbornenes
Tanja Tomkovic1, Nirmalendu Kuan2, Laurel L. Schafer3, and Savvas G. Hatzikiriakos1
1Chemical and Biological Engineering, The University of British Columbia, Vancouver, Canada; 2Chemistry, The University of British Columbia, Vancouver, Canada

Amine-functionalized polymeric materials are found potentially useful in a wide variety of applications. Combination of hydroaminationylation reaction and ring-opening metathesis polymerization was used to synthesize secondary amine-containing polynorbornenes. Various functionalities that exhibit different hydrogen bonding strengths were introduced. Extensive rheological characterization has shown the effect of the substituents in dictating the hydrogen bond ability within the polymeric materials and thereby, influencing the bulk material properties. Additionally, tertiary amine-containing polymers were synthesized to evaluate the hydrogen bond ability. The detailed rheological study has demonstrated a clear transition from liquid-like behavior of tertiary amine-containing polynorbornenes to solid-like behavior of secondary amine-containing polymers.

Wednesday 10:30 Emerald II

Dynamics of slide-ring gels: A step by step study
Sina Ghiassinejad1, Atul Kumar Sharma1, Charles-Andre Fustin1, and Evelyne van Ruymbeke2
1Institute on Condensed Matter and Nano-science, UCLouvain, Louvain-la-Neuve 1348, Belgium; 2The Division of Bio- and Soft Matter, IMCN, Université catholique de Louvain, Louvain-la-Neuve 1348, Belgium

In this work, we study the viscoelastic properties of slide-ring gel which was achieved by crosslinking of macrocycles on the different polyrotaxane strands. For getting polyrotaxane, a step by step synthesis protocol is followed in order to incorporate macrocycles (rings) along copolymers of linear poly(ethylene glycol) containing bulky end-groups for preventing the rings from unthreading. The viscoelastic properties of the samples obtained at each stage are then determined and analyzed with the help of the TMA tube model, in order to understand the role of the different components. In particular, we investigate the role of bulky end groups as well as the influence of the rings mobility on the dynamics of the chains. Based on these experimental results, we then extend our tube model in order to account for the influence of ring mobility on the rheological behavior of our systems, and to model the rheological behavior of slide-ring gel containing either fixed or free rings along the chains.

Wednesday 11:20 Emerald II

Rheological properties of compatibilized PE/PA multilayer films
Quentin Beuguel, Alain Guinault, Guillaume Miquelard-Garnier, and Cyrille Sollogoub
CNAM, PIMM laboratory, Paris 75013, France

The rheological properties of immiscible polyethylene/polyamide (PE/PA) multilayer films, compatibilized with a large amount of polyethylene-grafted-maleic anhydride (PEgMA), were investigated. The films were elaborated using a co-extrusion process equipped with layer multiplying elements, simultaneously increasing the number of layers up to ~2,000 layers and decreasing the layer thickness of each phase down to ~20 nm. In such systems, the number of interfaces is high and the compatibilization between both polymers has to be considered with attention, since it strongly influences their final properties. In molten state, the reactive bonding between maleic and amides groups at the interfaces is fast and leads to a strong interfacial adhesion between PE and PA. The formation of an interphase, i.e. a region of finite nanometric thickness where both polymers interact, and its role on the resulting materials properties is still misunderstood for compatibilized systems. Rheology appears to be a convenient and powerful tool to characterize this interphase. Here, rheological tests were performed in the linear domain and below the melting point of PA, enabling to analyze only the PE phase melt properties and preventing from further compatibilization reaction and thermal degradation of PA. The results show a solid-like behavior at low frequencies, attributed to a slower relaxation of PE chains in the presence of interphase. Both elastic and viscous moduli increase with decreasing PE thickness. A simple model, considering three phases (PE in bulk, PA in solid state and an interphase), enabled to fit the complex viscosity variation of multilayer films, letting the interphase viscosity as an adjustable parameter. This interphase viscosity decreases with PE confinement. This result could be attributed to a lower compatibilization efficiency or to conformation changes of PE chains close to the interphase, as the number of interfaces increases and the individual layer thickness decreases.
Rheology of statistical ethylene-octene copolymer melts
Domenico Ciaraldo, Veronica Vanzanella, Salvatore Costanzo, and Nino Grizzuti

Chemical, Materials and Industrial Production Engineering, Università degli Studi di Napoli Federico II, Napoli, NA 80125, Italy

Ethylene-octene copolymers (EOC) are systems where the sequence of ethylene monomers is spaced out by octene moieties. In fact, incorporating octene monomers (or other α-olefins) into ethylene chains is an effective strategy to tune the crystallization properties of the resulting copolymers and, subsequently, their mechanical properties. The past synthetic approach to obtain EOC used a metallocene-based catalyst, yielding random copolymers. Recent progress in chemical synthesis allowed for the development of the so-called chain shuffling technology where two catalysts having different monomer selectivity are used in the same reactor in order to obtain random multiblock copolymers [1-2]. At a relatively low octene content (approximately 10-20%), multiblock EOC behave as thermoplastic elastomers [3]. Tuning the stretching properties and processability by varying the octene molecular content, the number of blocks, and their length is interesting for mechanical applications. Furthermore, relating the rheological properties to the structure of these copolymers could provide a useful tool to extract information on the copolymer composition through rheological tests [4]. On the other hand, there are relatively few studies reporting on the link between the molecular architecture of EOC and their rheological properties. In this work, we present a systematic study of the linear rheological properties of EOC. We investigate the crystallization and melting of the hard phase by monitoring the evolution of the complex moduli as a function of temperature; in addition, we evaluate the frequency response at different temperatures and address the challenge of obtaining structural information (i.e. the entanglement molecular weight) from rheology.

[1] Auriemma et al., Macromolecules 2018
[2] Auriemma et al., Polymer 2018

Modified dual Kaelble equation – a new model for describing the temperature dependence of the viscoelastic properties of block copolymers
Olli-Ville Laukkanen1, H. Henning Winter2, and Jukka Seppälä3

1Institute of Physical Chemistry, RWTH Aachen University, Aachen 52074, Germany; 2Dept. Chemical Engineering & Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States; 3Department of Chemical and Metallurgical Engineering, Aalto University, Espoo 02150, Finland

Block copolymers (BCPs) are useful in many applications where a combination of different polymers yields a material with superior hybrid properties. In particular, the self-assembly of BCPs allows the design of nanostructured materials for sophisticated materials applications. Although BCPs have been studied extensively for over half a century, the temperature dependence of their viscoelastic properties is still poorly understood. In this study, the rheological properties of styrene-butadiene-styrene (SBS) triblock copolymer are measured in shear and torsion over a wide temperature range (-120 &degC ≤ T ≤ 180 &degC), extending well beyond the glass transition temperatures of the polystyrene (Tg,PS = 89 &degC) and polybutadiene (Tg,PB = -90 &degC) blocks. Only slight deviations from thermorheological simplicity are observed near the glass transition of PS, thus allowing the construction of rheological master curves over 36 decades of frequency using the time-temperature superposition principle. A particular effort is made to analyze the temperature dependence of the time-temperature shift factors αT. We note that the temperature dependence of the individual BCP components can be described by the modified Kaelble equation [1] both above and below their respective Tg's. Consequently, in the case of the SBS block copolymer, the temperature dependence of αT over the entire experimental temperature range is accurately described by a combination of two independent fits of the modified Kaelble equation. The inflection temperatures determined by the fits of the modified Kaelble equation closely coincide with the Tg's of the PS and PB blocks. We propose that the modified dual Kaelble equation can be used to describe the temperature dependence of viscoelastic properties in any BCP with two distinct glass transitions.

range which is associated with an interfacial tension between the phases. The dynamics of the polymer chains is probed by rheological (shear and elongational rheometry) and dynamic light scattering (DLS) experiments. The addition of pristine Pluronic F127 or a Pluronic-based multiblock copolymer leads to an additional relaxation process in shear rheological experiments which only appears in the presence of PVP because of the miscibility gap. The pronounced elasticity is caused by the interfacial tension between the two phases. Furthermore, a stress over- and undershoot are visible in stress-growth experiments in shear. At high shear rates, the phenomenon of rod-climbing can be observed which indicates the existence of normal stresses which are caused by a pronounced elastic behaviour. In elongational flow, an upper-convected Maxwell model is fitted to the data in order to determine the elongational relaxation time.

Wednesday 12:40 Emerald II

**The effect of rheological properties of the PEO solution on the sessile drop oscillation during the early stages of elastocapillary thinning transition**
Dae Yeon Kim and Kyung Hyun Ahn
Seoul National University, Seoul, Republic of Korea

The capillary break-up of an elastic fluid such as polymer solution evolves through a series of sequential stages. At the early and late stage of capillary thinning, several fluctuations and instabilities are observed. Especially, the oscillation of sessile drop and connected filament is generated at the transition from potential flow regime to elastocapillary regime. A shape of oscillation with time shows a damped sinusoidal function whose amplitude approaches zero as the transition progresses. This oscillation could disrupt the formation of uniaxial extensional flow field in filament. In an effort to define the factor which affects the oscillation, the presented study focuses on the change of frequency and amplitude decay ratio by several conditions.

The effect of rheological properties of polymer on the oscillation of sessile drop and the effect of particles on the development of oscillation during the capillary thinning process of a poly(ethylene oxide) solution has been experimentally studied. Dilute aqueous solutions of poly(ethylene oxide) of various concentrations and molecular weights (2x10^4-5x10^5) were used to achieve the variety in the viscosity and elasticity of fluid. The evolution of capillary thinning was captured using high speed camera. Then, obtained image sequence was processed by custom MATLAB-based image processing code to calculate the relaxation time and the height of sessile drop.

From the measured heights of sessile drop, the frequency of oscillation and amplitude decay ratio was calculated. The change of concentration and molecular weight of polymer did not affect the frequency of oscillation. The frequency remained constant under various conditions. On the other hand, the amplitude decay ratio was changed with concentration and molecular weight. The amplitude decay was accelerated with the increased viscosity of polymer. Whereas, it was decelerated with the increased molecular weight of polymer.

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**Symposium EM**

**Experimental Methods & Progress in Rheometry**

Organizers: Dimitris Vlassopoulos, Roland Kádár and Christian Clasen

Wednesday 9:30 Europe II

**Low-field Rheo-NMR for the study of soft materials**

Volker Räntzsch, Mürüvvet B. Özen, Karl-Friedrich Ratzsch, Gisela Guthausen, and Manfred Wilhelm
Karlsruhe Institute of Technology, Karlsruhe, Germany

Hyphenated characterization techniques based on rheology and nuclear magnetic resonance (NMR) have received great attention in the past 20 years because such combinations lead to correlated information on flow and molecular properties of soft matter, e.g. polymers, liquid crystals or colloids. Additionally, flow profiles (e.g. steady or oscillatory shear) both in the linear and non-linear regime can be applied to monitor and also to modify the state of a sample and measure its implications on molecular properties. Most RheoNMR designs have been realized for high-field NMR spectrometers using shear flow cells without a quantification of the rheological parameters. Here we present a low-field RheoNMR set-up based on a portable 30 MHz NMR unit that was integrated into a high end commercial strain-controlled rheometer (1). This unique combination can be employed to conduct a full rheological characterization ($G$, $G'$, $η$), FT-Rheology: $I_{1H}$, $Q_0$) while monitoring molecular dynamics in-situ via $^1H$ TD-NMR for temperatures from -15 to +210 °C. Possible applications include the measurement of quantitative composition in crystallizing soft matter (fats, polymers, etc.) and multiphase systems during the application of shear protocols (2, 3). To display the possibilities of this new technique, studies on the quiescent and flow-induced crystallization of polyolefins are presented. A short term steady-shear protocol was applied to study flow-induced crystallization as a function of different temperatures and flow conditions, respectively.

New tools and field configurations in magnetorheology

Jose R. Morillas¹, J. Yang², J Tajuelo¹, M Terkel¹, O Martinez-Can¹, R Hidalgo-Alvarez¹, and Juan de Vicente¹
¹Department of Applied Physics, University of Granada, Granada, Granada 18071, Spain; ²Department of Chemistry and Material Engineering, Logistic Engineering University, Chongqing, China

Magnetorheological (MR) fluids are colloidal systems prepared by dispersion of magnetisable particles in (non-magnetic) liquid carriers. Interestingly, they exhibit a remarkable rheological change (so-called MR effect) upon the application of a magnetic field. The reason for this is the magnetic field-guided colloidal assembly of the dispersed magnetisable particles. The self-assembly can be controlled through the field configuration (DC, AC or combinations) and the strongest MR effect is achieved in saturating fields [1]. In the first part of this communication we propose a new setup to measure the rheological properties of MR fluids under homogeneous magnetic fields in saturation. First, the device optimization is carried out using magnetostatic Finite Element Method simulations. Next, Computational Fluid Dynamics simulations are performed and validated against experiments and theoretical calculations for Newtonian liquids. Finally, yield stress fluids are addressed and in particular MR fluids [2]. In the second part of this communication we show our most recent advances towards the understanding of magnetorheology under non-stationary magnetic fields. For this purpose a triaxial magnetic field generator is constructed and preliminary experimental data are reported on the directed self-assembly and rheological evaluation of MR fluids.

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Rheological behavior of magnetic fluids under a tunable magnetic field: Numerical design and experimental analysis

Samir H. Sadek¹, Hossein H. Najafabadi¹, Laura Campo-Deaño¹, and Francisco J. Galindo-Rosas²
¹Departamento de Engenharia Mecânica, CETF, Faculdade de Engenharia da Universidade do Porto, Porto, Porto 4200-465, Portugal; ²Departamento de Engenharia Química, CETF, Faculdade de Engenharia da Universidade do Porto, Porto, Porto 4200-465, Portugal

An interesting approach for cleaning oil-spills consists of mixing synthesized magnetic nanoparticles and dispersing them in oil-polluted water in a vessel to form a ferrofluid in the oil phase. Then, in an oil-recovery vessel containing a Halbach array, the magnetic field thus separates the oil from the water phase much faster than gravity [1].

The efficiency of the Halbach array will depend profoundly on the rheological properties of ferrofluids, which are currently characterized by commercial rotational rheometers that undergo simultaneously shear flows and magnetic fields perpendicularly oriented. However, none of the available commercial extensional rheometers can apply an external magnetic field by controlling the current intensity. Recently, Galindo-Rosas et al. [2] developed an add-on allowing the application of an external magnetic field by means of permanent magnets to the fluid while characterized in the CaBER-I device[3]. Thus, a systematic study on the extensional properties of magnetic fluids controlling the intensity of the magnetic field is yet missing.

The present work introduces a new design of the add-ons, able to impose a tunable external magnetic field by controlling the current intensity through iron core solenoids. The design of the solenoids and its configuration has been developed numerically in a multiphysics software so that the magnetic field remains homogeneous throughout the whole volume of the fluid sample. Then, the scaffold case for the solenoids has been 3Dprinted and the experimental tool was used to characterize the extensional rheological response of different magnetic fluids under magnetic fields with different intensities.

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Rheological evaluations and capability assessments of ultrasonic spinning rheometry for non-Newtonian fluids

Taiki Yoshida¹, Yuji Tasaka¹, and Yuichi Murai²
¹Graduate school of Engineering, Hokkaido University, Sapporo, Japan; ²Faculty of Engineering, Hokkaido University, Sapporo, Japan

Rheological responses in non-Newtonian fluid flows (or deformations) will be unexpected due to non-linear behaviors, such as wall-slip, shear banding, viscoelastic instabilities, and so on. These phenomena have been ascribed as the cause of "Couette inverse problem", which is a considerable issue on uses of the rotational shear rheometer. Composed of the simple experimental setup, such as an open cylindrical container, we have developed ultrasonic spinning rheometry (USR) that is expected of overcoming the issue using ultrasonic velocity profiling technique.
As the basic concept of the rheometry, velocity profiles are substituted to the equation of motion. To evaluate rheological properties, multiple rheological properties can be determined by considering the rheological model equation from the velocity profiles without axial torque measurements. Introducing Maxwell model to the USR, we performed a linear viscoelastic analysis, which has many advantages to evaluate the fluid rheology; (i) Based on discrete Fourier transform, rheological measurements can avoid the influence of noise in the velocity profiling. (ii) USR can quantify a wider range of shear rates obtained from a single measurement. (iii) Spatiotemporal-rheological properties can be evaluated; O(1 s) and O(1 mm) as temporal and spatial resolution. In this study, the rheological evaluations of USR were compared with a parallel-disk rotational rheometer as comparative experiments. Newtonian (silicone oil), shear-thinning (carboxymethyl cellulose, CMC solution), and thixotropic (montmorillonite dispersion) fluids were examined as the demonstrations of the experiments. From the experiments, we remark the important feature that USR can evaluate the fluid rheology involving non-linear shear deformations, such as wall-slip, shear banding, shear localization, etc. Through the experimental proofs on rheological evaluations, the capabilities of USR function adequately with complementary relations for conventional shear rheometers.

**Wednesday 11:40 Europe II**

**Combined rheo-Raman analysis: Correlating viscoelastic behavior with chemical structure**

David A. Bohnsack¹, Bharath Rajaram¹, and Jennifer Ramirez²

¹TA Instruments - Waters LLC, New Castle, DE 19720, United States; ²Thermo Fisher Scientific, Madison, WI 53711, United States

Rheology offers powerful methods for studying a material's response to shear deformation and changes in environmental conditions. In addition to bulk rheology measurements, there is often a strong desire to explore the relationship between the sample microstructure, chemistry, and the observed mechanical response. Of these, structure visualization through microscopy and scattering techniques is well established in literature. In this study, we present a new rheo-Raman setup that permits chemical structure characterization during rheological measurements. Raman spectroscopy provides critical information about molecular structure and bonding and can elucidate intermolecular interactions of pure components and mixtures. Details are provided for a turnkey system that integrates a commercially available rheometer (Discovery Series HR-3, TA Instruments) with a Raman spectrometer (iXR, Thermo Fisher Scientific). The setup offers temperature control and ensures Class I laser safety through appropriate safety interlocks. Results are presented for the crystallization of a pure polyethylene glycol (PEG) melt studied by Differential Scanning Calorimetry (DSC) and simultaneous rheo-Raman spectroscopy. As the temperature is decreased, the polymer's liquid-to-solid transition is marked by a significant increase in the moduli. Simultaneous collection of Raman spectra indicates an increase in molecular interactions and order that directly coincides with bulk rheology. Additional examples of rheo-Raman spectroscopy are presented for commercial materials. In one case of a commercial cosmetic lotion, the temperature dependent decrease in viscosity directly correlates with changes in the C-C and C-H stretching modes that are sensitive to conformational disorder. The results highlight the importance of hyphenated rheometric techniques to fully understand the origins of material viscoelasticity.

**Wednesday 12:00 Europe II**

**New rheometrical tools for Rheo-SAXS and Rheo-SANS**

Joerg Laeuger

Anton Paar Germany, Ostfildern, Germany

The mechanical material properties as well as the flow behavior of complex fluids are strongly determined by their microstructure. In order to understand and customize the behavior of such of systems under flow conditions it is necessary to pay special attention to the structural changes that occur at the microstructural level. Therefore combined rheology small angle scattering techniques with light, neutron and x-rays have emerged as valuable tool over the last decades. The use of a commercial rheometer allows the application of more complex flow conditions and offers an “in situ” correlation between rheological behavior and the corresponding structural changes. A modular design of a scattering cell for a rheometer makes it possible to use the same basic unit for Rheo-SAXS and Rheo-SANS experiments. A high temperature system will be introduced as well as different new geometries and measurement options including a “dent” geometry for high viscous materials such as polymer melts. An extensional flow tool attached to the rheometer has been employed in Rheo-SANS investigations for copolymer-polystyrene blends and in Rheo-SAXS for observation of polymer crystallization during flow at small times and high elongation rates. Geometries for Rheo-GISANS are used to measure the reflectivity during flow and reveal information in thin sample layers during flow. Electrically isolated geometries can be used to obtain dielectric spectroscopy data during the simultaneous application of a flow field and the acquisition of SANS or SAXS data and provide additional information on the electrical conductivity during flow. For combined Rheo-SAXS measurement in a laboratory environment a rheometer measuring head has been attached to laboratory SAXS instrument. First results of this setup will be presented as well.

**Wednesday 12:20 Europe II**

**A novel approach to Sentmanat extensional rheometry: Applications to the study of extension induced crystallization**

Juliana Amirdine, Nicolas Boyard, and Teodor Burghielea

Laboratoire de thermique et énergie de Nantes, Nantes 44306, France

The extension is the dominant flow for a number of key industrial polymer processing operations including melt blowing, film extrusion and fibre spinning. Moreover, the extensional flows are known to promote the crystallization of molten polymers. Yet, there exist very few commercially available devices able to assess the extensional properties. Undoubtedly, the most popular and affordable tool is the Sentmanat device [1-2]. Initially designed for rubbers, this method has two main drawbacks in the case of molten polymers: gravity sagging and geometric inhomogeneity of the
sample at high Hencky strains. To circumvent the first drawback, we have designed an oil bath enclosure with optically transparent walls. This allows an accurate temperature control and minimizes the gravity sagging effects. As the second point is concerned, our device allows the in-situ monitoring of the geometric homogeneity of the sample. Furthermore, when coupled with polarized light illumination and high magnification telescopic imaging the device allows an in-situ measurement of the kinetics of the flow induced crystallization.


Wednesday 12:40 Europe II
Lossless and rapid sample preparation for oscillatory rheology via a novel vacuum compression molding process
Daniel Treffer
Management, MeltPrep GmbH, Graz, Styria 8020, Austria

Melt rheology provides valuable information about material properties that are of great importance for equipment design, process simulations and process understanding. The measurements are performed on small samples, in case of melt rheology, discs are used. However, the material to be investigated is usually a bulk material (powder, pellets) and require a sample preparation before the measurement can be performed. In most applications the samples are prepared via compression or injection molding. The weakness of both is that the volume of the sample chamber of both processes is fixed (not adaptable). Thermal expansion and contraction cannot be compensated, and samples may have voids and high internal stresses after the preparation. The analysis instruments, however, assume that homogeneous samples with defined are loaded for the measurement. Based on these assumptions material properties like storage and moduli are derived incorrectly. The measurement results contain artefacts and wrong values are determined.

The aim of this study was the development of a novel vacuum compression molding tool (VCM Tool) to overcome the common hurdles in the preparation of thermoplastic specimens.

VCM is a novel fusion-based method for sample preparation. The material is filled as bulk material at room temperature into a sample chamber. The chamber is formed by PTFE coated separation foils. The foils are arranged that the chamber is adaptable in height. One heating and cooling cycle takes less than 10 minutes. The separation foils are simply removed like a sticker after the preparation and no cleaning is required.

The VCM Technology is a rapid and straightforward approach to increase the quality of material data. The standard deviation of all conducted frequency sweeps could be reduced below 3% for all investigated materials. Even materials with particles sizes in the small µm range yielded excellent results. Artefact were reduced to an undetectable level.

Symposium GM
Granular Materials & Highly Filled Systems
Organizers: Joamin Gonzalez Gutierrez, Berenika Hausnerova and Tamás Börzsönyi

Wednesday 9:30 Europe III
3D granular flow of soft and hard spheres studied by ultrafast electron beam X-ray computed tomography (ROFEX)
Diego Sancho Martinez¹, Ralf Stannarius³, Martina Bieberle², and Frank Barthel²
¹Institute of Physics, Otto von Guericke University, Magdeburg 39106, Germany; ²Institute of Fluid Dynamics, Helmholtz-Zentrum Dresden - Rossendorf, Dresden, Germany

The discharge of a hopper filled with soft and hard granular materials was investigated. The 3D granular flow of soft, assumed frictionless hydrogel, and hard spheres were studied by ultrafast electron beam X-ray computed tomography (ROFEX). In this work, using digital particle image tomography with 1,000 cross-sectional images per second and per plane and with a spatial resolution of about 1 mm, the flow properties were determined quantitatively at different positions of the container, and the complete flow fields were reconstructed for the different materials used.
A description of shear viscosity for highly filled PIM material containing aluminium powder and stearic acid

Petr Filip1 and Berenika Hausnerova2
1Institute of Hydrodynamics of the Czech Academy of Sciences, Prague, Czech Republic; 2Faculty of Technology, Tomas Bata University, Zlin 76001, Czech Republic

Powder Injection Moulding (PIM) method represents a processing technique enabling production of very tiny geometrically complicated metal and ceramic parts integrated in one piece, thus eliminating a necessity of assembling geometrically simpler parts in one aggregate. Feedstock forming a starting material is composed of two entry components: metal or ceramic powder (including nanoparticles) and a carrier liquid, so called binder. This highly filled suspension (metal portion reaches 50-60 vol. %) is rather complicated material to be described both experimentally and theoretically. Even so relatively elementary rheological characteristic as shear viscosity is uneasy to predict. The theoretical and empirical predictions of this quantity are well elaborated for dilute and moderately concentrated suspension. However, with an increasing concentration availability of suitable models substantially reduces and the predicted evaluation (constitutive models) of shear viscosity depends exclusively on the only component - particle concentration. In practice, the suspensions used in the PIM method are not composed from only two components but presence of other materials -as e.g. surfactants contributing to higher packing, and hence, to better sintering- is also inevitable. The problem is how to model shear viscosity taking into account simultaneously metal particles and efficient agents. As far the authors are aware no such models exist. For the case of aluminium powder and stearic acid (surfactant) there was proposed a master curve approximating shear viscosity in the range 0 - 50 vol. % for powder and 0 - 5 vol. % for stearic acid. A deviation of the predicted viscosity from the experimental one is within the experimental error.

Acknowledgement: The author (B.H.) wishes to acknowledge GA CR for the financial support of Grant No. 17-26808S. The author (B.H.) appreciates the support by the Ministry of Education, Youth, and Sports of the Czech Republic - Program NPU I (LO1504).

Modeling sea ice fracture at very high resolution with VP rheologies

Damien Ringeisen1, Nils Hutter1, Martin Losch1, and L.-Bruno Tremblay2
1Alfred Wegener Institute, Bremerhaven, Bremen 27570, Germany; 2McGill University, Montréal, Canada

Recent high resolution pan-Arctic sea ice simulations show fracture patterns that are typical of granular materials but with intersection (fracture) angles wider than those observed from high-resolution satellite images (with a modal value of θ = 20°). In this work, we investigate the mechanism of formation and parameter dependencies of ice fracture in simple numerical uni-axial test on a 8 km x 25 km ice floe at an unprecedented resolution of 25 m for two different Visco-Plastic (VP) yield curves: an elliptical (standard in sea ice models) and a coulombic yield curve both with normal flow rule. In the standard VP model, the simulated angle of fracture is θ = 33.9°. The dependence of the angle of fracture on the ice shear strength is also contrary to that of typical granular materials with larger angle of fracture for higher shear strength. In this model, the divergence along the fracture lines (or LKFs) is entirely dictated by the ice shear strength with high shear strength resulting in convergence along LKFs and low shear strength resulting in divergence along LKFs. This is again contrary to typical granular materials. Moreover, the angle of fracture depends on the confining pressure in the uni-axial test with more convergence as the confining pressure increases, again contrary to granular material. In the Coulombic model, the angle of fracture is smaller (θ = 23.5°), but the solution is unstable because of the sea ice mechanical strength parameters, the sea-ice drift, sea-ice deformation (strain-rate) field in an inconsistent way. We consider this evidence to move away from the elliptical yield curve and associative (normal) flow rule.

Predicting the behaviour of highly-filled systems for FFF and PIM manufacturing

Cristina Berges, Juan Alfonso Naranjo, and Gemma Herranz
INEI-ETSI Industriales, University of Castilla-La Mancha, Ciudad Real 13071, Spain

The concept of combining additive manufacturing (AM) and Powder Injection Moulding (PIM) has recently attracted the interest of researchers and industry, due to the possibility of providing very similar prototypes to those final metallic or ceramic parts obtained by PIM. Based on our previous PIM experience, we suggest FFF Fused Filament Fabrication as an appropriate strategy to achieve comparable results by both technologies. Printing process of highly-filled systems in a conventional 3D printing machine implies an extensive optimization and the use of filaments previously designed with appropriate characteristics in terms of flexibility, rigidity and stiffness. Reaching high-quality green parts through PIM and FFF technologies, involves injection and printing processes, respectively. These stages, together with the debinding step (common to both approaches) are the keys for a feasible design of this new concept. In order to prove this PIM prototyping strategy and define a predictable criterion to select the optimal mixture for both FFF and PIM, several feedstocks have been characterized in terms of rheological properties. In this way, the differences in viscosity values at a temperature range have been studied and their behaviour under temperature and shear rate variations, which are expected during the processing of these highly-filled systems. After selecting the best system for FFF processing, it was subsequently employed as PIM feedstock and successfully injected. Finally, the properties of the obtained green parts were investigated by microscopy, density and surface roughness.
Length scales effects in granular column collapse

Romain Castellani¹, Anselmo Pereira¹, Lucas Sardo¹, Pierre Jop², and Rudy Valette¹

¹CEMEF, MINES ParisTech, PSL - Research University, Sophia-Antipolis, Sophia-Antipolis 06904, France; ²Surface du Verre et Interfaces, UMR 125 CNRS Saint-Gobain, CNRS, Aubervilliers, France

Column collapses appear as a classical benchmark for studying granular flows. An initially cylindrical granular column of height hi and radius ri is released resulting in a flow driven by gravity. Previous works on dry granular collapses [1-2] investigated axisymmetric column using various materials and studied the influence of the aspect ratio a = hi/ri on the final deposit radius rf. They observed two different regimes of collapse: a slumping regime, where the column spreads through an avalanche of its flanks, for a lower than a critical aspect ratio ac, and a spreading regime, where the whole column descends, for large a. Lajeunesse et al. concluded that the aspect ratio is the main parameter driving granular collapses. Lube et al. showed that the relative spreading (rf/ri)/ri scales as a^1 below a critical value of a close to 1.7 and scales as a^0.5 beyond. All studies showed that the total time of motion scales as (hi/g)^(0.5), g being the gravitational acceleration. In this work, we used a granular material (sandblasting sand) that exhibits a strong experimental dependency of its macroscopic friction to the inertial number in steady shear flows. We then identify a mu(I) friction law [3-4] and show experimentally that the relative spreading indeed varies with the column aspect ratio a but also on the inverse dimensionless grain diameter d/ri. The role of this additional length scale is then demonstrated using dimensional analysis and 3D finite element numerical simulations using the mu(I) rheology model.


Multiple shear bands in granular materials in slow shear

Sára Lévay¹, János Török², Lothar Brendel¹, and Dietrich E. Wolf³

¹Faculty of Physics, Department of Theoretical Physics, Uni. of Duisburg-Essen, Budapest Uni. of Tech. and Eco., Budapest H-1111, Hungary; ²Department of Theoretical Physics, BUTE, MTA-BME Morphodynamics Research Group, Budapest H-1111, Hungary; ³Faculty of Physics, University of Duisburg-Essen, Duisburg 47048, Germany

We study the qualitative differences in the behavior of a cohesionless granular material depending on the imposed strain rate: When sheared slowly, in a quasi static manner, the sample shows intermittent shear characterized by the presence of well defined shear bands. When, on the other hand, it is sheared fast, the displacement field is continuous. The question whether there is a well defined transition, remains open. We devote this presentation to the study of the crossover from slow to fast shear in the simple geometry of plane shear by means of discrete element simulations (using both molecular and contact dynamics). We show that there is indeed a well defined inertial number which separates the two regimes: At moderate shear rates, in the intermediate regime, multiple shear bands appear simultaneously which merge and appear as a continuous shear profile for large shear rates. Several quantities such as the lifetime of shear bands show qualitatively different statistics in the two regimes. We propose a mesoscopic, stochastic model which incorporates the effect of these simultaneous shear bands and we show how the corresponding quantities scale with the energy input rate up to the onset of this effect. The stochastic model and the DEM simulations also agree on the existence of a minimum of the shear stress and a maximum of the number of shear bands as functions of the energy input, however the positions do not coincide. The scaling analysis of the kinetic energy indicates that the number of shear bands is the more relevant quantity. In our study we attempt to gain a deeper insight into the process of shear. As our knowledge grows about the microscopic processes present there, applications related to the shear of granular materials can be further improved, let them be applications in soil mechanics, geotechnical engineering or pharmaceutical and food industry.

Relaxation of inhomogeneous granular flows

Lothar Brendel

Faculty of Physics, University of Duisburg-Essen, Duisburg 47048, Germany

In recent years, non-local models for the rheology of granular media have been successfully applied to steady state flows with inhomogeneities stemming from boundaries or body forces. We focus on the time domain and study a system with periodic boundary conditions where inhomogeneities result from the flow itself. We investigate the relaxation behaviour by means of DEM simulations and compare it to the predictions of different non-local models.

A new perspective on granular flow analysis in rotating drum

Angelica Maria G. Arseni, Francesco Greco, and Pier Luca Maffettone

Università di Napoli Federico II, Naples, Italy

Granular materials are ubiquitous in everyday life, in nature as well as in industry; therefore the prediction of granular fluid dynamics is of great interest in both physics and engineering research. A common complex granular flow is that occurring in rotating drums, which are widely employed...
as mixers, separators, dryers, reactors and granulators in different industrial processes. A continuum approach, where the solid phase is treated as a continuum, is suitable for large-scale flow modelling, as in the case of an industrial drum containing billions of particles. In this work, we present 3D Finite Volume (FV) simulations of dense granular flow inside a rotating cylinder, adopting the visco-plastic Jop-Forterre-Pouliquen constitutive model [1] for the granular medium stress tensor. The material parameters appearing in the constitutive equation are systematically varied to understand their effects on the main features of flow in the drum. The results obtained from our simulations are also compared with several experimental results available in the literature for the monodisperse and bidisperse case. We reproduce the flow configurations sequence in rotating drums, ranging from slumping to centrifuging [2], in good agreement with experimental results [3]. This validation opens up the feasibility of characterising a wide variety of regimes by changing both physical and geometric parameters, with the possibility of discovering new dynamical regimes, and of calculating several flow quantities difficult to be accessed through experiments.


Thursday 12:40 Europe III

Scaling of fibers: impact of form factor on flow properties
Ronan Chometon, Maxime Liard, and Didier Lootens
Sika Technology AG, Zürich, Switzerland

There is a need to develop new materials with very diverse and advanced properties which can be achieved by the process of hybrid materials which combines the interesting properties of several materials into a single one. Fiber-reinforced materials is an industrial example of such hybrids: the fibers are added and mixed with the slurry to improve its flexural strength. We demonstrate that the increase of the flexural properties is only effective when the fiber concentration is above a critical volume fraction because of packing difficulties in maintaining random orientation, similarly to the liquid crystal models. This transition occurs for fibers concentration close to the maximum packing and therefore the rheological properties of the mix is strongly modified. We show that the increase of the yield stress induced by the fibers can be understood with classical suspension model. Surprisingly, the effects of fiber form factor and fiber concentration are similar for both the rheological and the mechanical properties, despite being explained by different theories. Master curves have been successfully obtained by rescaling the fibers concentrations according to their form factor.

Symposium IP

Industrial Rheology & Processing

Organizers: Ulrich Handge, Clemens Holzer and Lazslo Gomze

Wednesday 9:30 Adria

Gelation phenomena in polypropylene and polyethylene as caused by phase separation, nucleation or crystallization
Markus Gahleitner, Jingbo Wang, Floran Prades, and Klaus Berreitner
St. Peterstr. 25, Borealis Polyolefine GmbH, Linz 4021, Austria

The use of rheological techniques for studying phase separation, nucleation and especially crystallization provides an additional technique for developing an improved understanding of processing phenomena of semicrystalline polymers. Temperature sweeps in the linear-viscoelastic domain have been established as a method for investigating gelation phenomena related to nucleation and crystallization behavior under quasi-quiescent conditions like in the works of Winter et al... In studying nucleation effects in polypropylene (PP) homopolymers and random copolymers by soluble nucleating agents of sorbitol- and triamide-type by this technique, the fibril network formation before the actual PP crystallization can be observed. The stability of such networks is, however, limited and the orientation of the fibrils enhances flow-induced structure formation here as well. It has now been found that quite similar effects are found with phase separation of low molecular weight waxes in polyethylene (PE) plastomers (single-site catalyst based homogeneous very low density PE). Especially PE-waxes can cause network formation and gelation, resulting in similar structures as for HDPE crystallization from solutions. In contrast, PP waxes are found to be distributed as micro-droplets which solidify well above the matrix crystallization temperature. It can be shown that the final phase morphology correlates well to the thermo-rheological behavior.
Wednesday 10:10 Adria IP2

**Rheological characterization of high density ethylene/α-olefin copolymers and its relation to molecular structure and post-yield axial deformation properties**

Joel Fawaz, Suleyman Deveci, Senthil K. Kaliappan, Umesh Gadgoli, and Bhagabata Das

*Borouge Innovation, Borouge Pte. Ltd., Abu Dhabi, Abu Dhabi 6951, United Arab Emirates*

In plastic industry, the use of rheology to characterize materials is critical, as it enables interpretations of different molecular structures, its processing and final article performance. In this study [1], high density poly(ethylene-co-1-butene) and poly(ethylene-co-1-hexene) samples were prepared with controlled molecular structures, via proprietary Borstar® process with a Ziegler-Natta catalyst, to determine the sensitivity of rheological measurements to molecular parameters. The rheological behavior was studied by conducting frequency sweep test at 5% strain and 190 °C using a stress-controlled rheometer. The results were related to the molecular structure such as molecular weight, molecular weight distribution, comonomer content and type, which were investigated by several analytical techniques. Additionally, the analytical results were correlated to post-yield axial deformation properties in the solid-state, i.e. natural drawing and strain hardening that are critical for predicting slow crack growth resistance properties of high density polyethylene designed for pressurized pipe application. Complex viscosity was found to systematically increase across the angular frequency range in alignment with the systematic increase in molecular weight. Consequently, shear thinning behavior was noted to decrease, with the increase in molecular weight, as the number of short chains that acts as lubricants decreased. The effect of comonomer type on viscosity of the samples became negligible as molecular weight and comonomer content decreased within the studied range. The increase in molecular weight and comonomer content resulted in a decrease in lamellae thickness, density and crystallinity. Therefore, it is postulated that there is a subsequent increase in entanglement density and tie molecules that resisted both natural drawing and strain hardening.


Wednesday 10:30 Adria IP3

**Tube model based constitutive equations for polydisperse linear and long-chain branched polymer melts**

Esmaili Narimissa and Manfred H. Wagner

1Chemical Engineering Program, Guangdong Technion Israel Institute of Technology GTIIT, Shantou, Guangdong 515063, China; 2Polymer Engineering and Physics, TU Berlin, Berlin 10587, Germany

Rheological equations of state are of great importance for simulation of polymer processing and for characterization of polymer melts. We consider tube model based constitutive equations developed in the last 40 years since the original publication of Doi and Edwards in 1978. The emphasis is on the concepts, assumptions, and material parameters introduced to model nonlinear viscoelasticity of polydisperse linear and long-chain branched (LCB) polymer melts, and the scope is limited to constitutive equations which can be expressed in terms of integral, differential, or integro-differential equations. Multi-mode models based on the concept of pre-averaged stretch such as the role-polym and the pom-pom models require a large number of nonlinear model parameters. Relaxing the assumption of a constant tube diameter, the number of nonlinear model parameters can be drastically reduced to 2 or 3, independent of the number of Maxwell modes needed to represent the linear viscoelasticity. The most recent constitutive model for linear and LCB polymer melts, the HMMSF model, requires only one parameter (the dilution modulus GD) for modeling extensional flows, and one additional parameter for accounting constraint release in shear flows, independent of the number of Maxwell modes used to define linear viscoelasticity.

Wednesday 11:20 Adria IP4

**Time temperature crystallinity superposition of an EVA copolymer**

Mario Minale, Liana P. Paduano, Luigi Grassia, and Claudia Carotenuto

*Department of Engineering, University of Campania Luigi Vanvitelli, Aversa, CE 81031, Italy*

In polymer processing the forming phase of the melt is followed by its solidification due to cooling. Crystallites are formed, an ordered structure can be detected, and the material rheological response significantly changes from liquid-like to solid-like. The knowledge of the mechanical response of the material during crystallization is therefore of seminal importance for process control and modelling. Homopolymers isothermal crystallization attracted some attention in the literature. Lamberti et al. [1] showed that for i-PP the same amount of crystallinity induces the same rheological hardening, regardless the crystallization conditions, thus proving a sort of crystallinity-rheological simplicity resembling the thermo-rheological one. Coppola et al. [2] measured the strength of the solidified PB arguing that it is dictated by some intrinsic features of the system, rather than by the crystallization conditions. Pantani et al. [3] proposed a sort of a time-crystallinity superposition for the i-PP with a non-uniform vertical shift of the moduli.

We hereby rheologically investigate both the isothermal and non-isothermal crystallization of a copolymer, Ethylene Vinyl Acetate (EVA), which does not suffer of thermal degradation problems as PB and PP. We changed the amount of amorphous phase by changing the relative amount of VA and extended the “use” and “advantage” of TTS to the case of a non-constant degree of crystallinity. To this end, we measured the frequency spectra of the EVA samples at different temperatures, varying from 110 to 20°C, i.e. during the crystallization process. Coupling the crystallization kinetics and the viscoelastic spectra at different temperatures, we here determine two independent shift factors, one for the time-crystallinity shift, and the other for the time-temperature-crystallinity-superposition.

Structure, shear and elongation rheology of multi-micro-nanolayers polymers based on polyethylene with varying macromolecular architectures

Ibtissam Touil1, Khalid Lamnawar2, and Abderrahim Maazou3
1Ingénierie des Matériaux Polymères, INSA Lyon, oyonnax 01100, France; 2Ingénierie des Matériaux Polymères, INSA Lyon, oyonnax, France; 3Ingénierie des Matériaux Polymères, INSA Lyon, Lyon, France

The aim of this study is to understand the confinement effects on the rheology and molecular dynamics in multilayer polymeric structures fabricated by the forced-assembly multilayer coextrusion process. Alternating multilayers of polyethylene (PE) and rigid polymers (higher Tg) have been studied, where rigid polymers act as confining system on PE (i.e., confined polymer). The PE with varying macromolecular architecture is incorporated therein. Various nano-structured multilayer structures with stable flow and layered architecture were then obtained using the layer multiplying technique. Various characterization techniques such as wide and small angle X-ray scattering (WAXS/SAXS), electron microscopes, dielectric and rheological spectroscopes were used to probe the structure, rheology and molecular dynamics of polyethylene in multi-layered systems. Interestingly, we found that confinements arising from the high Tg layers and the layer multiplication strongly affect the crystallization microstructure /morphology and molecular orientations of polyethylene. Moreover, the molecular and geometrical confinement are also found to remarkably influence the rheology and molecular dynamics of polyethylene in these multilayer systems. From micro- to nano-layers, rheological and dynamic behaviours are strongly dependent on the number of layers (or the individual layer thicknesses) and the compositions. Relevant mechanisms involving molecular rheology theories are proposed to elucidate the reasons underlying the changes especially in the extensional rheology. Results of this work will contribute to better understand the confinement effects in multi-layered assembly.

Some rheological and mechanical aspects of rolling sheets from molten metals and alloys

László A. Gömze and Ludmila N. Gömze
IGREX Engineering Service Ltd., Igrici 3459, Hungary

The rheological properties of the different materials [1-5] very strong depend on their compositions, structures, temperatures and processing technology. The rheological properties of the molten metals and alloys also strongly depend on their material compositions, temperatures and the times of crystalline nucleus formations. On the basis of rheological models of molten metals and alloys, mechanical stress equilibrium of elementary volumes and geometrical and kinetic parameters of rolling equipment the author successfully developed and mathematically described the followings:

- deformation characteristics and speed distribution of the melted materials in the gap between the rotating forming rollers;
- mechanical shear and pressure stress distribution developing in the molten metals and alloys passing through the gap of forming rollers;
- mechanical pressure distributions on the surfaces of the rollers of the high temperature forming equipment;
- the total energy requirement of rolling process of the melted metals and alloys.

The critical cross-section of the rolling machine gap and the values of the tensioning forces are also mathematically determined as function of rheo-mechanical properties of molten metals and alloys as well as function of compacting ratio and the geometrical and technological parameters of the rolling machine.

Keywords: alloys, mechanical stresses, molten metals, rheology, rolling, viscosity

Investigation of crosslinked rubber aging by Fourier transform rheology (FT-Rheology)

Shouliang Nie1, Jorge Lacayo-Pineda2, and Manfred Wilhelm1
1Karlsruhe Institute of Technology, Karlsruhe, Germany; 2Continental Reifen Deutschland GmbH, Hannover, Germany

The rheological properties of crosslinked rubber materials during aging [1] is of great importance, since they will determine the performance and safety of the products, e.g. the tires.

To characterize rheological properties, normally linear analysis is performed on the stress response of the rubber under oscillatory deformation. However, in the nonlinear viscoelastic regime, it is not adequate since this only give access to the linear portion of the already distorted stress response. Substantial information captured in the stress signal is lost. For nonlinear analysis, FT-Rheology [2-3] can be used to convert the stress signal into frequency domain and provide nonlinearity parameters, e.g. the third relative higher harmonic, $I_{3\omega}$.

In this work, the rheological nonlinearity of crosslinked rubbers filled with carbon black was studied in terms of $I_{3\omega}(\gamma_0)$ via strain sweep. The polymer networks were characterized by double quantum nuclear magnetic resonance (DQ-NMR) [4]. After aging at 70 °C for 14 days in air atmosphere, the polymer networks became denser, resulting in a decrease of $I_{3\omega}$ at large strain amplitude ($\gamma_0=70\%$) [5]. After hot-air aging at 120
ºC for 3 days, the polymer mesh size became more broadly distributed with more defects, leading to the rise of \( I_{3/1} \) at high strain amplitude. The nonlinearity at low strain amplitude (\( \gamma_0 = 2.5\% \)), which was derived from the carbon black involved networks, decreased after hot-air aging. This was assigned to the desorption of the polymer chains from the filler surface.


Non-linear rheology and strain-induced crystallization of PBT/PTHF thermoplastic elastomers
Matthias Nébouy¹, André de Almeida², and Guillaume P. Baeza³
¹MATEIS, INSA Lyon, Villeurbanne 69100, France; ²MATEIS, INSA Lyon, Villeurbanne, France; ³MATEIS, Polymer group, INSA-Lyon, Villeurbanne, -69621, France

Thermoplastic elastomers (TPEs) are widely used in the industry since the 1960s for their rubbery properties and ease of processing. They can be found in dashboard elements, wires sheaths and bitumen modifiers. Among them, PBT/PTHF segmented block copolymers occupy an important place because of their versatile mechanical behaviour, chemical resistance, thermal stability, and rapid crystallization. These materials, made of phase separated hard- and soft- domains, can exhibit quite different morphologies according to their chemical composition [1] and processing route [2]. Furthermore, we have recently shown that the hard-segments (PBT) crystallization, consisting surprisingly in a 2-steps process, was also strongly impacted by the chain rigidity [3].

In the present work, we propose to investigate the impact of non-linear mechanical solicitations applied prior to or during the crystallization. Steady shear experiments performed on TPEs with varying hard-segments content notably reveal a pronounced strain-induced crystallization resulting into a "long" viscosity plateau followed by a sudden increase of viscosity. While the latter was undoubtedly assigned to the TPE gelation, it was intriguingly observed at a constant strain amplitude, regardless of the strain rate. The evolution of the structure during this process was monitored through stress relaxation tests and X-ray scattering experiments opening the way to a deeper understanding of the phase separation mechanisms in such complex materials.

Normal stress differences and flow-type dependence in dense suspensions
Giulio G. Giusteri\textsuperscript{1} and Ryohei Seto\textsuperscript{2}
\textsuperscript{1}Department of Mathematics, Politecnico di Milano, Milan, Milan 20133, Italy; \textsuperscript{2}Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan

Dense suspensions of particles in viscous liquids are important fluids with a non-Newtonian rheology. They are found in many industrial applications (processing of food, paints, clays, concrete, etc.). Being able to understand and predict the behavior of such complex fluids is also relevant to environmental issues, as dense suspensions are present in landslides and floods. Recent computational results about the rheology of complex fluids is also pending particl.

In these experiments an unstable fluid filament held between two parallel plates undergoes capillary-thinning and breakup. Extensional properties of the fluid are then determined from the time evolution of the filament's minimum radius which we capture using a high-speed camera. The

Contributions of viscous dissipation in the flow behavior of soft glassy materials
Veronique Trappe\textsuperscript{1} and Marco Caggioni\textsuperscript{2}
\textsuperscript{1}Department of Physics, University of Fribourg, Fribourg 1700, Switzerland; \textsuperscript{2}Corporate Engineering Technologies, Procter & Gamble Comp, Cincinnati, OH, United States

We investigate the flow behavior of dense emulsions, for which the viscosity of the dispersing medium can be conveniently varied by temperature. Our experiments denote the importance of the medium viscosity in determining the functional form of the strain rate-dependence of the stress. We thus consider that elastic, plastic, and viscous dissipation needs to be accounted for and combine the elasto-plastic model with the Bingham model to describe our flow curves. Fits obtained by using this model describe the data as accurately as the Herschel-Bulkley model, and more importantly they provide physically meaningful values.

GO CaBER! - capillary breakup experiments on graphene oxide suspensions
Henry C. Ne\textsuperscript{1}, Andrew Corker\textsuperscript{1}, Eduardo Saiz\textsuperscript{2}, Esther Garcia-Tunon\textsuperscript{1}, and Rob J. Poole\textsuperscript{1}
\textsuperscript{1}University of Liverpool, Liverpool, United Kingdom; \textsuperscript{2}Imperial College London, London, United Kingdom

Graphene oxide (GO) colloids in solution, at high enough concentrations are known to be shear thinning, yield stress fluids (with their viscosity/viscoelastic properties known to be highly concentration dependent), forming strong networks at low concentrations (2 - 4vol\%) that in the absence of any other additives can be 3D printed using extrusion based processes; recovering to predominantly solid-like behavior (G'\textsuperscript{>}10kPa) when the shear is removed. Remarkably, the addition of GO at lower concentrations (1vol\% depending on the system) facilitates the formation of pastes to build free-standing 3D printed objects using materials such as; polymer solutions (PVA) and particulate systems (steel microspheres, SiC, and Al\textsubscript{2}O\textsubscript{3} platelets) which, in the absence of additives are unsuitable for 3D printing.

In the current work we explore the extensional properties of GO up to 0.3\% by volume using capillary breakup extensional rheometry (CaBER). In these experiments an unstable fluid filament held between two parallel plates undergoes capillary-thinning and breakup. Extensional properties of the fluid are then determined from the time evolution of the filament's minimum radius which we capture using a high-speed camera. The
measurements in extension are complemented by measurements in shear performed on a commercial rheometer (Anton Paar MCR 302). Our results indicate that even small amounts of GO flakes (0.02-0.3vol%) can significantly alter the pinch-off dynamics of a liquid bridge in comparison to Newtonian fluids of equivalent viscosity. GO solutions at concentrations that appear Newtonian in extension, already exhibit very strong shear thinning yield stress behaviour in shear experiments.

Wednesday 15:30 Europe I  
**CS28 Rheological behavior of magnetorheological fluids under precession magnetic fields: Experiments and particle-level simulations**  
M Terkel, J Tajuelo, O Martinez-Cano, Jose R. Morillas, and Juan de Vicente  
*Applied Physics, University of Granada, Granada, Spain*

Magnetorheological (MR) fluids are smart colloids prepared by dispersion of magnetizable particles in a liquid carrier. Under the presence of magnetic fields the dispersed particles become magnetized and aggregate along the field lines following deterministic aggregation dynamics. Eventually, these field induced structures are responsible for the viscosity enhancement and in some particular cases also for the appearance of a yield stress.

Most previous work in this field concern uniaxial DC fields that are suddenly applied on presheared suspensions. As a result, the particles self-assemble in gap-spanning, far-from-equilibrium, structures. In this contribution we subject MR fluids to carefully controlled intervals of uniaxial DC fields and precession fields in the velocity gradient direction. With this, bigger aggregates are formed and the MR effect is subsequently enhanced as demonstrated in both steady shear and small-amplitude dynamic oscillatory shear tests, which documented larger viscosities and G’ values, respectively, for an array of precession field configurations. Experimental results are found to be in good qualitative agreement with particle-level simulations and videomicroscopy observations.

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Wednesday 16:20 Europe I  
**CS29 Sedimentation rate of non Brownian inclusions in networks of rod like particles**  
Blandine Barabé¹, Deniz Z. Gunes², and Minne Paul Lettinga³  
¹Nestlé Research, Lausanne, Lausanne, Switzerland; ²Nestlé Research, Institute of Material Science, Lausanne, Switzerland; ³Forschungszentrum Jülich, Jülich, Germany

Gel and paste-like products are omnipresent in foodstuff, building and geological material. Their viscoelastic properties enable them to bear their own mass and those of fillers, that may be added for achieving improved properties of those systems, e.g. enriching their composition, or increasing their mechanical properties.

Successive shearing events may decrease, or even suppress, particle-bearing properties [1]. This may be the case when shearing the gel irreversibly changes its structure. Such effects are not desirable for consumer products, in which fillers should stay homogeneous in solution during process and shelf life.

For this reason, model systems were selected in order to understand better the recovery of gel macrorheological properties in the presence of inclusion(s). Yield stress fluids composed of anisotropic subunits, efficiently trap beads at low volume fractions. A model colloidal system of repulsive colloidal rod-like fd virus and Pf1 bacteriophages was studied [2]. Homogeneously dispersed large non-Brownian inclusions were suspended in solutions of fd virus or Pf1 bacteriophages. The aim was to determine whether conditions for which beads were trapped in solutions could be found. A further goal was to investigate whether for some set of conditions, the system of inclusions in the virus suspensions is stable enough at rest to be used for shear experiments.

The sedimentation rate of inclusions was investigated as a function of fd virus length, concentration and the solvent density. For interpretation, we used the Stokes terminal speed predictions with a modified viscous term to account for concentration effects. We measured the deviation between experiment and theory, for both virus lengths investigated. Furthermore we compared the experimental data for both rod lengths and showed that the decreasing trend is similar after rescaling with the overlap concentration.


Wednesday 16:40 Europe I  
**CS30 Concentrated non-Brownian suspensions under oscillatory shear flow: Dependence on the applied strain and frequency**  
Raffaella Martone, Claudia Carotenuto, and Mario Minale  
*Department of Engineering, University of Campania Luigi Vanvitelli, Aversa, CE 81031, Italy*

Concentrated suspensions are encountered in many different fields as: food processing, health and care industry, environmental engineering. They can show a very rich behaviour being a trait-union between dilute suspensions and granular flows. Even the simplest suspensions made of non-colloidal neutrally buoyant spheres in a Newtonian polymer can show intriguing features like the flow irreversibility due to multi-body interactions that make the particles trajectories chaotic even at low Reynolds numbers. Flow irreversibility may result in irreversible interactions that lead the
suspensions to evolve with the accumulated strain under oscillatory shear. It was shown the complex viscosity reaches a plateau value, for accumulated strains larger than 8000, which depends on the applied strain attaining its minimum in correspondence of an applied strain of about 1. This behaviour is due to a microstructure reorganization induced by the flow, as shown with numerical simulations, based on the Stokesian dynamics, by Bricker and Butler [J. Rheol. 51:735 (2007)] and, in principle, it should be frequency independent, since neither material characteristic times, nor flow ones are present. The Stokesian dynamics indeed predicts that the frequency cancels from the governing linear equations.

We here show that very surprisingly both the evolution of the complex viscosity with the accumulated strain and the plateau value do depend on the applied frequency. We focus on a non-Brownian suspension made of hollow glass spheres suspended in a Newtonian PIB at 40% volume fraction. After preconditioning the sample with a steady shear, we impose three different frequencies: 5, 50 and 200 rad/s and investigate the frequency dependence of the complex viscosity on both a stress-controlled and a strain-controlled rheometer. Depending on the applied strain and frequency, the final plateau value can be larger or smaller than the preshear viscosity.

Wednesday 17:00 Europe I  CS31

**Rheology of rod-shaped cellulose nanocrystal (CNC) particle suspensions in the presence of aqueous polymer solutions and their potential applications**

Yaman Boluk¹ and Hale Oguzlu-Baldelli²

¹Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta T6G 1H9, Canada; ²University of British Columbia, Vancouver, British Columbia, Canada

Rod-like CNC particles are generally produced by sulfuric acid hydrolysis of chemical wood pulp. CNC particles are typically 6-10 nm wide and 100-200 nm long. Negatively charged sulfate groups on CNC surfaces generate stable dispersions at low ionic strengths in aqueous dispersions. Conventionally it is known that CNC has not any thickening effect as concentrations less than 6-8% due to its low aspect ratio. We have shown that when CNC is used less than 1% in certain dilute to semi-dilute polymer solutions, interesting synergies and rheological behaviors arise in ways that cannot be predicted from its neither constituent. CNC self-organizes into mesoscopic physical structures in such polymer solutions and properties and interactions of these mesoscopic structures determine the macroscopic behavior of these systems. Such CNC suspensions have wide range of water based green products including as rheology modifiers in paints, coatings, drilling fluids and personal care products. The focus of this presentation is to discuss the structure, dynamics and rheology of cellulose nanocrystals (CNC) suspensions in the presence of aqueous semi-dilute polymer solutions. Unique rheological and mesoscopic scale phase behaviors of rod-like nanocrystalline cellulose (CNC) suspensions in aqueous media have been revealed in the presence of non-adsorbing polymers at semi-dilute concentrations. As an example, an impressive non-Newtonian thickening behavior (1000 Pa.s) was obtained as a result of incorporating 1.0% CNC suspension, which has the viscosity of 2x10^{-3} Pa.s into a 1.0% hydroxyl ethyl cellulose (HEC) suspension, which has only viscosity of 0.8 Pa.s. This behaviour is due to the depletion and structure formation of rod-shaped CNC particles by nonadsorbing polymers. The viscoelasticity of semi-dilute rod shaped cellulose nanocrystalline suspensions in the presence of non-adsorbing polymers were determined by oscillatory rheology in addition to their non-Newtonian shear thinning behavior under steady state shear flow.

Wednesday 17:20 Europe I  CS32

**Rheology of hyper-concentrated nanocellulose gels during lubricated compression**

Shubham Gupta¹, Florian Martoia², Laurent Orgéas³, and Pierre J.J. Dumont²

¹CNRS, 3SR Lab, Univ. Grenoble Alpes, Grenoble INP, Grenoble, France; ²CNRS UMR5259, LaMCoS, Univ. Lyon, INSA Lyon, Lyon, France

Nanocelluloses such as Cellulose Nanofibrils (CNF) or Cellulose Nanocrystals (CNC) are mainly extracted from plants or wood in the form of colloidal aqueous suspensions. CNFs are slender and tortuous nanofibres (length 1 > 1 μm and width d ≈ 5-100 nm). CNCs are rod-shaped nanoparticles (l ≈ 100-200 nm, d ≈ 5-20 nm). Nanocelluloses have attracted a considerable attention due to their outstanding mechanical properties. They can be used to produce various types of materials such as foams, nanocomposites or continuous filaments using various processing routes during which nanocellulose suspensions behave as complex hydrogels. For a better control of the flow conditions of these gels during their processing, it is crucial to characterize and model their rheology under various loading conditions such as shear and compression in concentrated and hyper-concentrated regimes (from 1%wt to 20%wt). Thus, we developed an original methodology to prepare concentrated (1%wt) to hyper concentrated (15wt%) nanocellulose suspensions with CNCs, TEMPO-oxidized CNFs and enzymatic CNFs, i.e., with three different particle types and colloidal stabilities. The prepared gels were then subjected to uniaxial compression experiments performed in perfect slip conditions at various strain rates. Some of the compression experiments were carried out with optical visualization and Digital Image Correlation (DIC) to measure local strain-field measurements on the sample surface. Stress-strain curves showed two distinct regimes: first a linear increase followed by a plateau associated to a flow stress. The experiments also revealed the effect of the types and concentrations of nanocellulose suspensions as well of strain rates on the rheological properties of these gels. From DIC measurements, flow heterogeneities in the form localized deformation bands and water segregation could be observed under various testing conditions.

Note: The affiliation of the first author, Shubham Gupta, is Univ. Grenoble Alpes, Grenoble INP, CNRS, 3SR Lab and Univ. Lyon, INSA Lyon, CNRS UMR5259, LaMCoS
Rheology test methods and data interpretation model for fibre reinforced semi-solid cement-based materials for extrusion
Xiangming Zhou
Brunel University London, Uxbridge, United Kingdom

Manufacturing of cement-based products predominantly remains based on old batch-processing techniques such as casting and pressing, which limits the applications and performance of the materials and products formed. This paper reports on research into transforming the manufacturing of precast cement-based products from in batches to a continuous process by way of extrusion. A key to a successful and successive extrusion process is rheology. Cement-based materials suitable for extrusion feature coupled viscous, elastic and plastic properties with traditional rheology test method, such as using a shear-driven rheometer, does not work for such semi-solid, dough-like materials. A range of non-traditional rheology test methods, such as ram extrusion, capillary extrusion, orifice extrusion, upsetting, direct shear box test, and tri-axial test, have been developed/modified to characterise the viscous, elastic and plastic properties of semi-solid, dough-like cement-based materials tailored for extrusion. In addition, data interpretation models have been proposed for various rheology test methods for extrudable cement-based materials. It has been found that most rheology test method itself cannot derive the coupled elasto-viscoplastic rheology properties of semi-solid cement-based materials for extrusion. A holistic approach of employing a range of rheology test methods is therefore needed to give a full picture of the coupled elasto-viscoplastic rheology properties of cement-based materials for extrusion. Finally, various shapes of fibre-cement products developed via extrusion at laboratory and factory scales are introduced with the intention to further promote, extrusion, as a new offsite manufacturing techniques for concrete products for modular construction which is currently demanded by construction industry to achieve low cost and low environmental impact production.

Keywords: Capillary extrusion, Cement-based Materials; Extrusion; Orifice extrusion, Ram extrusion, Rheology, Shear box test, Tri-axial test, Upsetting

Symposium NF

Non Newtonian Fluid Mechanics & Flow Instabilities (in honor of Prof. Mike Webster)
Organizers: Tim Phillips, Russel Davies, Natalie Germann and Corneliu Balan

Ageing, yielding and shear banding in an elasto-plastic model
Hugh J. Barlow1, Andrew Clarke2, and Suzanne M. Fielding1
1Soft Matter and Biological Physics, Durham University, Durham, Durham DH1 3LE, United Kingdom; 2Schlumberger Cambridge Research, Cambridge, Cambridgeshire CB3 0EL, United Kingdom

We introduce a two-dimensional tensorial lattice-based elasto-plastic model for the rheology of yield stress fluids. The model incorporates both full force balance (including after each local plastic yielding event), and the rheological ageing behaviour that is widespread in soft glassy materials. We examine the emergence of shear bands separately in shear startup and following the imposition of a step stress. These bands are shown to be transient but very long-lived, and we characterise carefully the lifetime of the bands before a statistically homogeneous steady state is recovered. We also consider the interplay between these long-lived bulk shear bands, and avalanches of plastic events that flicker in and out of existence across the sample.

The Kaye effect: New insights from experiment, theory and modelling
Jack King and Steven J. Lind
School of Mechanical, Aerospace and Civil Engineering, University of Manchester, Manchester, United Kingdom

The Kaye effect is a phenomenon whereby a jet of fluid poured onto a surface appears to leap on impact, rather than stagnate or coil as expected. Since it was first described in 1963, several authors have attempted to explain the mechanism by which the phenomenon occurs, although to date no complete explanation for the behaviour exists. The effect is often used as an example of interesting and unexplained phenomena in popular science and outreach. Current evidence points towards the existence of an air layer between the jet and the heap which enables slip. We show experimentally that the Kaye effect does not occur in a vacuum, indicating that the air layer is crucial for the effect to occur. By conducting a theoretical analysis based on control volumes we show that viscoelasticity plays a key role in the Kaye effect, and this role is two-fold. Firstly, viscoelasticity appears to increase air entrainment, and secondly, it reduces the pressure required to bend the jet, allowing a thicker air layer to be sustained. We present the numerical simulations of viscoelastic jets showing how viscoelasticity qualitatively affects jet buckling, increasing the chances of slip, and therefore the initiation the Kaye effect. These new findings provide insight into a problem that has puzzled theologists for over half a century.
**Wednesday 15:10 Emerald I**

**LIFT of viscoplastic fluids**

Maziyar Jalal1, Klein Schaarsberg Martin2, Claas-Willem Visser2, and Detlef Lohse2
1Applied Mathematics and Theoretical Physics, University of Cambridge, Cambridge, United Kingdom; 2University of Twente, Enschede, The Netherlands

Laser Induced Forward Transfer (LIFT) is a direct-write method of printing. LIFT exploits the energy of a laser (continuous or pulsed) to locally transfer material, from one surface to another. Herein, we experimentally study the LIFT of viscoplastic materials; a class of non-Newtonian fluids that represent a wide range of printing inks in LIFT technology such as hydrogels in 3D bio-printers or metallic pastes in electronic printing devices. We use Carbopol solutions. The elasto-viscoplastic material features yield stress and storage modulus of 10s of Pascals. Above the yield stress, the elastic properties are negligible and the material behaves like a shear thinning fluid with flow indices of about 0.4. In experiments, we focus a 5ns laser pulse inside a thin layer of the viscoplastic material. The optical breakdown results in bubble formation inside the layer that yields to the jet formation. We visualize the jet dynamics using high-speed imaging and categorize different regimes of jetting, depending on the laser energy, focal height, and material rheology. The early stage of the layer deformation is highly inertial and independent of the rheological properties. At large time, the apparent viscosity and the surface tension become important and define the shape of the jet. We provide a theory to find a characteristic velocity that is a-priori known and define non-dimensional groups of modified Reynolds and Weber numbers to classify the observed morphologies in a regime map. In the end, we show the application of the method in bio-3D-printing and printing circuits for flexible electronics and discuss how our results can be used in optimizing the 2D or 3D printing with viscoplastic materials.

**Wednesday 15:30 Emerald I**

**Water entry of yield-stress droplets**

Anselmo Pereira1, Romain Castellani2, Rudy Valette1, Elie Hachem2, Maziyar Jalal3, and Detlef Lohse4
1CMEF, MINES ParisTech, PSL - Research University, Sophia-Antipolis, Sophia-Antipolis 06904, France; 2MINES-ParisTech, PSL Research University, Sophia Antipolis, France; 3Applied Mathematics and Theoretical Physics, University of Cambridge, Cambridge, United Kingdom; 4University of Twente, Enschede, The Netherlands

We study through experiments and direct numerical simulations the water entry of yield-stress droplets. Experimentally, the impact of carbopol droplets on water surfaces is analysed by using a high-speed camera. Numerically, the phenomenon is taken into account thanks to an adaptive variational multi-scale method for three materials (air, water, and Bingham fluid) with surface tension. Following the impact on water free surfaces, these Non-Newtonian fluids undergo at least three stages: a spreading one (1), related to the impact acceleration, driven by the viscous dissipation and during which the droplet reaches its maximum deformation; a droplet-water interaction stage (2) along which the viscoplastic material tends to recover its initial morphology before being finally dominated by the yield-stress (3), which prevents further deformations. Different final shapes are observed. Their link with the fluid rheology is discussed in the light of scaling laws, kinematic and energy exchange analyses.

**Wednesday 16:20 Emerald I**

**Filament-stretching dynamics of yield-stress fluids**

Pantelis Moschopoulos, Alexandros Syrakos, Konstantina Psaraki, Yannis Dimakopoulos, and John Tsamopoulos

Chemical Engineering, University of Patras, Patras, Greece

We study the extension of a material that is confined by two coaxial disks initially forming a cylindrical filament when the disks are pulled apart. The material may be an emulsion, suspension or foam and so it exhibits a viscoplastic response. It follows the Herschel Bulkley model and yields according to the von Mises criterion. The evolution of the bridge shape, particularly its minimum radius, velocity and stress fields are monitor. Assuming axial symmetry, the governing equations are solved using our newly developed Penalized Augmented Lagrangian method [1]. The code is validated by comparing its predictions to experiments by Balmforth et al. [2] and Niedzwiedz et al. [3]. Satisfactory agreement is found for a wide range of values of the Bingham number (Bn, ratio of yield stress to capillary forces). A similar comparison study with the predictions of a 1D slender filament approximation shows that at high values of Bn, the 1D model fails to predict not only the shape of the bridge-breakup but also where and when this occurs. We show that this discrepancy stems from the simplified von Mises criterion in the slender approximation. A complete parametric study is performed where the effect of the Bn, shear thinning, stretching velocity and initial aspect ratio, are systematically examined. Finally, we investigate how the usually smaller material elasticity affects the bridge dynamics and whether universality exists during the pinch-off of viscoplastic materials.


**Wednesday 16:40 Emerald I**

**Spreading behaviour of complex fluids, from film formation to application properties**

Christophe Kusina1, Jean-Baptiste Boitte2, Odile Aoubrun2, and Annie Colin1
1CBI-MIE, ESPCI Paris, PARIS 75005, France; 2L’Oréal Recherche et Innovation, Chevilly-Larue, France

Complex fluids (i.e. emulsions, solid dispersions, gels) with non-Newtonian rheology are often found in several industries (food, cosmetics...) as products used by consumers. These products target different performances (optical, mechanical, optical...), which are generally dramatically
affected by their spreading behaviour. From a scientific point of view, numerous parameters have to be taken into consideration to simulate the real life spreading of a product through in vitro experiments. The spreading, due to the shear effect induced by the gesture, challenges the rheological properties of the complex fluid in dynamic conditions which causes changes in product microstructure. However, these physicochemical phenomena and the link between structure and property during the spreading of a cosmetic product on the skin still raises many questions. For that purpose, we developed an innovative blade coating system that mimics the spreading of a product and observed the microstructure of the formed deposit and how it evolves with time. With this system, we studied the fundamental parameters that are involved in the film formation of model complex fluids (i.e., capillary number, spreading velocity, yield stress and the elasticity of the blade). We investigated the effect of above parameters in order to obtain a better understanding of the spreading phenomena. On the other hand, we also investigated industrial applications of model complex fluids. For example, back and forth movements during spreading create a pattern on the deposit surface depending on the composition of the complex fluid. These patterns are due to both rheological behaviours of fluids (shear thickening or yield stress effects), and to unavoidable Plateau-Rayleigh destabilization within the film. Since these patterns create thickness heterogeneities in the film, they may impact product performances and have to be further investigated.

Wednesday 17:00 Emerald I

Long waves in power law liquid flow down on oscillating plane
Evgeny Mogilevskiy and Regina Vakhitova
Faculty of Mechanics and Mathematics, Lomonosov Moscow State University, Moscow 119992, Russia

Many liquids used for industrial applications, e.g., paints, concrete, soap, petroleum, etc. are non-Newtonian. The shear stress in these fluids depends on shear rate, and such dependence affects transport properties.

We consider a free surface flow on non-Newtonian fluid over a vertical plane. It is well-known that this flow is unstable due to Kapitsa instability, and long waves appear on the free surface. We assume that the supporting plane oscillates in a longitudinal direction and study how mean characteristics (the flow rate, the film thickness) and the flow stability depend on amplitude and frequency of these oscillations.

We model a non-wavy flow and study its stability. The non-wavy flow has flat free surface and constant thickness, and the velocity field has one non-zero component which depends on time periodically. For this flow, we have a non-linear PDE and find its solution numerically. We compared our results with experimental data presented in V. Sobolik Rheol. Acta. 1994. 33 (2) and found good correspondence.

For the stability analysis, we use the Integral Boundary Layer approach. Assuming that disturbances have small wavenumber (long waves) and their frequency is much lower than the plane oscillations frequency. We obtain equations describing the evolution of the film thickness and local flow rate on the disturbances time scale.

We showed that the oscillations of the supporting plane change both mean thickness of the thin film flow down and its stability characteristics. For pseudoplastic fluids, the thickness decreases. For all fluids, the oscillations stabilize the flow for long-wave disturbances. There is a critical value of oscillations amplitude which makes the flow stable, and this value has a finite limit while the oscillation frequency tends to infinity.

The work is supported by the Russian Science Foundation (project 18-71-00049)

Symposium SM

Polymer Solutions, Melts & Composites
Organizers: Giovanni Ianniruberto and Evelyne van Ruymbeke

Wednesday 14:30 Emerald II

Thermo-rheological effects of plasticizer types and concentrations on cellulose diacetate with varying molar masses
Rafael Erdmann¹, Oscar Eduardo Vernaez Hernandez¹, Stephan Kabasch¹, and Hans-Peter Heim²
¹Bio-based Plastics, Fraunhofer Institute UMSICHT, Oberhausen 46047, Germany; ²Institute of Material Engineering, Polymer Engineering, University of Kassel, Kassel 34125, Germany

The thermo-rheological effects of adding different types and amounts of plasticizer to cellulose diacetate were studied using Dynamic Mechanical Thermal Analysis (DMTA) and Oscillation shear rheology (SAOS). Depending on the plasticizer type and concentration the zero shear viscosity, i.e., the first Newtonian plateau, can be adjusted before shear-thinning behavior occurs. The control of the viscoelastic performance is of special interest for extrusion foam processes (comparable to XPS-processes), where low shear rates between 1 and 30 s⁻¹ arise. In this study, the effects of the type of plasticizer and its concentration as well as the molar mass of cellulose diacetate on the entanglement density and the viscoelastic properties of the material are examined. Three different plasticizers have been used in the cellulose acetate blends in concentrations between 15 to 40 wt.-%. The plasticizer concentration and temperature affect the viscosity more pronouncedly than the plasticizer type used does. Furthermore, the plasticizer significantly influences the apparent measured entanglement density of cellulose acetate.
Time-dependent behaviour in analyte-, temperature- and shear-sensitive Pluronic PE9400/water systems

Nuria Calero¹, Jenifer Santos¹, Coro Echevarría², José Muñoz³, and Maria Teresa Cidade⁴

¹Departamento de Ingeniería Química. Facultad de Química, University of Seville, Seville, Spain; ²Departamento de Ciência dos Materiais e CENIMAT, Universidade Nova de Lisboa, FCT-NOVA, Caparica 2829-516, Portugal

Phenomenological scaling using the Carreau model to obtain characteristic time(s) and characteristic modulus(s) as scaling factors. Phenomenological scaling uses the mean relaxation time and the mean modulus as a scaling factor from the terminal behavior of solutions. The concept of the phenomenological scaling is similar to that of the viscosity-fitting scaling: use of scale factors which can be determined for any viscoelastic fluid regardless of molecular weight distribution. Two scaling methods were applied to the linear viscoelasticity of the cellulose solutions with different molecular weights and molecular weight distributions. The results of each scaling were compared by the superposition of master curves obtained from each scaling. The effects of molecular weight distribution were observed by the dependence of the scaling factors on concentration and molecular weight of cellulose.

Scaling analysis on the linear viscoelasticity of cellulose 1-ethyl-3-methyl imidazolium acetate solutions

Mi Kyung Kwon¹, Junhaeng Lee², Kwang Soo Cho³, and Se Geun Lee¹

DGIST, Daegu, Republic of Korea; ¹Kyungpook National University, Daegu, Republic of Korea

Many researches have studied the viscoelasticity of cellulose/ionic liquid solutions through the conventional scaling rules which assume the monodisperse polymer. However, they are not suitable for cellulose since natural polymers such as cellulose have molecular weight distribution. We compared the viscosity-fitting scaling [1] and the phenomenological scaling to replace the conventional scaling. Conventional scaling uses characteristic time(s) and characteristic modulus(s) as scaling factors, but it is difficult to define the plateau modulus for polydisperse solutions. On the other hand, the viscosity-fitting scaling is obtained by using the Carreau model to obtain characteristic time(s) and characteristic modulus(s) and use it as a scaling factor. Phenomenological scaling uses the mean relaxation time and the mean modulus as a scaling factor from the terminal behavior of solutions. The concept of the phenomenological scaling is similar to that of the viscosity-fitting scaling: use of scale factors which can be determined for any viscoelastic fluid regardless of molecular weight distribution. Two scaling methods were applied to the linear viscoelasticity of the cellulose solutions with different molecular weights and molecular weight distributions. The results of each scaling were compared by the superposition of master curves obtained from each scaling. The effects of molecular weight distribution were observed by the dependence of the scaling factors on concentration and molecular weight of cellulose.

Phase state and rheology of cellulose/ionic liquid/non-solvent triple systems

Anna V. Kostyuk, Viktoriya Y. Ignatenko, Tatiana S. Anokhina, Sergei V. Antonov, and Sergey O. Ilyin

A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow 119991, Russia

At the formation of the cellulose films, there is a contact between the cellulose solution and its non-solvent. Thus, it is important to know phase diagram for cellulose - solvent - non-solvent triple systems. Such diagrams have been obtained for N-methylmorpholine N-oxide, N,N-dimethylacetamide/LiCl, NaOH and ZnCl₂ solutions as the cellulose solvents. However, no such triple diagrams were found in literature for cellulose solutions in ionic liquid.

In this research, we investigated cellulose - 1-ethyl-3-methylimidazolium acetate - non-solvent systems. As non-solvents causing cellulose precipitation we used water and isopropanol. Besides, we used dimethyl sulfoxide which formally is a cellulose non-solvent but actually is a cellulose co-solvent in combination with the ionic liquid.

Rheology of the cellulose solutions in solvent/non-solvent mixtures with different ratios of the components was investigated in detail. The transitions of solutions to gel state as well as of gels to two-phase systems with variation of the component concentration and temperature were demonstrated. The components' interdiffusion coefficients and the morphology of cellulose films were evaluated by laser interferometry method.

This research was supported by the Russian Foundation for Basic Research (project # 17-08-00499).
**Influence of polyalkylmethacrylates on the rheological behavior of lubricants**

Justine Dorengé, Jean-François Tassin, Christophe Chassenieux, and Fanny Briand

*1Université du Mans, Total, Le Mans 72560, France; 2Université du Mans, Le Mans 72000, France; 3Marketing & Services, TOTAL, Solaize 69360, France*

Nowadays, the reduction of car fuel consumption is an important concern for oil companies for a green planet purposes. It implies among other the reduction of friction between moving parts through the improvement of lubricant properties. A lubricant is composed of base oil and several additives. Among them, polymeric compounds are commonly used to modify the rheological properties, more especially to limit the decrease of viscosity with temperature. The principle of action of this type of additives, called Viscosity Index Improver (VII), is based on the swelling of polymer chains with temperature due to an increase of the solvent quality for the macromolecules. In this presentation, we will show how the chemical structure can influence the viscosity of model systems consisting in a base oil containing polyalkylmethacrylates at concentrations slightly below \( T_c \). We will focus on the characterization of intrinsic viscosity over a large temperature range (between -10°C and 135°C). These system show an usual increase of this parameter above a critical temperature and the link between structure and the swelling temperature will be described. Since stability of the formulations under use is a key issue, a degradation study in a conventional test has been carried out, followed by a detailed characterization of the polymer chains after degradation. We will emphasize how the molecular weight and more precisely the hydrodynamic volume of the polymer control the degradation. The consequence of degradation on the molecular weight distribution will be described. Finally, in addition to rheological properties of the solution, their behavior under tribological tests is a key issue. We propose a map; using dimensionless parameters, to represent the film thickness in a rolling spherical contact and show that different regimes depending on the chosen polymer are observed.

**Effect of asphaltene addition on rheology and structure of polymers**

Viktoriya Y. Ignatenko, Anna V. Kostyuk, Sergei V. Antonov, and Sergey O. Ilyin

*A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow 119991, Russia*

It is well recognized that composites formed by adding nanoparticles to polymers can have significantly enhanced properties in comparison with the unfilled polymer. At the present time exhaustion of the light crude oil supplies has stimulated an increasing interest to heavy crude oil production and processing. Processing of heavy crude oil is a difficult and laborious procedure which includes removing of heavy components that can poison catalytic systems in oil refinery and contribute to heavy crude oil viscosity. Asphaltenes are one of such harmful components of oils. Since the size of asphaltenes molecules is about few nanometers and their molecular structure contains flat fragments consisting of several aromatic cycles, they can be considered as nanofillers close in structure to graphene, which is generally regarded as one of the most promising and widely used carbon nanofillers for polymer modification at the moment.

The asphaltenes were obtained from Ashalchinskaya heavy crude oil by precipitation with hexamethyldisiloxane. Then the asphaltenes were added to different polymers such as polypropylene, polystyrene, and polyetherimide. The phase state and morphology as well as rheological and thermophysical properties of the composites containing up to 30% of asphaltenes were considered. The glass transition temperature, melting and crystallization temperatures were evaluated using DSC. The flow curves and frequency dependencies of storage and loss moduli were obtained using a rotational rheometer. It was found that asphaltenes are partially soluble in polymer medium and thus play a role of plasticizers. However, in the case of high asphaltene content, they are able to act as a reinforcing phase.

It was demonstrated that asphaltenes can be regarded as cheap and promising nanofillers for thermoplastic polymers.

This research was supported by the Russian Ministry of Education and Science, contract # 14.613.21.0069 (identification code is RFMEFI61317X0069).

**Isostructural softening of the filler network in SBR/silica nanocomposites**

Hoang G. Trinh, Marlène Deslotre, Fabien Dutertre, Jean-Charles Majesté, Florent Dalmas, and Guilhem P. Baeza

*1MATEIS, Polymer group, INSA-Lyon, Villeurbanne, - 69621, France; 2IMP-LRMP, Université Jean Monnet, Saint Etienne, - 42023, France*

A new formulation of the widely used nanocomposites based on SBR (ca. 250 kg mol\(^{-1}\)) and fractal silica fillers is proposed by substituting the usual covering and coupling agents by poly-propylene glycol (PPG) oligomers (4 kg mol\(^{-1}\)). We study in a systematic way the structural evolution as well as the change in linear and non-linear mechanical properties of two series of samples varying: (i) the silica volume fraction (\( \Phi_{Si} = 0, 5, 10 \) and 15 vol.% in PPG free samples, and (ii) the amount of PPG for a given silica content \( \Phi_{Si} = 15 \) vol.%: While the first series are used as a reference, showing expected trends (e.g. increase of the plateau modulus), the second series reveal in contrast, a surprising PPG insensitivity of both the silica structure (investigated with SAXS, FIB-SEM and TEM) and the properties "at rest" (linear rheology and dielectrics). However, increasing the deformation amplitude (in both shear and tension tests) discloses the great effect of the oligomers, opening possibly the way to a fruitful decorrelation between the low and high deformation performances of tires. Although this study is focused on the investigation of uncrosslinked materials, we will also provide some results on more operative industrial formulations in which the filler network rigidity appears as an independant trigger for the tailoring of the mechanical properties.
Decoupling polymeric and colloidal contributions to the rheology of self-suspended grafted nanoparticles

Daniele Parisi¹, Eileen Buening², Benencwicz C. Brian³, Sanat K. Kumar⁴, and Dimitris Vlassopoulos⁴
¹Materials Science and Technology, FORTH-University of Crete, Heraklion, GR 70013, Greece; ²Chemical Engineering, Columbia University, New York, NY, United States; ³Chemistry and Biochemistry, University of South Carolina, Columbia, SC, United States; ⁴Chemical Engineering, Columbia University, New York, NY, United States

Melts of polymer-grafted nanoparticles have been shown to exhibit colloidal features and represent a class of materials known as self-suspended nanoparticles [1]. The structure and rheology of these systems have been investigated in detail, however a clear connection between internal particle microstructure and macroscopic properties remains elusive. Here we address this challenge by using a series of well-characterized nanoparticles having the same core hard silica particle, same grafting density and varying molar mass of the grafted chain. In particular, we investigate the linear rheological response of SiO2-PMA nanoparticles. We find a very rich viscoelastic response exhibiting dual relaxation dynamics that can be decoupled into a polymeric and a colloidal contribution. The dual nature of the system exhibited in the rheological spectra is quantitatively modeled by using: i) a simple chain conformation model to detect the dry-to-wet brush transition, ii) the branch-on-branch (BoB) model for star polymers to describe the relaxation of grafted chains [2], and iii) Mode Coupling Theory (MCT) [3] for the long-time colloidal contribution. We compare the results against data with other grafted particles and multiarm star polymers and present results on the nonlinear shear response in the polymer-dominated and colloid-dominated regimes. These results suggest the possibility to tailor the flow properties of soft composites by varying the internal structure of nanoparticles and expanding the dynamic arrest ideas to melts of nanoparticles. Moreover, they open new routes for rationally designing membranes with desirable separation abilities and mechanical properties.


Numerical simulations of short fiber polymer composite in the extrusion process

M. Masoudian¹, N. Sharifi-Mood², and J. M. Marchal³
¹Product Lifecycle Management, SIEMENS Industry Software GmbH, Nuremberg, Germany; ²SIEMENS Industry Software, Bellevue, WA, United States; ³SIEMENS Industry Software, Louvain-la-Neuve, Belgium

Fiber-reinforced polymeric composites are extensively manufactured by various melt processes such as extrusion, injection, and compression molding. Generally, in a suspension of fiber, the flow field alters the orientation of the fibers; at the same time, the presence of fibers changes the stress response of the suspension. In this work, we investigate melt rheological effects on predicted fiber orientation in an extrusion problem by using numerical techniques. Continuum approach based on Advani et al. [1] was adopted to predict the orientation of rigid short fibers with uniform volume fraction in the suspension. Furthermore, an Arbitrary Lagrangian-Eulerian (ALE) method was developed to track the free surface in melt extrusion process simulation. We first determine the parameters associated with the constitutive equation (viscoelastic (VE) and generalized Newtonian (GN) models) based on experimental rheometry data by means of the material calibration solver of Simcenter STAR-CCM+. This includes various non-linear shear and extentional flows along with Small Amplitude Oscillatory Shear (SAOS) tests in the linear regime. Our numerical approach was fully verified by comparing the fluid flow properties and fiber orientation in an extrusion process with the results reported in the literature recently [2]. Additionally, we investigate the influence of polymer melt properties on the die swell and the orientation of short fiber in the die and extrudate regions. Finally, by utilizing the fully two-way coupled approach, we numerically determine the detailed flow pattern of a suspension of short fiber in a GN fluid during the extrusion process. All simulations were performed completely with Simcenter STAR-CCM+.


Symposium EM

Experimental Methods & Progress in Rheometry

Organizers: Dimitris Vlassopoulos, Roland Kádár and Christian Clasen

Multi-parameter in-process monitoring of clay dispersion during melt compounding with PLA

Paulo F. Teixeir¹, Fiorenza Sutera², Roberto Scaffaro², José A. Covas¹, and Loïc Hilliou¹
¹IPC - University of Minho, Guimarães, Portugal; ²DICAM - University of Palermo, Palermo, Italy

The time evolution of organoclay particle size and volume fraction, as well as the shear viscosity, are measured in-line for a series of Poly(lactic acid)/organoclay composites, using a rheo-optical die coupled to a prototype modular corotating twin screw extruder [1]. The small angle light scattering patterns and light attenuation recorded during transient experiments indicate that clay dispersion develops through melt intercalation...
between the clay galleries, thereby expanding the aggregates size, and eventually leads to aggregates break-up, i.e., exfoliation. The simultaneous recording of shear viscosity also indicates that smaller viscosities promote a faster melt intercalation and exfoliation but hinder the extent of clay dispersion. The effect of screw speed on the clay dispersion mechanism is also studied. The methodology used in the present study validates the well accepted mechanism for clay dispersion and can be applied straight away for the monitoring of PNC manufacturing during practical production. The methodology is also of particular interest for the development of highly thermo-mechanically sensitive materials such as biodegradable polymer blends and composites, which are the subject of intense research due to the societal awareness on environmental issues associated with plastics.


Wednesday 14:50 Europe II
High-frequency rheometry of polymer melts and colloidal glasses: validating the loss angle measuring loop
Athanasiou Athanasius, Dimitris Vlassopoulos, and George Petekidis
Institute of Electronic Structure & Laser, Foundation for Research and Technology Hellas, FORTH, Heraklion, Greece
We revisit and improve the technique of sliding plate piezo-operated rheometry in order to provide a versatile platform for measuring the linear viscoelastic properties of various soft matter systems. The sensitive loss angle measuring loop is validated explicitly against reference data from entangled amorphous polymer melts obtained with conventional rotational rheometers by means of time-Temperature Superposition (tTS). Errors are traced and theoretical corrections are shown to be feasible when strong non-linearities are present. This gives confidence in measuring more complex systems where tTS does not apply. We also demonstrate the ability to probe the short-time dynamics of hard-sphere colloidal glasses. Important high-frequency features such as the limiting behavior of the high-frequency elastic modulus, the respective moduli crossover related to beta-relaxation and the associated limiting, in phase with strain-rate, dynamic viscosity, are captured. This promising technique can complement the rheological map of many commercially available products. By providing direct insights to interactions at nano-metric particle separations it will augment the design of novel materials with properties tailored to specific applications.

Wednesday 15:10 Europe II
A novel Orthogonal Superposition (OSP) drive and flow cell: Testing a wormlike micellar solution, a colloidal suspension, and a polymer melt
Thomas B. Schweizer1, Jan Vermant1, and Jörg Läuger2
1Soft Matter Materials Group, ETH Zurich, Zürich CH-8093, Switzerland; 2Anton Paar Germany, Ostfildern 73760, Germany
Orthogonal superposition (OSP) rheometry may evolve into a new and elegant standard technique for investigating non-linear viscoelastic and thixotropic fluids with widely differing time scales, due to for example anisotropic molecular orientation or anisotropic breakdown of a particle microstructure. As the main shear flow and the superimposed oscillation are orthogonal to one another, the flows are decoupled thus making the analysis of the experiments quite transparent as the orthogonal superposition moduli retain their physical meaning of storage and loss moduli, and the underlying spectra are linear perturbation spectra. The effects of flow on microstructure can hence be investigated through mechanical spectroscopy underflow. The shear induced structural anisotropy of a wormlike micellar solution and a colloidal particle network have been investigated by the new OSP setup for Anton Paar’s MCR702 rheometer. It consists of the standard measuring motor for shearing and a linear motor developed specifically for the OSP technique for the orthogonal dynamic sensing. Contrary to existing setups, placing a novel designed OSP cell in the convection oven allows also for studying particle or short fibre filled polymer melts. First results are presented for a polystyrene melt.

Wednesday 15:30 Europe II
Miniaturized characterization of polymers: From synthesis to rheological and mechanical properties in 10 mg
Susana Petisco-Ferrero, Ruth Cardinaels, and Lambért van Breemen
Polymer Technology, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands
Rising consumer demands and advances in technological applications drive a continuous search for advanced polymeric materials. Newly developed and increasingly complicated synthesis methods often result in minute amounts of novel polymers, which seriously hampers a thorough screening of the rheological and mechanical material characteristics. Hence, there is a large need for miniaturized testing methods, both for the liquid as well as the solid state properties of polymers. This miniaturized testing is hampered by the contradicting requirements of small sample sizes (and thus surface areas) and sufficiently large generated torques and forces. In the present work, we show a methodology that allows rheological and mechanical characterization on small pillars of 1 mm diameter. The small cylindrical samples are prepared by extrusion of polymer rods followed by molding and cutting. For the characterization of the rheological behavior in small amplitude oscillatory shear, we use eccentric rheometry. Herein, the sample is placed off-centric, which results in a large increase in the generated torque without the need for increasing the sample size. By combining experimental data and numerical simulations, we show that the choice of the pillar aspect ratio is essential to maintain a homogeneous sample deformation and thus to extract correct rheological parameters. For the characterization of the intrinsic mechanical behavior, compression experiments at different strain rates are performed with a rotational rheometer. Thereby, the deformation kinetics demonstrating the increase of the yield stress with deformation rate was mapped out. Our methodology was validated for the semi-crystalline polymers polypropylene and polycaprolactone but in essence it is applicable for any material. Hence, it can be concluded that a full material characterization, both in the liquid as well as solid state, can be performed with only 10 mg of material.
Blends, Emulsions, Foams & Interfacial Rheology

Symposium BE

Examining the suitability of interfacial shear rheometers for probing polymers at the A/W Interface
Daniel Ashkenazi1, Stelios Alexandris2, Dimitris Vlassopoulos2, and Moshe Gottlieb1
1Chemical Engineering, Ben Gurion University, Beer Sheva, Israel; 2IESL, Foundation for Research and Technology Hellas, Heraklion, Crete 71110, Greece

The rheological and dynamic properties of complex fluid interfaces play an important role in a variety of industrial applications and biological processes. The challenges involved in determining these properties by means of interfacial shear rheometry for complex fluid interfaces formed by biological or synthetic amphiphilic molecules has been recently outlined in detail [1,2]. Even for the case of simple polymer chains deposited on the water/air interface, the challenges are formidable. The type of interaction between the polymer chain and the aqueous subphase, the 2-d conformation of the chains, the static and dynamic flexibility of the backbone, the morphology of the polymeric layer, the likelihood of forming multilayered islets rather than monolayers, and in some cases even the history of polymer deposition on the interface, all affect the measurement of the rheological properties. In this work we report on the results obtained by systematic measurements with three different interfacial shear rheometers namely, ISR, bicone, and DWR for several homopolymers with varying hydrophilicity and molecular characteristics (molar mass, flexibility). Measurements are carried out at different surface concentrations and in the case of the bicone at different interfacial thicknesses. We find large variations in the values obtained by the different interfacial rheometers as well as issues of sensitivity and reproducibility. The results will hopefully provide guidelines for the appropriate molecular parameter space to obtain reliable rheological measurements.


Selective localization of carbon black in polymer blends: Rheological and structural consequences
Zdeněk Starý, Martina Nevoralová, and Valentina Dragecovic
Institute of Macromolecular Chemistry CAS, Prague, Czech Republic

Immiscible polymer blends are perspective materials offering property profiles, which cannot be obtained by using single polymers. Application scope of polymer blends is, however, often limited by their insufficient mechanical properties and structure instability. In recent years conductive polymer composites draw an increased scientific attention as materials for packaging, electromagnetic shielding and sensors. To reach a desired electrical conductivity, formation of percolated structures consisting of conductive filler particles is necessary. This in turn affects processing properties negatively. Selective localization of conductive particles in one phase or at the interface decreases the filler concentration necessary for percolation. Moreover, enhanced interfacial adhesion and stabilization of blends phase structure is often reported. In this contribution immiscible polystyrene/poly(methylmethacrylate) (PS/PMMA) blends filled with carbon black (CB) are investigated in a broad composition range. In these blends carbon black is localized preferentially in polystyrene phase. The influence of carbon black on blends phase structure is evaluated and consequently rheology and electrical conductivity is discussed. Pronounced differences in the morphology of unfilled and filled blends were observed in cases, in which PS phase containing CB forms a minor phase. Dispersed morphology with spherical particles and sharp interfaces turned by addition of 3 vol.% of CB into partially co-continuous morphology with irregular domain shapes. This morphology change was detected even in blends with PS content as low as 10 vol.%. The rheology of the blends was largely influenced by the addition of CB in the systems with PS matrix. The applicability of mixing rules for description of rheology of filled polymer blends is discussed.

This work has been financially supported by Czech Science Foundation (grant 17-05654S).

Phase separation upon shearing and relaxation of immiscible polymer blends stabilized with Janus nanorods
Felipe Paiva1, Arman Boromand2, João M. Maia1, Veronica Calado1, Argimiro Secchi3, and Shaghayegh Khani1
1Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202, United States; 2Department of Mechanical Engineering and Material Science, Yale University, New Haven, CT, United States; 3School of Chemistry, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil; 4COPPE Chemical Engineering Graduate Program, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

It is well-known that shear flow can direct the assembly of particles at fluid interfaces. In particular, studying the effect of shear flow and its cessation as a tool of external manipulation/actuation in soft metamaterial systems is important for fine-tuning the microstructure. Furthermore, in the case of Janus rigid surfactants, both shape and chemical anisotropy within the same particle offer a way to control particle orientation and...
self-assembly at the interfacial level. However, the aggregation behavior of such particles under shear flow and their relaxing behavior is far from being well-understood. Hence, in the present work, Dissipative Particle Dynamics is used as a way to computationally assess the phase separation of binary polymer blends stabilized by Janus nanorods and how the nanoparticles assemble at the interface. This is done for various shear rates and Janus rod weight fractions. A very rich behavior has been verified consisting of tilting, tumbling and Janus aggregate break-up at a flat interface between two polymer phases. Results highlight the interplay between hydrodynamic and capillary torques on the particles at the interface and Janus aggregates have also been found to rebuild upon flow cessation. Additionally, at sufficiently high shear rates, Janus–compatibilized dilute polymer blends exhibiting a droplet morphology deform and relax to a metastable cylindrical morphology, which is in turn less stable when Janus rods are absent. Results obtained shed light on the potential of using shear flow to nanoscopically engineer interfacial structure and on flow-alignment phenomena in general. Studying the possibility of yielding oriented nanoparticles and morphologies upon flow cessation may have potential applications in novel liquid-crystalline displays, photovoltaics, and optical and electronic devices in general.

Wednesday 17:20 Europe II

**Numerical modelling of polydisperse polymer blends**

Wing-Hin B. Wong, Martien A. Hulsen, and Patrick D. Anderson  
*Eindhoven University of Technology, Eindhoven, The Netherlands*

Polymer blends are an important class of materials where a great variety of material properties can be obtained by manipulating the blend morphology. We investigate blends where the morphology consists of droplets dispersed throughout a matrix fluid, focusing on the droplet size distribution (polydispersity). In practical flow problems, the number of droplets is computationally intractably large. We therefore use a macroscopic model [1] to describe these droplet morphologies based on Peters et al. [2]. We group droplets together in fields of polydisperse populations, where each subpopulation of droplets is described by an average droplet size and stretch ratio that evolve under the influence of the viscosity ratio and the local capillary number. The model has been implemented in a finite element framework in order to simulate complex flows.

We first show results for simple shear and Poiseuille flow. This gives insight in the influence of the shear rate on the droplet morphology and polydispersity evolution without convection effects. Next, we show results for the morphology evolution in a 2D eccentric cylinder flow, illustrating the applicability of the model in a complex flow. The next step is to extend the model to 3D, which we are currently working on. We expect to show results for the morphology development in a 3D mixing flow at the conference, demonstrating that our model is a powerful tool for describing the morphology of disperse polymer blends in industrially relevant geometries, under the influence of processing flow conditions and material properties.


Wednesday 17:40 Europe II

**Startup steady shear flow from the Oldroyd 8-constant framework**

Chaimongkol Saengow¹, Alan J. Giacomin¹, and Rossana Pasquino²  
¹*Chemical Engineering Department, Queen's University, Kingston, ON K7L 2N9, Canada; ²Chemical Materials and Industrial Production Engineering, Università degli Studi di Napoli Federico II, Naples, Italy*

One good way to explore fluid microstructure, experimentally, is to suddenly subject the fluid to a large steady shearing deformation, and to then observe the evolving stress response. If the steady shear rate is high enough, the shear stress and also the normal stress differences can, overshoot, and then, they can even undershoot. We call such responses nonlinear, and this experiment shear stress growth. This paper is devoted to providing exact analytical solutions for interpreting measured nonlinear shear stress growth responses. Specifically, we arrive at the exact solution for the Oldroyd 8-constant constitutive framework. This framework includes a rich diversity of special cases, including, for instance, the corotational Jeffreys and the Johnson–Segalman fluids. In this paper, we test these special cases against the measured behaviours of wormlike micellar solutions. We find that, at high shear rates, these solutions overshoot in stress growth without subsequent undershoot. We find that the corotational Jeffreys fluid to be inadequate at high shear rates for shear stress overshoots, and that the Johnson–Segalman predicts these more accurately.

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**Wednesday Afternoon**

**Chemical Materials and Industrial Production Engineering, University of Limerick, Limerick, Ireland**

**Annual European Rheology Conference 2019**
Fuel cells (FC) are energetic devices that convert chemical energy of reactants (typically hydrogen and air) into electricity and heat. Among the fuel cells types, Solid Oxide Fuel cells (SOFC) operate at high temperature and present the advantages such as higher electrical conversion efficiency and fuel flexibility. The two main used geometries for SOFC stack are planar or tubular and they are usually fabricated by conventional manufacturing methods such as uniaxial pressing, slip/tape casting or extrusion. However, the introduction of components with more complex geometries in this field has been yet barely explored and could overcome some limitations that SOFC devices face today to enter the market: performance, durability and scalability. [1] In this work, Ceramic Injection Moulding (CIM) has been employed to manufacture zirconia anodes with controlled porosity and flat geometry. [2] The different stages of CIM process have been successfully optimized. Porosity in the manufactured parts has been tailored from near-zero up to almost 70 vol. % values by adding different concentrations of pore generators (graphite and corn starch). The addition of pore generators has an influence on the ability of the binder to efficiently homogenize the ceramic powder in the feedstock. Moreover, rheological studies were carried out and melt flow index values were determined. In this way, the flow behaviour, the viscosity properties and the pseudoplasticity of mixtures containing pore generators in comparison with the zirconia mixtures without additives was investigated.


Acknowledgements: This work has been supported by a JCCM project financed with FEDER funds.

Wednesday 14:50 Europe III

Silo outflow of soft frictionless spheres

Diego Sancho Martinez1, Torsten Trittel1, Tilo Finger1, Maja Illig1, Ahmed Ashour1, Tivadar Pongo2, Tamás Börzsönyi2, and Ralf Stannarius3

1Institute of Physics, Otto von Guericke University, Magdeburg 39106, Germany; 2Institute for Solid State Physics and Optics, HAS Wigner RCP, Budapest, Budapest, Hungary

The outflow of hard grains with different shapes from 2D and 3D silos has been extensively studied in the past. Today’s availability of incompressible but deformable hydrogel grains in large quantities opened the door to extend such studies to grains that are soft and nearly frictionless. We conduct a quasi-2D silo experiment with hydrogel spheres and with mixtures of soft and hard spheres. These materials show qualitatively and quantitatively new features compared to hard grains: Even when the orifice size is only slightly larger than two sphere diameters, the silo does not clog. By decreasing the orifice size below two sphere diameters, the flow becomes increasingly intermittent with transient clogs, finally leading to a permanently clogged state. The clogging probability of soft grains depends on the container fill height, unlike hard grains which flow practically independent of the fill level. The Janssen effect, a saturation of the pressure with increasing fill height, is ineffective for soft frictionless materials. The pressure at the silo bottom increases linearly with fill height (hydrostatically) in the range covered by our experiments. Beverloo’s, equation, which describes the mass flow rate, remains valid. By means of x-ray tomography, we determine the packing fraction, contact numbers and force chains of soft spheres randomly packed in a container.

Wednesday 15:10 Europe III

Numerical simulation of the rheology of frictional spherocylinders

Dániel B. Nagy1, Philippe Claudin2, Tamás Börzsönyi1, Ralf Stannarius3, and Ellák Somfai3

1Institute for Solid State Physics and Optics, HAS Wigner RCP, Budapest, Budapest, Hungary; 2Physique et Mécanique des Milieux Hétérogènes, ESPCI, Paris, France; 3Institute of Physics, Otto von Guericke University, Magdeburg 39106, Germany

The dissipation during granular flow is characterized by the so-called effective friction coefficient, which is defined as the ratio of shear stress and confining pressure. This is in contrast to fluid flows, where dissipation is described by the viscosity. In the case of granular flows, the effective friction originates from microscopic contacts between the particles. Describing the rheology, one needs to measure the effective friction as a function of the dimensionless shear rate (the inertial number), which can be interpreted as the ratio of the macroscopic timescale of the shear flow and the timescale of the microscopic rearrangements of the flowing particles. The rheology of spherical particles has been studied previously by several authors. In our work, we focus on elongated particles, which are ubiquitous in industry and agriculture. They show more complex
rheological properties, since elongated particles are rotating in the shear flow and hinder each other's movement. In our simulations, we quantified how this complex dynamics changes the rheological properties of the system. We also study the origin of a unique behavior, the appearance of a secondary flow in certain geometries.

Wednesday 15:30 Europe III
Training, memory and universal scaling in amorphous frictional granular matter
Saikat Roy¹, Mahesh Bandi², George Hentschel¹, and Itamar Procaccia¹
¹Department of Chemical & Biological Physics, Weizmann Institute of Science, Rehovot, Israel; ²Collective Interactions Unit, OIST Graduate University, Okinawa, Japan

Memory formation and retention via hysteresis is a non-equilibrium process because the system requires external forcing to get across the energy barrier from one state to the other. Consequently, universal laws and universal exponents which provide adequate theoretical characterization of equilibrium transitions are very difficult to find in non-equilibrium hysteretic processes. Here, we report a joint experimental and theoretical investigation of cyclic training of amorphous frictional granular assemblies, with special attention to memory formation and retention. Measures of dissipation and compactification are introduced, culminating with a proposed scaling law for the reducing dissipation and increasing memory. This scaling law is expected to be universal, and insensitive to the details of the elastic and frictional interactions between the granules. We thus expect this will be of broad interest for geologists through material scientist and statistical physicists.

Symposium PS
Polyelectrolytes, Self-Assembling Fluids & Gels
Organizers: Alexander Malkin and Olga Philipova

Wednesday 16:20 Europe III
Rheological scaling of ionic liquid-based polyelectrolytes in ionic liquid solutions
Atsushi Matsumoto¹, Del Giudice Francesco², and Amy Q. Shen¹
¹MicroBioNanofluidics Unit, Okinawa Institute of Science and Technology Graduate Univ., Onna-son, Okinawa 9040495, Japan; ²Systems and Process Engineering Centre, Swansea University, Swansea, United Kingdom

Polymerized ionic liquids (PILs) are a special class of polyelectrolytes with ionic liquid (IL) species being covalently attached to the repeating unit. The rheological properties of PIL in IL solutions are strongly influenced by the electrostatic screening between IL and PIL chains. However, the effect of IL electrostatic screening on the rheology of PIL in IL solutions remains elusive. To address this challenging yet important question, we conduct detailed rheological characterization of a model system containing a PIL (PC₂-TFSI: poly(1-butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) in a mixture of a salt-free solvent (DMF: dimethylformamide) and an IL (Bmim-TFSI: 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) solution, spanning dilute and semi-dilute polymer regimes. We compare the specific viscosity ηsp and the longest relaxation time λ of PILs measured at various Bmim-TFSI concentrations from 0 M (pure DMF) to 3.42 M (pure IL) with the scaling predictions for ordinary polyelectrolyte solutions. We find good agreement at low IL concentrations, but significant deviations at higher IL concentrations. We capture this discrepancy by proposing and validating a modified scaling law accounting for the modified screening length in concentrated electrolyte solutions. We demonstrate that extended PIL chains initially shrink due to the charge screening effect at low IL concentrations, but revert to expanded configuration at higher IL concentrations due to the charge unscreening effect. Our results shed new insights on the conformation of PIL in IL solutions, and provide a valid reference for the study of general polyelectrolyte solutions at high ion concentrations, where the Debye-Huckel theory is no longer valid.

Wednesday 17:00 Europe III
Nano-liquids formed by colloidal particles and their interaction with polymer matrix
Alexander Malkin, Mariya Y. Polyakova, Andrey V. Subbotin, Galina N. Bondarenko, and Valery K. Kulichilin
Laboratory of Polymeric Rheology, A.V. Topchiev Institute of Petrochemical Synthesis, TIPS RAS, Moscow 119991, Russia

Colloidal systems are usually considered as multicomponent and multiphase dispersions. Such systems are widely spread in Nature and technology. In opposite, we examined the rheological properties of the quite other type of colloid-like systems which are homogeneous up to a nano-size level. These compounds occupying an intermediate position between polymeric molecules and colloidal particles are created by grafting of functionalized organic chains on silica nucleus. So, they are nano-liquids though usual nano-particles are always solids. They are often called silica-sol. We examined a series of such objects of different size (and MW) but having the same molecular structure. These compounds are viscoelastic in a wide temperature range. At room temperature, the dependence of the viscosity on MW is very strong being approximated by the power law with the power of the order of 8. However a new physical model for the viscosity of liquid nano-fluids has been proposed. The model is based on scaling arguments. The system of liquid nano-particles is considered as impenetrable elastic objects which tightly fill the volume. The viscosity is determined by the relaxation time which is proportional to the coefficient of friction (proportional to the surface area) and depends on the potential barrier overcome by the particle when moving a distance of order of the particle radius. At some temperature, the transition takes place due to rearrangements of internal bonds inside nano-particles which leads to the formation of physical gel. The examination of the low-
temperature IR-spectra shows that we have the case of water-induced gelation while there is no free water. The final part of the work consists of the study of the rheology of nano-liquids - PDMS mixtures in the whole concentration range. Small nano-particles are completely compatible with PDMS while the phase inversion takes place in this pair for high MW nano-particles.

This work was supported by the Russian Science Foundation (Grant 17-79-30108).

Wednesday 17:20 Europe III

**Rheological reentrant transition in microgel-surfactant mixtures**
Sarah Goujard¹, Jean-Marc Suau², Clémentine Locatelli-Champagne², and Michel Cloître¹

¹Soft Matter and Chemistry, ESPCI, Paris, France; ²Coatex SAS, Genay, France

Stimuli-responsive microgels are colloidal particles made of cross-linked polymeric networks that undergo a volume transition in response to changes in pH, temperature, or solvent quality. As particle swelling provokes a dramatic increase of the volume fraction, randomly close-packed suspensions with remarkable viscoplastic properties and optical transparency can be obtained at very low polymer content. These features are exploited to design rheological modifiers used in cosmetics, pharmaceuticals, and food products.

Here we explore a strategy that consists in triggering the swelling of microgels by adding surfactants as guest-molecules, which adsorb onto the polymeric network and induce swelling. Once the surfactant adsorption onto the backbone is maximum - meaning the backbone is saturated by guest-molecules -, surfactants form micelles outside of microgels that act as depletant, provoking a decrease in viscosity. The great challenge is to control and model the volume transition and the rheological properties in terms of enthalpic and entropic interactions that develop between the polymeric network and the guest molecules.

Using rheology, fluorescence techniques, and SAXS investigations we elucidate the microscopic mechanisms that connect the composition of microgel/surfactant mixtures to rheological properties such as the yield stress. In addition to providing exquisite solutions to the design of a new rheology modifiers for personal care products, this host-guest paradigm opens the route to other applications, for instance to adsorb toxic residues from complex formulations.

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**Symposium IP**

**Industrial Rheology & Processing**

Organizers: Ulrich Handge, Clemens Holzer and Lázsló Gomze

Wednesday 14:30 Adria

**On-line monitoring of polymerization reactions by coupling rheology and optical spectroscopy**
Maik Nowak and Sorin Pulbere

Material Physics, Advanced Materials & Systems Research, BASF SE, Ludwigshafen 67056, Germany

For reactive polymer systems the numerical simulation of common manufacturing processes like mold filling demands much more complex models than required and widely established for unfilled or also filled thermoplastics. Recent publications report the prediction of even reactive foams. The obvious benefit of such simulations is the reduction in development time and setting the right process parameters to ensure the desired product part quality. In order to precisely describe the materials behavior through all process steps, not only the dynamic mechanical properties of the system but also the kinetic parameters of the chemical reaction have to be determined for an enhanced material modelling. Therefore transient, at best simultaneous in-situ measurements are required of both the rheological properties and also reaction quantities such as conversion or density. One of the main challenges in that matter is to mimic most closely the actual process situation under laboratory conditions. With that objective a rheometer parallel plate accessory was specifically designed to imitate a reactive injection molding process for a compact material.

Ensuring that the extremely crucial mixing of the components was done as thoroughly and quickly as feasible, the experimental results confirmed the strong dependency of the properties of a polyurethane cast elastomer on the process conditions. In particular the temperature protocols were proven to be decisive to obtain process relevant data. Additional chemical information was obtained by simultaneously coupling rheometry with optical spectroscopy, like NIR or Raman. With this kind of coupled measurements as a calibration set for chemometrics the time dependent mechanical results and the respective conversion of the reactive system could be predicted from the transient optical spectra. This correlation was found to be in good agreement with results from strictly isothermal microcalorimetry. Eventually coupling this method with spectroscopy will be pursued in the near future.

Wednesday 14:50 Adria

**Molecular architecture from integrated computer models for synthesis, characterization, and rheology**
Chinmay Das and Daniel Read

University of Leeds, Leeds, West Yorkshire LS2 9JT, United Kingdom

Computational models [1] based on the tube theory allows quantitative predictions for the rheological responses of arbitrarily branched polymers in both the linear and nonlinear regimes. The inverse problem of determining the branching structure of industrial resins is a much harder problem because different mixtures of differently branched molecules can lead to similar flow properties. In this talk we show that by integrating...
computational models of polymer synthesis, characterization and flow together [2] one can determine the underlying molecular structure and the effective rate constants in the model with better confidence than could have been possible by modelling any one experiment separately. This also allows us to predict the synthesis conditions required for synthesizing polymers with certain desired flow properties and to predict the optimum operating window for enhanced flow properties while avoiding reactor fouling.


Wednesday 15:10 Adria

Computational modeling of the selective laser sintering process: from two to multiple particles
Caroline Balemans, Arne Jacobs, Martien A. Hulsen, and Patrick D. Anderson
Eindhoven University of Technology, Eindhoven, The Netherlands

Selective laser sintering (SLS) is an upcoming 3D printing technique for industrial applications. Products are built of polymer powder that is locally heated in a layer-by-layer fashion. To improve this technique, we need to understand the relation between the printing process and the mechanical properties of the products. We developed a computational model using the finite element method to assess the behavior of two polymer particles. Firstly, we analyzed the viscoelastic flow problem of the sintering process using both the Giesekus model and the eXtended Pom-Pom model [1] to describe the complex behavior of the polymer [2]. Secondly, we included the temperature-dependent flow behavior of the system to study the effect of process and material parameters [3]. Finally, we are considering the crystallization kinetics to predict and tune the morphology of the products, because crystallization plays an important role in the final microstructure. Furthermore, we extended the two-particle model to a geometry with more particles in a row and with multiple layers, to gain important insights in the actual process in a SLS printer. In this presentation, we will discuss the most important findings of the two-particle model and show the results of the extended geometries.


Wednesday 15:30 Adria

Viscoelastic rubber extrusion simulation with wall slip and comparison to experiments
Tijmen Mateboer and Jakob Buist
Professorship for Polymer Engineering, Windesheim University of Applied Sciences, Zwolle, Overijssel 8000 GB, The Netherlands

Unvulcanized rubber extrusion is a key process in the tire industry. In recent studies extrusion flow problems are often addressed with numerical simulations with viscoelastic models and the balance equation. Traditionally, in such flow problems, it is assumed that the fluid adheres to the wall surface: “no slip” condition. However, in some studies the no slip assumption leads to a discrepancy between experiments and simulation in terms of pressure drop and extrudate swell.

This study focused on simulations of rubber extrusion with slip included and verification by industrial extrusion experiments. Both a butadiene rubber (BR) and a tire rubber compound were used. Extrusion experiments with both rubbers were performed at a wide range of flow rates. Slip velocities were determined by comparing rheological measurements with a rheometer with grooved surfaces and a rheometer with smooth surfaces.

The rheological behavior ($G'$, $G''$) was measured with the RPA2000 cone-cone oscillatory rheometer. A PTT model was fitted onto the measurements in order to describe the viscoelastic behavior of the rubber.

Viscoelastic extrusion simulations were performed with slip included and without slip. The simulations of BR without slip was found to overpredict the pressure drop inside the die. The simulation with slip included showed agreement with the experiments for a large range of flow rates. The extrusion simulation of the tire rubber compound without slip was also found to overpredict the measured pressure drop. The pressure drop decreased when slip was included in the simulation, but the simulated pressure drop appeared still greater than the measured pressure drop.

Wednesday 16:20 Adria

A numerical study of anisotropic thermal transport in polymer melts and networks
David Nieto Simavilla1, Wilco M. H. Verbeeten1, and Doros Theodorou2
1SIRG Department of Civil Engineering, Universidad de Burgos, Burgos, Burgos 09006, Spain; 2Chemical Engineering, National Technical University of Athens, Athens, Attika, Greece

Over the last decades, experimental evidence has shown that thermal conductivity becomes anisotropic in polymer melts and networks subjected to deformation. Surprisingly, the strong coupling between thermal properties and rheology in polymeric materials is often neglected in macroscopic numerical simulations used to design manufacturing processes. We propose a molecular-to-continuum approach to validate and help to explain the experimental results. Such an approach is necessary to develop a robust methodology for the simulation of non-isothermal flows and predict the material final properties after processing. Among the experimental evidence, three findings are remarkably useful to implement anisotropic thermal transport into macroscopic flow simulations: 1) the existence of a linear relationship between anisotropy in thermal conductivity and stress (i.e. the stress-thermal rule); 2) the universality, or independence of polymer chemistry, of this rule; and 3) its validity beyond finite extensibility.
While 1) can be explained using simple molecular arguments, 2) and 3) are not well understood. The number one challenge is that thermal transport theories for neither solids or liquids can be applied directly to polymers, due to the complexity of the relationships between deformation and structure. We use molecular simulation techniques to test the validity of the three key findings discussed above under uniaxial extension and shear. Combining molecular dynamics and connectivity altering Monte Carlo methods, we are able to study deformation-induced changes in the thermal conductivity over a wide range of deformation rates. Our results show the stress-thermal rule to be valid and the stress-thermal coefficient to be independent of the deformation type or rate. In addition, we will discuss how MD simulation techniques help us gain fundamental insights into the transport mechanisms governing thermal transport and leading to anisotropic thermal conductivity in polymers.

Wednesday 16:40 Adria IP14

Minimum concentration of poly(ethylene oxide) in water solution ensuring good quality of electrospun nanofibres
Jana Zelenkova, Petra Peer, and Petr Filip
Institute of Hydrodynamics of the Czech Academy of Sciences, Prague, Czech Republic

Successful electrospinning of polymer solutions is limited among other parameters by a range of concentration of the polymer used in a solvent. Too low concentration indicates minimum of contacts between the individual macromolecules and hence, no possibility to create nanofibres. The question is how to estimate the lowest value of concentration for specific materials above which the nanofibrous mat can be obtained (under otherwise fixed other parameters such as the process ones). One of the indications is given by a course of specific viscosity. For a solution of poly(ethylene oxide) in water we can approximate dependence of the specific viscosity on concentration by two or three linear segments depending whether log-log or semi-log coordinates are used. The points of line refraction have a correspondence with an existence and quality of electrospun nanofibres as will be demonstrated.

Acknowledgement: The authors wish to acknowledge GA CR for the financial support of Grant No. 17-26808S.

Wednesday 17:00 Adria IP15

Playing with the chemistry of copolymers to establish rheological criteria to select materials for pressure driven or fused filament 3D printing
Itxaso Calafel¹, Robert H. Aguirresarobe¹, Naroa Sadaba², Miquel Boix³, Ignacio J. Conde³, Belen Pascual³, and Antxon Santamaria¹
¹Polymer Science and Technology Department, POLYMAT, University of the Basque Country, San Sebastian, Gipuzkoa 20018, Spain; ²Mining-Metallurgy Engineering and Material Science, POLYMAT, Bilbao, Bizkaia 4013, Spain; ³Innovation and Technology Department, ERCROS S.A., Monzón, Huesca, Spain

Additive manufacturing techniques for 3D printing have gained ground in recent years producing a revolution in the processing technologies of different materials, such as metals, ceramics, polymers and composites. In polymers, fused filament fabrication (FFF) is more employed than melt-extrusion additive manufacturing, but the later offers advantages like higher dimensional accuracy, ability to work at low pressures and direct feeding with polymer pellets. In both cases there are rheological implications that should be considered to understand the physics of 3D printing and create a route to overcome trial and error method for the selection of the polymers. As pointed out by Mackay in a recent paper [1], the improvement of the additive manufacturing process requires careful rheological measurements. At least the following rheological features should be contemplated: Fair viscosity to ensure the expected printing velocity; fast adhesion of deposed layers and a cooling process that guarantees good mechanical properties. Recently we have reported [2] how to play with the microstructure of acrylate/vinyl chloride random copolymers to tune the viscoelastic properties and so obtain good conditions for 3D printing in a pressure driven device. However, the elaborated random copolymers were not suitable for fused filament fabrication. This led us to deepen on the rheological features to discriminate between polymers able to be employed in each of the additive techniques. In this work we analyze the different properties and, in particular, the link between filament buckling and rheological parameters. For this goal, we work with one phase (random) and two phases (block) copolymers, demonstrating that phase separation (i.e amorphous/crystalline, matrix/droplet or matrix/filler) is a necessary condition for fused filament 3D printing.


Wednesday 17:20 Adria IP16

Effects of rheological properties on thin-film formation flows for coating processes
Jaewook Nam
Chemical & Biological Engineering, Seoul National University, Seoul, Republic of Korea

Slurries, pastes, suspension foams and emulsions are frequently handled in industrial processes. When the microscopic structures inside such materials consisted of particles such as polymeric microgels, liquid or gas droplets, are developed significantly, they allow the materials to maintain the shape or deform in the same way as solids below a certain level of stress. But above this critical stress, the materials behave like a liquid. This threshold stress is called yield stress.

The yield stress is already significant in many engineering fields, including food processing, ceramic slurries processing for semiconductor, measuring rheological parameters for fresh concrete paste, etc. However, the yield stress is not widely considered in a continuous liquid coating process for high-speed thin-film productions.
The liquid coating process is used to produce various films or sheet-like products, such as adhesive tapes, optical films, display panels, etc. It is also a strong candidate for nanoparticle assembly film production. Slot coating is a popular high-precision coating methods because the film thickness is directly controlled by the flow rate and substrate speed rather than coating liquid properties [1,2]. However, many high-performance multi-functional films for electronics and optical devices require nano- or micro-sized particles inside a coating liquid. This study presents fundamental aspects of film formation flows [3] used in coating processes and the impact of rheological properties on the operating limits of a coating method in both experiments and computations [4].


Wednesday 17:40 Adria

Elongational flow behavior and high-speed rotary bell atomization of non-Newtonian coatings with and without particles

Walter Oswald\(^1\), Lutz Goedeke\(^2\), and Norbert Willenbacher\(^1\)

\(^1\)Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, Baden-Württemberg 76131, Germany; \(^2\)Fluid Mechanics, Technical University of Dortmund, Dortmund, Nordrhein-Westfalen 44227, Germany

High-speed rotary bell atomization is the dominating coating technique in the automotive industry. This is due to the high coating quality at high transfer efficiency and short process time. In this application, atomization is initiated by the disintegration of single ligaments near the bell edge. Understanding this process is essential for control of resulting coating layer properties and for preventing coating defects. Most previous studies on high-speed rotary bell atomization focused on Newtonian fluids, and the effect of elongational flow behavior and the presence of particles on the spraying process was not considered, although industrial paints are pigmented non-Newtonian fluids. This experimental study investigates the influence of flake-shaped particles on shear and elongational flow behavior as well as on the breakup of ligaments during atomization using acrylic thickener solutions with different glass flake concentrations. Elongational flow resistance was characterized using Capillary Breakup Elongational Rheometry (CaBER). Steady shear viscosity was determined from rotational rheometry. Ligament breakup length was extracted from recorded images using a self-written MATLAB\(^\circledR\) code. Droplet size of the resulting spray was determined using phase-Doppler anemometry. Increasing elongational relaxation time results in an increase of ligament breakup length for a series of the model system without particles. Adding glass spheres to the thickener solution neither changes elongational flow behavior nor ligament disintegration. In contrast, increasing amount of glass flakes leads to a pronounced increase of elongational relaxation time and a decrease of breakup length of ligaments during atomization but does not affect shear viscosity. This distinct effect of particle shape on capillary filament thinning as well as ligament disintegration was also found in industrial automotive basecoats including aluminum flakes. Finally, it should be noted, that droplet formation is not affected by the flake-like particles.
Thursday Morning

Symposium PL

Plenary Lectures

Thursday 9:00 Europe I

Digested? - The design and in-vivo validation of satiety controlling food
Nathalie Scheuble¹, Fredric Carriere², Andreas Steingoetter³, and Peter Fischer¹

¹Institute of Food, Nutrition and Health, ETH Zurich, Zurich 8092, Switzerland; ²Enzymologie Interfaciale et Physiologie de la Lipolyse, Aix-Marseille Université, Marseille 13402, France; ³Institute for Biomedical Engineering, University Zurich and ETH Zurich, Zurich 8092, Switzerland

Malnutrition, which includes overeating as well as nutrient deficiencies is one of the most pressing problems towards a healthy population and personal well-being. From a variety of approaches the stimulated release of satiety hormones offers a soft control on food intake [1]. In a conceptual study we present the design of food systems and its fate during human gastric and intestine digestion including its physiological resonance. A feedback loop between bulk and interfacial rheology, in-vivo gastric magnetic resonance imaging, and physiology in humans and rats does not only establishing the in-vitro/in-vivo correlation of fat digestion but also provides pathways to limit or stimulate food uptake. Besides controlling nutritional uptake, the mechanical performance of food after consumption is also a key factor affecting hydrophobic drug release [2]. In summary, the designed food systems as well as the analysis of their physicochemical changes during digestion provide in-vivo based guidelines for functional food formulations.


Symposium CS

Colloids & Suspensions

Organizers: Michel Cloitre, Guillaume Ovarlez and Norbert Willenbacher

Thursday 10:00 Europe I

Rheology of soft-patchy particles made of Telechelic Star Polymers
Esmaeel Moghimi¹ and Dimitris Vlassopoulos²

¹Foundation for Research and Technology - Hellas, Heraklion, Greece; ²Institute of Electronic Structure & Laser, Foundation for Research and Technology Hellas, FORTH, Heraklion, Greece

Telechelic Star Polymers (TSPs) are macromolecules made of diblock copolymers grafted on a central anchoring point. Each diblock arm has a fraction of a solvophobic (at the outside) and (1-a) solvophilic monomers. The dual nature of their arms makes TSPs particularly sensitive to variations of the external conditions, such as temperature or ionic strength, which allows each particle to self-assemble into a soft particle with attractive patches on the surface. This gives rise to an unprecedented richness in the morphology of resulting material, which has been explored by computer simulations. The consequences on the dynamics have not been considered yet. Using a powerful combination of experiments and computer simulations with appropriately designed and synthetized TSPs (based of styrene-isoprene blocks with isoprene inside and different f, a and molar mass), we demonstrate that these systems are simple, robust and tunable. They can self-assemble hierarchically into soft-patchy particles and mechanically stabilized structures. Rheological experiments exhibit a liquid- to solid-like transition upon cooling. Small angle X-rays (SAXS) experiments demonstrate that this is associated to a disorder to order transition with the formation of hexagonal structures. An intriguing re-entrant liquid transition is detected on further cooling. Based on SAXS experiments this transition is associated to formation of a mixture of hexagonal and cubic structures. Moreover, we examine the direct impact of inter-particle attraction strength on the yielding behavior of TSPs during start-up shear flow.
Thursday 10:20 Europe I
Structure and rheology of a suspension of colloidal particles with shape and charge anisotropy
Vincent Labalette\textsuperscript{1}, Yannick Hallez\textsuperscript{1}, Martine Meireles\textsuperscript{1}, and Jeffrey Morris\textsuperscript{2}
\textsuperscript{1}LGC, Université de Toulouse, CNRS,INPT, UPS, Toulouse 31062, France; \textsuperscript{2}Physico-Chemical Hydrodynamics, The Benjamin Levich Institute, New York, NY 10031, United States

The rheology and microstructure of a colloidal suspension of electrically charged plate-like particles are studied numerically. Hydrodynamic and electrostatic interactions are both considered at the particle scale to understand the local force balances driving the macroscopic behavior of the suspension better. Many-body hydrodynamic interactions are calculated via Accelerated Stokesian Dynamics (ASD) in which the plate-like particles are quasi-rigid aggregates of hard spheres bound by springs. Electrostatic interactions between platelets are first introduced by using pairwise DLVO-type interactions between the spheres constituting the platelets. The microstructure and mechanical response (viscosity, yield stress...) of suspensions of uniformly or heterogeneously charged platelets are discussed as a function of the Péclet number, electrostatic interaction range, intensity and anisotropy. In a second step, we comment on the consequences of using the pairwise additivity approximation for electrostatics by comparing the aforementioned results with those produced with a more precise numerical scheme coupling full many-body electrostatic calculations and the ASD for hydrodynamics.

Thursday 10:40 Europe I
Suspensions of granular particles embedded in fumed silica gels
Soichiro Makino, John R. Royer, and Wilson Poon
University Of Edinburgh, Edinburgh, United Kingdom

Binary suspensions composed of non-Brownian 'granular' particles embedded in a colloidal gel formed by much smaller, attractive particles are encountered in many common industrial products, such as cement, toothpaste and battery electrode materials. While colloidal gels and granular suspensions have been well-studied individually, there has been relatively little work on these more complex gel-granular binary systems. The interplay between the granular and gel phases can lead to time and history dependent changes in their rheology and microstructure. This complexity can in turn lead to processing challenges and manufacturing defects, particularly in highly demanding applications such as suspension casting of battery electrodes. Here we investigate the rheology of a model binary suspension system composed of large, repulsive silica spheres and small, attractive fumed silica particles dispersed in polyethylene glycol. On their own, the large spheres exhibit shear thickening while the fumed silica forms a colloidal gel. By varying the surface treatment of the fumed silica, we can vary the particle interactions, and hence the strength of the gel. Thus, this model system provides the opportunity to isolate the role of the small-particle interactions in the rheology of the mixed binary suspensions.

Thursday 11:30 Europe I
Settling dynamics of two spheres in a suspension of Brownian rods
Gaurav Kumar and Giovanniantonio Natale
University of Calgary, Calgary, Alberta T2N1N4, Canada

Sedimentation of solids in complex fluids is of great interest in several industrial operations, e.g. oil and gas exploration where these fluids are used as drilling fluids. In these systems particles with characteristic lengths that differ of several order of magnitudes interact. These interactions control the rheology of the whole system and consequently they affect the settling dynamics. As model system, we numerically investigate the settling of two rigid spheres in a dilute suspension of Brownian rods. The purpose of this study is to study the coupling between the settling of the spheres and the orientation of the nanoparticles affect the overall settling dynamics. The Brownian motion of the nanorods introduces a finite relaxation time in the suspending medium which is modeled as a continuum. Moreover, the suspending fluid can be considered thixotropic since the orientation state of the nanorods will always want to go back to its isotropic state. When the spheres are falling along their center line, the spheres experience two contributions: (1) Newtonian drag force and (2) Non-Newtonian force due to the presence of Brownian nanorods. The interactions between the two settling spheres is evaluated as function of Pe, distance between the centers of the spheres and the spheres' diameters. Repulsive and attractive interactions are found depending on the configuration of the system. Attraction between the two spheres was observed when both spheres are of the same size. By changing the spheres' sizes, a repulsive force can also be obtained. These forces were calculated numerically as a function of center-to-center distance between them at different Péclet numbers (Pe) (0.001-10) when both were of same size. Also, a study was conducted when either of the particles was larger in size compared to another, keeping distance between them constant and forces were calculated as function of size of the particle again at different Pe.

Thursday 11:50 Europe I
Oscillatory shear response of the rigid-rod model in nematic regime
Marco De Corato\textsuperscript{1} and Giovanniantonio Natale\textsuperscript{2}
\textsuperscript{1}University of Barcelona, Barcelona, Spain; \textsuperscript{2}University of Calgary, Calgary, Alberta T2N1N4, Canada

Nematic phase of rigid-rod molecules presents rheological complexities given the intrinsic anisotropy of the molecules and spatial variation of an average molecular orientation (director) in the bulk. The Doi-Hess rigid-rod [1,2] model has been shown to predict correctly the rheological response and orientation dynamic of nematic phase. This microscopic model has been investigated in simple shear and elongational flow but it has not been investigate in transient flows. Oscillatory shear flow is a model transient flow which introduces a transient and periodic perturbation to the system. Recently, large amplitude oscillatory shear (LAOS) has attracted interest given the rich rheological response that is obtained. This
enables more precise and complete characterization of complex materials. However, the interpretation at the microstructural level of the LAOS response is still limited to specific systems. For the first time, we aim to investigate the response of the rigid-rod model in oscillatory shear flow. We perform numerical simulations of the Doi-Hess equation for the molecular orientational distribution function using Brownian dynamics and an expansion in spherical harmonics. Here we focus on linking the rheological response and the microstructural evolution in LAOS. The stress components show even and add modes in LAOS that reflects the symmetry breaking coming from the Nematic state. Moreover, we demonstrate that oscillatory flow can be used as a technique to introduce discontinuities in rheological properties during flow.


Thursday  12:10  Europe I

**Fluctuating stresses and viscosities of colloid suspensions**

*Duraivelan Palanisamy and Wouter K. Den Otter*

*Multiscale mechanics, Engineering Technology, University of Twente, Enschede, Overijssel 7522 CJ, The Netherlands*

The viscosity of colloidal suspensions is important to biological and industrial flow processes. We show that current theoretical and numerical approaches based on explicit colloids moving in an implicit solvent, with the hydrodynamic (self-)interactions accounted for by the Brownian equation of motion and the stress expression, yield inconsistent values for the viscosity. This situation is remedied by revising the inclusion of fluctuating hydrodynamic stresses on the colloids. We present numerical results on a variety of isolated non-spherical particles, using a recently introduced efficient simulation approach [1], illustrating the necessity of these corrections to obtaining consistent values of the Einstein viscosities of dilute solutions of these particles. Viscosities for suspensions of ellipsoidal particles, for a wide range of aspect ratios and for Peclet numbers from the Brownian-dominated regime to the shear-dominated regime, are compared against theoretical predictions on the shear-thinning behaviour of these suspensions.


Thursday  12:30  Europe I

**Emergence of long-lived and long-ranged stress correlations in glass-forming colloidal dispersions**

*Florian Vogel¹, Annette Zippelius², and Matthias Fuchs¹*

¹*University of Konstanz, Konstanz, Germany; ²University of Göttingen, Göttingen, Germany*

A theory for the non-local shear stress correlations in glass-forming colloidal dispersions is derived from first principles. It captures the crossover from viscous to elastic dynamics at the liquid to glass transition and explains the emergence of long-ranged stress correlations in colloidal glasses. They can be traced to the coupling of shear stress to transverse modes, which is ignored in the classic Maxwell model. The dynamics in the solid phase is dominated by Goldstone modes in the long wavelength limit. These Goldstone modes are the consequence of the spontaneously broken translational symmetry on a local level. The modes are diffusive, because transverse momentum is not conserved -- excluding propagating transverse sound. These results are derived within a hydrodynamic theory, generalising Maxwell’s model to finite wavenumbers, after the dynamics has been decomposed into potentially slow modes, associated with the order parameter, and fast microscopic degrees of freedom.

Thursday  12:50  Europe I

**Simulating flexible filament suspensions and their sedimentation**

*Adam K. Townsend, Simon F. Schöller, Timothy J. Westwood, and Eric E. Keaveny*

*Department of Mathematics, Imperial College London, London, United Kingdom*

Microscopic flexible filaments and rigid fibres suspended in and interacting with fluids arise in many industrial processes and biological contexts and, due to their elasticity, are a staple ingredient of non-Newtonian fluids. In this talk, we present a comprehensive, scalable methodology for simulating suspensions of flexible filaments, overcoming timestep limitations due to numerical stiffness while also resolving fully 3D filament deformations due to bending and twisting through the use of quaternions. This approach is applicable to both active and passive filaments: here, we specifically examine the dynamics of sedimenting passive filaments. We look at these filaments in isolation, in small groups, and, finally, in large clouds and in homogeneous suspensions, and compare our results with those found previously for rigid filaments. Our simulations show how flexibility can complicate, but also simplify filament trajectories, and lead to enhanced settling speeds and non-trivial dynamics in large clouds.
Symposium NF

Non Newtonian Fluid Mechanics & Flow Instabilities (in honor of Prof. Mike Webster)
Organizers: Tim Phillips, Russel Davies, Natalie Germann and Corneliu Balan

Thursday 10:00 Emerald I
Numerical modeling of 2D melt fracture instability in viscoelastic flow
Youngdon Kwon
School of Chemical Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do 16419, Republic of Korea

Computational modeling the 2D Poiseuille flow along and outside a straight channel with a differential viscoelastic constitutive equation, we demonstrate unstable dynamics involving bifurcations from steady flow to periodic melt fracture (sharkskin instability) and its further transition regime to a chaotic state (gross fracture). The numerical simulation first exposes transition from steady flow to weak instability of periodic fluctuation, and in the middle of this periodic limit cycle (in the course of increasing flow intensity) a unique bifurcation into the second steady state is manifested. Then a subcritical (Hopf) transition restoring this stable flow to stronger periodic instability follows, which results from the high stress along the streamlines of finite curvature with small vortices near the die lip. Its succeeding chaotic transition at higher level of flow elasticity that induces gross melt fracture, seems to take a period doubling as well as quasiperiodic route. By simple geometrical modification of the die exit we illustrate as well reduction or complete removal of sharkskin and melt fracture. The result as a matter of fact suggests a convincing evidence of the possible cause for the sharkskin instability and it is thought that this fluid dynamic transition has to be taken into account for the complete description of melt fracture. The competition between nonlinear dynamic transition and other possible origin like wall slip will ultimately determine the onset of sharkskin and melt fracture. Therefore, the current study conceivably provides a robust methodology to portray every possible type of melt fracture if combined with an appropriate mechanism that also results in flow instability.

Thursday 10:20 Emerald I
A curvature dependent mass-correction scheme for the Level-Set method
Artur Sucena1, Manuel A. Alves2, Fernando T. Pinho1, and Alexandre M. Afonso1
1Departamento de Engenharia Mecânica, Faculdade de Engenharia da Universidade do Porto, Porto 4200-465, Portugal;
2Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Porto 4200-465, Portugal

Numerical simulations are presented in this work, with the aim of describing the behaviour of two-phase flows, in particular, the liquid-droplet flow of viscoelastic Boger fluids [1]. The interface between the two fluids is described using the Level-Set method [2], implemented in a Finite Volume Method in-house solver. The Level-Set method represents the interface with the use of the so-called Level-Set function, which is given by the signed distance to the interface. While the Level-Set method does not guarantee mass conservation, several mass correction schemes were already developed to deal with this problem. These methods generally distribute this error in the mass throughout the whole interface, which can lead to imprecisions in the shape of the interface in the long run, since the dissipation is higher in zones of the interface of high curvature. To better address this problem, this work proposes a mass correction scheme that depends on the curvature, leading to a better definition of the interface while still guaranteeing mass conservation.


Thursday 10:40 Emerald I
Energy dissipation rate-based viscosity measurement method for pressure-driven flows of non-Newtonian fluids
Hye Kyeong Jang1, Sun Ok Hong2, Ju Min Kim2, and Wook Ryol Hwang1
1Gyeongsang National University, Jinju, Republic of Korea; 2Ajou University, Suwon, Republic of Korea

In the present work, a novel viscosity measurement method is presented, which can be applied to a pressure-driven flow of an inelastic non-Newtonian fluid in an arbitrary geometry. The method is established on the balance of the rate of energy dissipation such that the external power will be dissipated within the system as the viscous dissipation in a laminar regime. The procedure includes the two flow numbers, which depends on the flow geometry only (nearly independent of the fluid properties): the energy dissipation rate coefficient that associates the total energy dissipation to the Reynolds number and the effective shear rate coefficient that relates the flow rate to the effective shear rate. After proving the method analytically for a simple flow of a power-law fluid in a circular pipe, and three different flows with complicated geometries are tested for the numerical and experimental validation: (i) axisymmetric expansion-contraction flows with numerical simulations; (ii) flows in a Kenics mixer with numerical simulations; (iii) experiments for flows in a complex microfluidic array with xanthan gum solutions. The error in viscosity estimation has proved to be less than 1% in numerical simulations and 10% in experiments. The present method is well-suited for on-line monitoring of in-situ viscosity in various non-Newtonian fluid flows of industrial processes due to its simplicity in the algebraic expression of viscosity as a function of the pressure drop, the flow rate and the two flow numbers.
Thursday 11:30 Emerald I

**Uncertainty in frictional pressure loss modelling of pipe flow for a non-Newtonian drilling fluid**

Solveig Riisøen and Fionn Iversen  
*Drilling and well modelling, NORCE AS, Bergen 5183, Norway*

In drilling operations, models are used to estimate the pressure profile in the well for both planning and process management. Sufficient modelling accuracy is required to help ensure that the driller stays within the available wellbore pressure window, thereby avoiding well control incidents. A good understanding of the uncertainty of the modelled flow frictional pressure loss is therefore needed. Method of measurement (and variability) of drilling fluid rheological properties, required as input for modelling of pressure gradient, strongly impact this uncertainty. The reported study has evaluated the impact of the method of measurement of rheological properties on the uncertainty of the modelled pressure loss. The frictional pressure loss has been estimated using the rheological characterization of a drilling fluid as measured with an Anton Paar high-precision rheometer. The rheometer measurement has been carried out with shear rate as control parameter, while for the reference pipeline flow the readily available control parameter is the pressure gradient. A key discrepancy therefore lies in the uncertainty in the relation between shear rate and pressure gradient in non-Newtonian pipe-flow. The main contributors to the uncertainties of the frictional pressure loss are investigated with focus on experimental errors, regression analysis and choice of rheology model. The drilling fluid used in this study is the polymer solution of Poly-Anionic Cellulose (PAC) with viscoelastic shear thinning behaviour. By identifying and quantifying the main sources of uncertainties for pressure loss modelling this work shall contribute to optimize the drilling process in a more efficient and safe manner. The results are of importance for other industries dealing with non-Newtonian pipe-flow, where it is of interest to estimate the pressure uncertainty range.

Thursday 11:50 Emerald I

**3-D simulation of pulsatile blood flow using a haemorheological model**

Soha Niroumandi¹, Azadeh Jafari², and Shidvash Vakilpour¹  
¹Faculty of new Sciences and Technologies, University of Tehran, Tehran, Iran; ²School of Mechanical Engineering, College of Engineering, University of Tehran, Tehran, Iran

Blood is a complex suspension of erythrocytes, leukocytes and platelets suspended in plasma that possesses several non-Newtonian rheological characteristics such as thixotropy, viscoelasticity and shear thinning in low shear rate typically less than 100 (1/s). These include, for normal blood, sluggish flow in the venous system and parts of the arterial vasculature where the geometry has been altered and RBC aggregates become more stable, such as downstream of a stenosis and inside a saccular aneurysm. In this study, the time evolution of the pulsatile non-Newtonian characteristics of the flow of human blood in a rigid wall cylinder is described by a new constitutive equation proposed by Owens [1]. This constitutive equation describes the aggregation and disaggregation of erythrocytes in normal human blood at different shear rate. The spectral/hp element method and third-order Adams-Bashforth method is employed for the spacial and time discretization respectively. Velocity correction splitting scheme method has been applied for the pressure force decoupling algorithms. The effect of hemodynamic parameters of pulsatile blood flow on flow pattern is investigated in this study. Our numerical results affirm red blood cells migration away from vessel walls, resulting in a region of reduced cell concentration close to the walls. Furthermore, Oldroyd-B is a simplified version of a homogeneous Owens's constitutive equation for blood flow at fairly high shear rate. So, the results of non-Newtonian stress with both Owens and Oldroyd-B constitutive equation are also discussed in this study. All simulations of this study have been done with the C++ toolbox, Nektar++ (https://www.nektar.info/), which is an open source software library currently being developed for non-Newtonian fluid flows in our research group.


Thursday 12:10 Emerald I

**Characterization of the effective slip in non-Newtonian fluid flows over corrugated surfaces in terms of the energy dissipation rate**

Jia Chen and Wook Ryol Hwang  
*School of Mechanical Engineering, Gyeongsang National University, Jinju 52828, Republic of Korea*

Complex local flow fields particularly near the corrugated surfaces can be accurately reproduced with the effective slip representation on an interface, in which a "normalized" slip length can be considered as a surface parameter even for a non-Newtonian fluid flow. In this work, we will investigate the estimation of the "normalized Navier-slip" at an imaginary smooth surface over patterned surfaces with various non-Newtonian fluids. On the basis of momentum balance and energy dissipation rate, expressions of the "normalized slip length" has been derived analytically with an effective viscosity and effective shear rate in a simple flat channel flow with corrugated surfaces on the bottom. In addition, some effects including aspect ratios, various non-Newtonian fluid models and pattern shapes will be investigated as well as the limiting cases (flat bottom and a Newtonian fluid). To verify appropriateness of this approach, example problems have been tested and compared with direct simulations with the corrugated surfaces. We report that the dimensionless normalized slip length appears almost constant as a function of the effective shear rate (or flow rate), which implies the normalized slip length is independent of rheological properties but depends nearly on the flow geometry itself. Interfacial flows are of great interest in nature (e.g. ground water flows) and in industries (composites manufacturing, oil/gas exploration, flows through membranes) and the quantification of the effective slip in this work with non-Newtonian fluids may provide a general computational framework in describing complex fluid flows near the interfaces either over corrugated surface or porous media.

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Three-dimensional flow characteristics around a bulge structure in a cavity swept by a viscoelastic fluids
Hiroshi Suzuki, Masaki Wada, Ruri Hidema, Shigeo Hosokawa, Kosuke Hayashi, and Akio Tomiyama
1Department of Chemical Science and Engineering, Kobe University, Kobe 657-8501, Japan; 2Department of Mechanical Engineering, Kobe University, Kobe, Japan

A small amount of surfactants added in water causes effective drag reduction in a pipe flow due to its viscoelasticity. This technique has been widely used for the thermal energy transportation systems, such as district heating/cooling systems. However, heat transfer reduction also occurs in a heat exchanger. In the previous studies, the authors reported flow penetration into a cavity between ribs mounted on heat transfer surface occurs due to a Barus effect at a certain low Reynolds number. Thus, heat transfer is enhanced in a heat exchanger with rib-like heat transfer promoters. Through the previous flow visualization experiments, a unique flow structure in a cavity was found at a certain middle Reynolds number. A flow separated from the upstream top corner of the cavity reverses at the middle position of the cavity and penetrates to the upstream bottom corner of the cavity. After that, the flow sweeps the cavity bottom and goes away from the cavity. Thus, the separated flow showed a bulge-like motion, and then it was called a bulge structure. In the previous study, this bulge structure was predicted to occur due to three-dimensional flow characteristics in the cavity. In this study, three-dimensional velocity fields around the bulge structure have been investigated by a spatial filter velocimetry based on a time-series of particle images taken with two high-speed video cameras. From the results, it was found that the flow at the upstream region of the cavity expanded not only in the normal direction but also in the spanwise direction. Then, the fluid was supplied spanwisely to the outer region and then the low velocity region appeared in the center region of the upstream bottom region of the cavity.

Due to the mass continuity, the fluid was supplied from the downstream region of the cavity to the upstream bottom region. This was concluded to be the mechanism for the bulge structure formation.

Symposium SM
Polymer Solutions, Melts & Composites
Organizers: Giovanni Ianniruberto and Evelyne van Ruymbeke

Dynamical heterogeneities, yield stress, plastic flow and strain hardening in glassy polymers: Theory
Didier R. Long, Paul Sotta, Luca Conca, and Thomas Merlette
1Laboratoire Polymères et Matériaux Avancés, CNRS - Solvay, Saint Fons 69192, France; 2CNRS - Solvay, Saint Fons, France

A model for the dynamics of non-polar amorphous polymers, based on percolation of slow domains, has been developed and solved, succeeding in reproducing many features of polymers, from the linear regime up to yield. We extend this model to large strain amplitudes. We propose that local deformation induces monomer orientation at the monomer scale analogous to nematic order. The consequent strengthening of monomer-monomer interaction results in slowing-down of the dynamics. Our model allow for calculating stress-strain curves up to the strain hardening regime with moduli of order a few tens to a few hundreds of MPa. Consistently with experimental observation, this modulus decreases upon increasing temperature until the strain hardening regime disappears altogether. Though the high molecular weight is an essential feature for strain hardening, we show that this effect cannot be explained by entanglements and has a molecular origin. We interpret the strain hardening regime as the consequence of a continuous increase in the fraction of strongly oriented monomers with locally increased glass transition temperature and enhanced ageing process. This is the first model solved in 3D which takes into account dynamical heterogeneities and proposes a consistent description with other features such as Stokes law violation, Tg shifts in confinement, ageing and rejuvenating process upon heating and the scale x of dynamical heterogeneities with no new adjustable parameter such as the so-called Eyring activation volume which has no clear interpretation. Our model allows also for calculating the whole spectrum of relaxation times with its spatial distribution which may allow for calibrating/checking the model thanks to experiments. Understanding the microscopic origin of this mechanism opens the path for designing polymers with enhanced ultimate properties.
interactions and the effect of an external magnetic field on the rheological properties of responsive biopolymer networks, temperature controlled flow and viscoelastic measurements are performed by using an opto-magneto-rheological cell built up in the MSC laboratory [1]. A magneto-viscous effect has been clearly evidenced by an increase of the low shear viscosity and the linear viscoelastic moduli with an increase of magnetic field. This behavior could be explained by different microstructures which depend on shear rate and magnetic field. This explanation has been supported by in situ optical visualization. A link between microstructure and macroscopic rheological properties is clearly obtained with the analysis of optical images.


**Symposium EM**

**Experimental Methods & Progress in Rheometry**

Organizers: Dimitris Vlassopoulos, Roland Kádár and Christian Clasen

Thursday 11:30 Emerald II

**Particle sedimentation in a dental resin investigated by dielectric analysis (DEA) using IDEX-sensor**

Bernhard Moeginger1, Lara Kehret1, Thomas Haenel1, and Berenika Hausnerova2

1Angewandte Naturwissenschaften, Hochschule Bonn-Rhein-Sieg University of Applied Sciences, Rheinbach 53359, Germany; 2Faculty of Technology, Tomas Bata University, Zlin, Czech Republic; 3Netzsch Gerätebau GmbH, Selb, Germany

Acrylic resins are the base of most light curing dental resin composites being highly particle filled to meet a manifold of requirements. Practically two aspects are important: 1st handling and flow behavior during cavity filling investigated by rheometer experiments, and 2nd curing behavior investigated by DEA in terms of ion viscosity during irradiation due to the fast reaction rate. IDEX-sensors are flat sensors with comb-like interdigitated electrodes whose grid field has a finite reach into the sample approximately given by the electrodes distance. This allows for measuring curing reactions depth dependently or sedimentation of suspensions to optimize the composites. As DEA measurements with IDEX-sensors are easy to perform the idea is to apply it for quality assurance purposes of particle filled suspensions to control filler contents. Therefore, dental resin composites with filler filler contents from 25 to more than 70wt% were investigated with respect to their initial ion viscosity. The initial ion viscosity is dominated by high ion mobilities in the liquid resin whereas the solid filler particles contribute only little to it. Assuming a homogeneous particle distribution, filler volume content changes affect apparently the mean ion concentration of the resin. Thus, for a resin with a given initial ion viscosity one can calculate the filler content dependent initial ion viscosities of suspension. However, the measured values exceeded systematically the predicted ones for filler contents below 50wt% what could be explained by sedimentation. Therefore, a measuring cell was designed allowing sample heights much larger than the reach of the fringe field. Starting with a homogeneous suspension, sedimentation can be observed as an increase of the ion viscosity until reaching a maximum value. Then, the measuring cell is turned upside down and the ion viscosity starts to decrease until a minimum value is reached. First results of sedimentation measurements are shown for diluted dental resin composites.

Thursday 11:50 Emerald II

**Rate dependent relaxation spectra and a novel approach to comparison of parallel and orthogonal superposition dynamic moduli**

A Russell Davies3 and Daniel J. Curtis2

1School of Mathematics, Cardiff University, Cardiff, Wales CF24 4AG, United Kingdom; 2College of Engineering, Swansea University, Swansea, Wales SA1 8EN, United Kingdom

In 1971, in a seminal paper,† Yamamoto derived integral relationships between dynamic moduli and rate-dependent relaxation spectra in parallel superposition of oscillatory shear on steady shear flow, where both the flows and deformation gradients exist in the same plane. These integral relationships are more complicated than their counterparts for orthogonal superposition (where the oscillatory and unidirectional flow fields occur in orthogonal planes) since they involve not only the spectrum, but also its derivative with respect to unidirectional shear rate. In this talk we show how the derivative may be eliminated from Yamamoto’s theory, which makes it possible (1) to determine rate-dependent relaxations spectra directly from parallel superposition rheometry; (2) to convert from parallel dynamic moduli to orthogonal in a stable manner; (3) to interpret parallel superposition dynamic moduli to allow direct comparison with orthogonal superposition moduli in the study of rheological anisotropy (as a consequence of flow induced alignment in, for example, particulate suspensions). Our approach facilitates interpretation of parallel superposition data without the complication of a secondary derivative.

† M Yamamoto. Transactions of the Society of Rheology, 15:2, 331-344, 1971
Implementing shear flow in a versatile simulation environment
Sebastian Bindgen\textsuperscript{1}, Pierre De Buyl\textsuperscript{2}, and Erin Koos\textsuperscript{1}
\textsuperscript{1}Soft Matter, Rheology and Technology, KU Leuven, Leuven 3001, Belgium; \textsuperscript{2}Institute for Theoretical Physics, KU Leuven, Leuven 3001, Belgium

In rheology, computational experiments are an important addition to laboratory experiments. They deliver complete particle-level observables and can probe length and time scales not accessible by traditional experimental techniques.

The Lees-Edwards boundary condition \cite{Lee1972} is a method to generate a shear flow in a molecular system and allows one to study the non-linear rheology of, e.g., colloidal or polymeric systems. Despite being introduced more than 45 years ago, there is no proper implementation available in an open-source molecular dynamics simulation package. Current solutions often use a biased thermostat or a SLLOD \cite{Morris1984} implementation that forces the particles on a linear shear profile without a clear physical justification.

Here, we demonstrate our implementation of the Lees-Edwards boundary condition in the software package ESPResSo \cite{Arnold2013}. The implementation is based on pair-wise thermostatting using the DPD (dissipative particle dynamics) technique \cite{Espanol1995} and, hence, does not require a user-specified bias to be enforced. It offers steady shear, oscillatory shear and step strain protocols. We demonstrate our implementation using different examples including polymer chains and suspensions of aggregating particles. A special focus will be put on the online analysis of stresses, hydrodynamics, and cluster structures as well as their impact on flow phenomena.

Due to the interplay with the versatile ESPResSo software package, this implementation offers a new pathway to directly obtain rheological quantities, which may be of particular interest for complex industrial flows. This package is freely available and designed to be easy to use by any researcher interested in modelling realistic flow phenomenon.

\begin{thebibliography}{99}
\bibitem{Arnold2013} Arnold, Lecture Notes in Computational Science and Engineering, Vol. 89: 1, (2013)
\end{thebibliography}

Characterization of physical aging by time-resolved rheometry: Fundamentals and application to bituminous binders
Olli-Ville Laukkanen\textsuperscript{1}, H. Henning Winter\textsuperscript{2}, and Jukka Seppälä\textsuperscript{3}
\textsuperscript{1}Institute of Physical Chemistry, RWTH Aachen University, Aachen 52074, Germany; \textsuperscript{2}Dept. Chemical Engineering & Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States; \textsuperscript{3}Department of Chemical and Metallurgical Engineering, Aalto University, Espoo 02150, Finland

Physical aging is a ubiquitous phenomenon in glassy materials that results in the time evolution of rheological properties. Due to the prevalence of physical aging in numerous industrial processes and technological applications, its effects need to be taken into account in the design, manufacture and use of many everyday products. For example, physical aging in bituminous binders has a major impact on the durability of asphalt pavements. In this study, we demonstrate that time-resolved rheometry (TRR) \cite{Mours1994} is a powerful technique to monitor and analyze the time dependence of linear viscoelastic properties during physical aging. The advantages of TRR over the traditional Struik's physical aging test protocol \cite{Struik1966, Struik1977} are discussed. In the experimental section, TRR is applied to study physical aging in a set of bituminous binders. Small-diameter parallel plate rheometry \cite{Laukkanen2017} is employed to perform cyclic frequency sweep experiments over extended periods of time (up to 8.6 days). It is observed that sample mutation is relatively slow (mutation number $N_m << 1$) during physical aging, thus allowing rheological measurements to be conducted on quasi-stable samples. The results show that crystallinity increases the degree of physical aging in bitumen. Physical aging is observed to occur both below and above the nominal glass transition temperature, and this is attributed to the broad glass transition of bitumen. The time-aging time superposition is found to be valid in bitumen. When bitumen is modified with styrene-butadiene-styrene triblock copolymer, both horizontal and vertical shifts are necessary to create smooth time-aging time master curves. It is speculated that the vertical shifts are induced by the formation of continuous polymer-rich network structure in bitumen.

\begin{thebibliography}{99}
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We propose a constitutive model to describe the mechanical behavior of cement pastes. The model is capable of predicting time dependence and irreversibility caused by the continuous hydration process that occurs in oil well cement pastes during cementing operations. The model is developed for a specific cement paste according to a recently proposed method [1] with a modification to accommodate cement setting predictive capability. The fluidity (reciprocal of viscosity) is directly employed to indicate the structuring level of the microstructure. The model relies on the results of several rheological experiments to determine the nature and parameter values of novel material functions that arise in the model development. The material function that carries the cement setting information is the yield stress function, which turns out to be an exponentially
increasing function of time. Except for minor differences observed at low shear rates, good agreement is observed between the data and the model predictions.


Thursday 12:10 Europe III

**Finite strain thermomechanical behavior of filled rubbers: Hydrostatic pressure effect**
Jonathan Champagne¹, Cristian Ovalle², Karine Le-Gorju³, Helene Montes⁴, François Lequeux⁵, and Sabine Cantournet⁶

¹Mines ParisTech, ESPCI, Hutchinson, Corbeil-Essonnes, IDF 91100, France; ²Centre des Matériaux, Mines ParisTech, Corbeil-Essonnes, IDF 91100, France; ³Caractérisation et Essais Mécaniques, Hutchinson, Chalette sur Loing, Centre 45120, France; ⁴SIMM, ESPCI, Paris, IDF 75005, France

Within some aeronautical applications, confined rubber are subjected to high hydrostatic pressure. The link between both hydrostatic pressure and temperature effects on the material's rheology is studied. The proposed constitutive law will have to integrate, in addition to common internal variables temperature and strain, the hydrostatic pressure, related with the structure effect.

A numerical code is used to carry out a finite element analysis on geometrically-confined cylindrical specimens under uniaxial compression. The specimen center is characterized by an hydrostatic pressure state [1] whereas the outbond is characterized by an uniaxial stress state. In other words, the confined compression effect results in an hydrostatic pressure state.

Shear tests are carried out on confined cylindrical specimens at controlled temperature T and various static compression load. This compression load leads to an hydrostatic pressure p_h deduced from the aforementioned finite element analysis. Results show a rise of shear stiffness K and dissipation with decreasing T or increasing p_h. Considering the shift factor a_T, shear stiffness master curves are built regardless the shear strain amplitudes.

Our discussion relies on the physico-mechanical approach for the non-linear modeling of filled rubbers proposed by [2]. By rewriting the aforementioned local model for a confined compression case and by means of a multiscale analysis, we can explain the experimental T-p_h superposition as a consequence of the fillers regrouping effect within the elastomer. Finally, the physical meaning of the shift factor a_T will be discussed and, in particular, its dependency with shear strain amplitudes.


Thursday 12:30 Europe III

**Experimental investigation of start-up flows of time dependent materials**
Cezar O. Negrao¹, Lucas G. Pereira¹, Roque M. Duarte Jr.¹, Tainan G. Santos¹, and Diogo V. Andrade²

¹Academic Department of Mechanics, Federal University of Technology - Parana, Curitiba, Parana 81280-340, Brazil; ²Laboratoire Navier, IFSTTAR, Université Paris-Est, Champ-sur-Marne, Île-de-France 77420, France

Flow start-up is an important problem in many industries which are usually interested in reducing restart time or in obtaining the minimum pressure required for the start-up. In the petroleum and gas industry, for instance, significantly high pressure or time required for starting up gelled crude oils may make the design of pipelines unfeasible. The current work aims to investigate experimentally the start-up flow of time dependent materials by using a laboratory-scale flow loop. The experimental rig, basically composed of a siring pump, a 50 m long pipeline built in coil shape and a fluid reservoir, is placed inside a thermally controlled chamber. The flow loop controls the inlet pressure or flow rate so as to obtain either the minimum pressure and time required for the start-up or the maximum pressure reached for a given flow rate. In order to better understand time dependent material responses, three different fluids were evaluated: a Newtonian (glycerin), a viscoplastic (Carbopol solution) and a thixotropic (laponite solution). Flow curves obtained with the flow loop for the three fluids were compared with rheological data so as to validate the experimental rig. Despite the good agreement for the three fluids, there is a clear evidence of wall slip for the Carbopol solution. Images of fluid motion at the pipeline outlet taken during controlled pressure experiments show that the minimum wall stress required for the flow start-up coincides with the fluid yield stress obtained from the rheometer flow curve. Controlled flow rate experiments clearly evince viscous effects, pressure propagation, shear history, inertia, elastic effects and thixotropy during flow start-up. The experimental data was also compared to the results of a one-dimensional mathematical model with good agreement.

Thursday 12:50 Europe III

**Deformation of soft solid foams investigated using Finite Element Modelling (FEM) and ultra-fast X-Ray tomography: Application to the study of food chewing mechanisms**
Melissa Assad-Bustillos, Sofiane Guessasma, Anne-Laure Reguere, and Guy Della-Valle

Biopolymers Interactions and Assemblies, INRA, Nantes 44316, France

Soft solid foams are encountered in many parts of our daily life, either as materials or even as living organisms. In spite of this wide interest, the detailed study of their damage mechanisms under mechanical load is still in progress. Today, the concomitant development of imaging and
numerical methods has made possible more detailed studies of such mechanisms. This work focuses on two cereal foods, sponge-cake (SC) and brioche (B), considered as solid foams, to enlighten the process of human mastication. Their mechanical properties have been characterized under large compression levels (>90% in height reduction). Two distinct non-linear mechanical behaviors were observed: B showed plastic deformation and SC displayed hyper-elastic behavior. The evolution of the cellular structure of the two foods under compression was captured using high resolution ultra-fast X-ray microtomography at the European Synchrotron Radiation Facility (ESRF), according to two geometries: plane/plane and grooved surface/plane, the latter allowing large shear deformation. The compression response of the samples was recorded in situ at all stages. The resulting 3D images provide necessary information in order to implement realistic numerical models developed using COMSOL® Finite element computation was used to derive the mechanical model representing the compressive response up to densification as compared to experimental data. Densification was modelled as a local increase in stiffness, implementing an exponential function of the applied load. The mechanical response of both foods was accurately represented. By predicting the mechanical and microstructural changes of two soft cereal food foams under conditions that mimic oral processing (compressive loading, associating shear deformation), these results allow a more accurate description of the mechanisms that govern food mastication. They opens prospect to design food products adapted to the elderly population. This work was supported by AlimaSSenS (ANR-14-CE20-0003).

Symposium PS

Polyelectrolytes, Self-Assembling Fluids & Gels

Thursday 10:00 Europe III

Rheology of double networks composed of polymer and micellar chains

Andrey Shibaev, Ilias Iliopoulos, and Olga Philippova

1Physics department, Moscow State University, Moscow 119991, Russia; 2ENSAM, Paris 75013, France

The paper is devoted to the study of phase behavior, microstructure and rheological properties of self-assembled networks based on wormlike surfactant micelles of varying negative charge and polymer weakly interacting with the micelles. It is shown that the mixed networks demonstrate a synergistic increase in viscosity as compared to pure component solutions, which was attributed to the formation of entanglements between polymer and micellar chains and to the elongation of micelles induced by polymer. These findings demonstrate the effectiveness of the addition of weakly interacting polymer for the modulation of rheology of wormlike surfactant micelles thus opening a new way for manipulating the rheological properties of viscoelastic surfactant solutions and gels.

Acknowledgment. The work was financially supported by Russian Foundation for Basic Research (project N 19-53-15012).

Thursday 10:20 Europe III

Non-monotonic rheological behaviour of hydrogels consisting of mixtures of supramolecular hydrogelators

Emmanouil Vereroudakis, Daniele Parisi, René Lafleur, Minaspi Bantawa, Emanuela Del Gado, E. W. Meijer, and Dimitris Vlassopoulos

1Institute of Electronic Structure & Laser, Foundation for Research and Technology Hellas, FORTH, Heraklion, Greece; 2,3 Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, The Netherlands; 4Institute for Soft Matter Synthesis and Metrology, Georgetown University, Washington, DC, United States

The synthesis of strong and resilient networks which can uptake large amounts of water while exhibiting enhanced processability and self-healing has emerged as a research topic of prime significance because of the ability to tailor their rheology and their similarity with networks of biological macromolecules such as polypeptides and proteins. Here, we investigate the unusual rheological properties of a class of hydrogels made of fibrillar supramolecular polymers based on the 1,3,5-benzene-tricarboxamide motif decorated with aliphatic chains terminated by a tetra(ethylene oxide) chain (3OH-BTA) and in particular their tunable mechanical response. The 3OH-BTA unit is known to self-assemble into long, persistent fibrillar structures which form physical networks akin to those of entangled polymers. A second novel motif comprised from a telechelic poly(ethylene glycol) chain decorated with 3OH-BTA units on both ends (BTA-PEG-BTA) was investigated as well. The BTA-PEG-BTA motif can also form gel-like materials in water albeit with different mechanical response compared to 3OH-BTA networks. Importantly, by mixing the 3OH-BTA and BTA-PEG-BTA units in different compositions we observe a non-monotonic mechanical response, suggesting the presence of interactions between the two building units that enable fine tuning the mechanical properties. We discuss the origin of this behavior and its consequences on the tunability of hydrogel response. Our findings are supported by simulations which can give us important insight on the structure and rheology of the network formed by such a class of materials, especially in mixtures where two different types of transient bonds (in terms of strength and range) are present and control the overall response.
Thursday Morning

**Symposium MN**

**Micro, Nano Fluidics & Microrheology**

Organizers: Pouyan Boukany, Manlio Tassieri and Francisco J. Galindo-Rosas

Thursday 10:00 Europe II

**High-throughput microfluidic characterization of erythrocyte shape and mechanical variability**

Felix Reichel¹, Johannes Mauer², Ahmad A. Nawaz¹, Gerhard Gompper², Jochen Guck¹, and Dmitry A. Fedosov²

¹Center for Molecular and Cellular Bioengineering, Technical University Dresden, Dresden 01307, Germany; ²Institute of Complex Systems, Forschungszentrum Juelich, Juelich 52425, Germany

The motion of red blood cells (RBCs) in microchannels is important for microvascular blood flow and biomedical applications such as blood analysis in microfluidics. The current understanding of the complexity of RBC shapes and dynamics in microchannels is mainly based on several simulation studies, but there are a few systematic experimental investigations. Here, we present a combined study, which systematically characterizes RBC behavior for a wide range of flow rates and channel sizes. Even though simulations and experiments generally show good agreement, experimental observations demonstrate that there is no single well-defined RBC state for fixed flow conditions, but rather a broad distribution of states. This result can be attributed to the inherent variability in RBC mechanical properties, which is confirmed by a model that takes the variation in RBC shear elasticity into account. This represents a significant step toward a quantitative connection between RBC behavior in microfluidic devices and their mechanical properties, which is essential for a high-throughput characterization of diseased cells.

Thursday 10:40 Europe II

**The dynamics of flexible Brownian fibers in viscous flows**

Anke Lindner¹, David Saintillan², Yanan Liu¹, Olivia du Roure¹, and Brato Chakrabarti²

¹PMMH, ESPCI, Sorbonne Université, Paris, Ile-de-France 75005, France; ²University of California San Diego, San Diego, CA, United States

The morphological dynamics, instabilities and transitions of elastic filaments in viscous flows underlie a wealth of biophysical processes and are also key to deciphering the rheological behavior of many complex fluids and soft materials. Here, we combine microfluidic experiments with actin filaments as a model system and computational modeling with non-local slender body theory to elucidate the dynamical regimes and morphological transitions of elastic Brownian filaments in a simple shear flow. The filament dynamics and transitions are primarily governed by a dimensionless elasto-viscous number comparing viscous drag forces to elastic bending forces, with thermal fluctuations only playing a secondary role. The transitions are characterized by a buckling instability and the appearance of localized high-curvature bends that propagate along the filaments in apparent “snaking” motions. We present a complete characterization of filament morphologies and transitions as a function of elastoviscous number and scaled persistence length and demonstrate excellent agreement between theory, experiments and simulations.

Thursday 11:30 Europe II

**On the hemodynamics around 2D microbot prototypes**

Tomás Rodríguez¹, Francisco J. Galindo-Rosas², and Laura Campo-Deañño¹

¹Departamento de Engenharia Mecânica, CEFT, Faculdade de Engenharia da Universidade do Porto, Porto, Porto 4200-465, Portugal; ²Departamento de Engenharia Química, CEFT, Faculdade de Engenharia da Universidade do Porto, Porto, Porto 4200-465, Portugal

Having such a small size, microbots might just represent the next frontier for minimally invasive medicine. Over recent decades, the notion of miniaturisation has come to grow amongst the medical community, as efforts are being put into the development of increasingly smaller medical devices. Research areas like microfluidics have proven to be instrumental in the study of the human body as a carrier for such microrobotic systems, by combining micro scale accessibility with several well-established flow characterisation techniques. In this work, the focus goes to the hemodynamics of these devices inside the submillimeter blood vessels of the body, with special emphasis on the morphology of the robots and how it translates to the flow patterns, pressure drop, velocity field, etc., while dealing with the complex rheology of the medium. With this in mind, the flow of blood analogue fluids around 2D microbot prototypes in a straight capillary-like microchannel was investigated experimentally. In order to do so, two simplified microbot models – a circular one and an elliptical one (with an aspect ratio of $1:4$) – were individually placed at the fully developed region of a $10$ mm long rectangular microfluidic channel (resembling the flow past a confined cylinder problem). The blockage ratio ($\beta$) was $\sim 28\%$ and the flow conditions tested varied from creeping flow up to $Re \sim 100$. Pressure drop and micro-Particle Image Velocimetry ($\mu$PIV) measurements were performed using Newtonian and viscoelastic blood analogues, leading to several remarks on the dynamic efficiency of both geometries in whole blood conditions.
**Thursday 11:50 Europe II**

**Numerical simulations of particulate fouling in microchannels**

Marco Trofa, Gaetano D'Avino, Giovanna Tomaiuolo, Francesco Greco, Pier Luca Maffettone, and Stefano Guido  
*Università di Napoli Federico II, Napoli, Italy*

The development of micro and nanotechnologies has provided the possibility of synthesizing, analyzing, and manipulating particles with micrometric and submicrometric characteristic dimensions under continuous flow conditions. In many systems, the suspended particles show adhesive properties leading to undesired phenomena such as fouling and clogging. Fouling is the continuous deposition of particles on an initially clean surface, whereas clogging is the mechanism that interrupts the transport of particles in confined geometries. Although these phenomena have been thoroughly studied, the complete mechanism is far from being fully understood. In this work, we study the initial growth of an aggregate at the wall of a slit microchannel by using Computational Fluid Dynamics (CFD) combined with the Discrete Element Method (DEM). We consider a suspension of “soft” micro particles in a Newtonian liquid, with a simple model to describe particle-particle adhesion. The parameters considered in the simulations are taken from our recent experimental study on cluster growth in a microreactor. The results are presented in terms of cluster morphology and growth rate, quantified by the projected area onto the slit wall. A reasonable agreement with experimental data is found.

**Thursday 12:10 Europe II**

**Particle migration in confined viscoelastic channel flows of polymer solutions: A quantitative study**

Antoine Naillon, Clement de Loubens, William Chèvremont, and Hugues Bodiguel  
*Univ. Grenoble Alpes., CNRS, LRP, Grenoble 38000, France*

Flows of particles in viscoelastic liquids are involved in numerous geological, biological or industrial applications. We focus in this work on confined flows at low Weissenberg where it has been shown that viscoelasticity is responsible for cross-stream migration of the particles. The associated force scales as a^3, where a is the particle size, which ensures a very high sensitivity in sorting applications. This phenomenon has been the focus of a few theoretical studies in the late seventies, and has regained interest during the past decade in the context of nano and microfluidics. However, the theoretical predictions have not been directly experimentally tested and validated. The aim of this work is to provide a quantitative study of the viscoelastic migration of particles that occurs in confined flows of viscoelastic fluids, and to extend it to the case where an additional body force is acting on the particle. We developed a technique to recover the 3D trajectories of particles using a standard optical microscope. It is based on a 2-dimension particle tracking velocimetry coupled with the detection of the out of focal distance. Thanks to this technique, we manage to characterize the transverse particle migration kinetics in confined flows of a polymer solution. The method is applied in various systems and experimental conditions, to reach a robust comparison with theory. One of the challenge being related to the precise characterization of the short (1-10 ms) range of the relaxation time of the solution, we used the slow retraction method of filament breakup experiment. The theory of Ho and Leal is tested and extended to predict the evolution of the PDF of the particle positions. The agreement with the experimental data is excellent, up to a prefactor which we discuss. Strikingly, when a body force is imposed (electrostatic) to slow down the particles in the flow, they migrate in the opposite direction, from the centre to the walls. LBM simulations are carried to describe this effect.

**Thursday 12:30 Europe II**

**Controlling particle trajectories in confined flows via particle shape**

Mathias Bechert1, Jean Cappello2, Marine Daïeff2, François Gallaire1, Anke Lindner2, and Camille Duprat3  
1Laboratory of Fluid Mechanics and Instabilities, EPFL, Lausanne, Switzerland; 2PMMH, ESPCI, Paris, France; 3LadHyX, Ecole polytechnique, Palaiseau, France

Transport properties in confined geometries show very specific characteristics, as for example lateral drift for fibers inclined with respect to the flow direction. Due to viscous friction with top and bottom walls transported particles act like moving obstacles and induce strong flow perturbations. These perturbations are at the origin of the observed lateral drift, oscillatory movement between lateral walls or the deformation of flexible fibers. When fiber shape is perturbed by adding for example an additional arm, an L shaped fiber is formed, and fiber symmetry is broken. This induces fiber rotation until a stable equilibrium orientation is reached. Lateral drift is then observed until interaction with side walls becomes important. Tuning the fiber asymmetry allows for a precise control of particle trajectories, including the approach of side walls, robust even against small perturbations. Our investigation combines precise microfluidic experiments as well as numerical simulations based on modified Brinkman equations. The knowledge gained here can be used for targeted delivery or particles capture inside microchannels.

**Thursday 12:50 Europe II**

**Viscoelastic ordering of particles in a straight microfluidic channel**

Francesco Del Giudice1, Gaetano D'Avino2, Francesco Greco2, Pier Luca Maffettone2, and Amy Q. Shen3  
1College of Engineering, Swansea University, Fabian way, United Kingdom; 2Università di Napoli Federico II, Napoli, Italy; 3OIST, Onna-son, Niigata, Japan

Controlling the trajectories of particles suspended in fluids flowing in microfluidics devices is crucial in a variety of applications such as counting, sorting, analysis, and detection. Recent studies have shown that fluid viscoelasticity can be used to align the flowing particles on the centerline of a straight microchannel (3D focusing). In many applications, however, it is also desired to achieve “particle ordering”, i.e., the self-assembly of aligned particles in equally-spaced structures. This is the case, for instance, of the encapsulation of particles in droplets where the frequency of droplet formation must be synchronized with the frequency of particles entering the encapsulation area. In this contribution, we show by experiments and simulations that, once 3D focusing is achieved, fluid viscoelasticity drives self-assembly of equally-spaced particle trains. A
suspension of 20 µm particles in an elastic, shear-thinning hyaluronic acid solution flowing in square-shaped microchannel with height of 100 µm is employed. At high Deborah numbers, the particles self-assemble in equally-spaced structures. Simulations are carried out for a system of particles aligned along the channel centerline by solving the particle motion equations where the velocities are taken from direct numerical simulations on a three-particle system. The spacing efficiency is evaluated by varying the particle concentration, fluid rheology, and flow rate. A good quantitative agreement between experiments and simulations is found. A simple qualitative argument on the train stability based on the pair particle dynamics is used to understand the underlying mechanism leading to particle ordering.
Thursday Afternoon

Symposium GM
Granular Materials & Highly Filled Systems

Organizers: Joamin Gonzalez Guttierez, Berenika Hausnerova and Tamás Börzsönyi

Thursday 14:40 Europe I  GM14
Rheology of granular media on ground and in space
Matthias Sperl
Materials Physics, German Aerospace Center DLR, Cologne, Germany

An ultimate goal and benefit for society of granular rheology should be the achievement of similar predictive power as standard computational fluid dynamics has for, e.g., the design of airplanes. This is especially true in space where in contrast to Earth-bound applications trial and error as an optimization strategy are practically impossible. A challenge encountered when performing rheological experiments in space under varying gravity conditions is the very impact of gravity on these experiments regarding such aspects as confinement of the material as well as the significance of effects like secondary convection. Such experimental difficulties call in question a proper rheology in such environments. Combining experimental and theoretical strategies for both macroscopic shear as well as in comparison passive and active microrheology, a route towards the rheological characterization of granular media in space shall be given.


Thursday 15:00 Europe I  GM15
Optimisation of the interfacial bonding in polypropylene filled with different types of glass spheres produced by extrusion-based additive manufacturing
Martin Spoerk and Joamin Gonzalez-Gutierrez
Institute of Polymer Processing, Montanuniversitaet Leoben, Leoben, Styria 8700, Austria

A decent interface between fillers and the polymer matrix is a pre-requisite for optimal mechanical performance of polymer composites. Especially for extrusion-based additive manufacturing, an increasingly popular manufacturing technique for thermoplastics that is also known as 3D-printing, an optimised morphology is a must for complex composites, as the processability fully relies on morphological aspects. Filler agglomerations in the filament, for example, regularly result in clogged nozzles and buckling of the filament in the printing head. In turn, a prominent change in morphology can drastically alter the rheological behaviour of the composite. Consequently, the interfacial weld strength and, thus, the overall mechanical properties of 3D-printed parts can change. The present study determines the consequences of different compatibilisers, coatings, and glass sphere types on the properties of highly-filled PP composites that are most relevant for 3D-printing, namely morphological, rheological, tensile, thermal, impact, and dimensional properties. It is found that the most promising compound, comprising of 30 vol.-% coated borosilicate glass spheres and a compatibiliser based on maleic anhydride, reveals a homogeneous filler distribution and an exceptional filler-matrix interface. These findings combined with optimised processing settings that overcome the increase in viscosity offer an improved processability, dimensional accuracy, and mechanical properties compared to neat PP.

Thursday 15:20 Europe I  GM16
Rheological investigations on free-flowing and cohesive powders in different states of Aeration, using a ball measuring system
Andreas Kottlan¹, Denis Schütz², and Stefan Radl³
¹Institute of Process and Particle Engineering, Graz Technical University, Graz, Austria; ²Rheology, Anton Paar GmbH, Graz, Austria

For many industrial applications, knowing the bulk properties of powders is a crucial factor. This affects developments in the pharmaceutical industry as well as research on new materials and production processes. Even though, the simulation of idealized, particulate systems has become state of the art, a comprehensive description of industrially utilized powders is still challenging, if not impossible. Conducting measurements is imperative to gain knowledge about the flow behaviour of a powder, either for direct application in engineering or for the validation of simulations. We investigate an alternative method for measuring the apparent viscosity of granular materials, meeting challenges associated with free-flowing and cohesive powders. The method is based on the measurement of a typical drag force, acting on a sphere when dragged through a powder bed. From the measured torque signal, the apparent viscosity is calculated via Stokes drag law. To connect the measured viscosity with a typical flow
metric, a theory providing an averaged shear rate has been developed. Results obtained with the newly developed sphere-based measuring system are compared to data from other well investigated flow setups. The results suggest that our method is capable of measuring the apparent viscosity of free-flowing and cohesive powders. Furthermore, we demonstrate that the derived shear rate theory suitably approximates the complex flow field in the measuring setup for a range of applications. We believe that, this method can be a tool enabling researchers to gain deeper insights to the flow behaviour of powders, especially into that of the cohesive ones. These insights may be one piece of the puzzle for future developments.

Thursday 15:40 Europe I
Flow and clog of grains in silos
Kiwing To
Institute of Physics Academia Sinica, Taipei 11529, Taiwan
In experiments of mono-disperse plastic beads falling out of a cylindrical silo through a circular exit at the bottom, no continuous flow can be sustained when the diameter D of the exit is about 5 times that of the beads. If the exit of the silo moves horizontally (e.g. circular motion or linear oscillation) with respect to the wall of the silo, finite flow rate can be sustained even at small D. If the exit rotates at off-center distance R with angular frequency ω, the flow rate W increases with R^2. Similarly, if the exit oscillates with amplitude A and oscillation frequency f, W increases with Af. On the other hand, if D is large, W varies non-monotonically with either the angular frequency ω or oscillation frequency f. Since silos and hoppers are very common appliances that are used as transporting or distributing granular materials in food, coal and pharmaceutical industries which suffer high losses due to clogging, our work will not only enhance our basic understanding of the phenomenon of clogging but also improve the design of hoppers and silos for less clogging.

Thursday 16:30 Europe I
The concept of jamming in filled rubbers
Xiaorong Wang
School of Chemical Science and Engineering, Tongji University, Shanghai, China
Soft rubbers filled with nano-sized carbon black and silica are utilized in numerous applications, including gaskets, damping materials, conveyor belts, hydraulic hoses, and automobile tires. Recent advances that draw upon the common features among filled rubbers and other frustrated systems are encouraging. The present discussion is dedicated to the remarkable similarities between the dynamic strain-induced nonlinearity of the modulus and the physics of the glass transition of glass forming materials, as well as the jamming transition of vibrated granular materials. This analogy stems from the fact that filler particles in the rubber matrix agglomerate and tend to form a jamming network. The filler network is transient in nature and can be broken or fluidized through shear deformation. The agglomeration and de-agglomeration of filler are typical jamming and de-jamming processes. Therefore, particle-filled rubbers with respect to deformation may display many unusual glass-like phenomena, including the asymmetric kinetics, crossover effects, and heterogeneous relaxing. The newly collected evidence also suggests that particle-filled systems under deformation may display feature fluctuations that is reminiscent of critical phenomena of a transition. This evidence suggests that although jamming is kinetic, it may also be thermodynamic in nature. The coexistence of kinetic and thermodynamic descriptors of this phenomenon suggests that a new physics exists in these materials. Based on those experimental results, we propose a unified phase diagram for describing the transition that has incorporated variables that are all derivable from Hamiltonians and may facilitate crucial comparisons between theories and experiments.

Symposium IP
Industrial Rheology & Processing
Organizers: Ulrich Handge, Clemens Holzer and László Gomze

Rheological behavior of glass ceramic pastes used as sealants for solid oxide fuel cells
Svenja Dittrich, Karl G. Schell, Ethel C. Bucharsky, and Michael J. Hoffmann
Institute for Applied Materials IAM-KWT, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany
Glass ceramics are used as sealant materials between interconnector and electrolyte to separate air and fuel in solid oxide fuel cells (SOFC). They are electrically insulating, gas tight and chemically stable at high temperatures. The screen printing process of the glass ceramic paste is one of the most important steps during fuel cell stack assembly. It offers several advantages for large-scale production compared to other deposition methods such as thickness control, easy design and low cost. The topography and quality of printed films should be reproducible and strongly depend on the flow and relaxation behavior of the paste. In this study, the influence of paste composition on paste rheology is investigated and correlated with the film contour.

For the glass ceramics an alkaline earth silicate glass with a particle diameter d50 of 15 μm is used, which contains small amounts of zirconium dioxide and yttrium oxide. This powder is dispersed in a commercially available suspension medium. The rheology of paste formulations with different solid contents, as well as amounts of dispersing and networking agent, is evaluated by rotary and oscillatory rheometry. An important property for the printability of the paste is its shear thinning behavior, through which the viscosity decreases at high squeegee pressure.
Additionally the paste structure recovers when the shear stress is reduced. By adjusting the composition, films with a thickness of about 150 μm can be deposited reproducibly.

Thursday 15:00 Emerald I

New tool for process rheology
Fridolin Okkels
Fluidan, Kgs. Lyngby 2800, Denmark

Many industries that are producing or handling Non-Newtonian liquids have a challenge in measuring and controlling the rheological properties during the production. For a broad range of liquid products such as paints, household-products, beverage concentrates, and pharmaceutical semi-solids, the rheological properties play a crucial role in the functionality, shelf life, and/or user experience of the product. Controlling such properties during production, rely on being able to measure the rheology as an integrated part of the production, and except from using in-line viscosimeters that measure a single viscosity-value, a sample must be manually taken from the production and measured on a stand-alone rheometer to get a more detailed rheological characterization. Presently, such a measurement often takes between 15 minutes and 2 hours, depending on e.g. temperature conditioning. This introduces a substantial delay in the production flow, especially when cycles of adjustments/rework are required or if the production is continuous. A new on-line, temperature-controlled, process rheometer [1], developed by the start-up company Fluidan, will be evaluated here. It automatically measures a full flow curve and the viscoelastic properties (G', G'') at time-intervals of 1-5 min. depending on the overall viscosity of the product. It has already been tested on semi-solids [2]. As in-line viscometers can be seen as "viscosity-sensors", the new tool can be seen as an actual "rheology-sensor" that can stream rheological data directly from the production to the quality control unit. Beside the clear benefits from a production point of view, such a tool will also ensure that liquid products keep having the right functionalities that are valued by the general consumer. The changes in industrial practice that is enabled by on-line rheology is discussed.


Thursday 15:20 Emerald I

Rheology and self-adhesion of uncrosslinked butadiene-acrylonitrile rubber
Valentine Hervio and Costantino Creton
Laboratory of Soft Matter Science and Engineering, ESPCI Paris, Paris 75005, France

The adhesion of unvulcanized elastomers, to themselves (self-adhesion) or to other materials, is industrially very important for the manufacturing of rubbers, and in our specific case, for the fabrication process of helicopters’ fuel tanks.

We investigated the self-healing behavior of an unfilled and unvulcanized acrylonitrile-butadiene random copolymer (commonly called nitrile butadiene rubber NBR). We have shown that unlike more classical non-polar elastomers such as polyisoprene or polybutadiene, shows very poor self-adhesion properties. We suggest, supported by DSC and linear rheology experiments, that because of its polarity, our material tends to self-organize with time and form nano-clusters of polar groups. This organization can be seen as some physical crosslinking, preventing both the flow at low frequency in linear rheology, and the diffusion of the polymeric chains in the bulk and at the interface.

Different strategies were explored to disrupt these supramolecular objects knowing that when sheared at high temperature the material flows at low frequency.

First, we blended NBR with small molecules (tackifiers), expecting that for polar tackifiers, the polar clusters could be disrupted. Second, we impregnate the surface of the elastomer with solvent to break and dilute the physical interactions between polar groups, and accelerate the interdiffusion of the polymer at the interface between two pieces of uncrosslinked NBR.

We find that while the rheological properties are not much affected, both strategies are efficient in improving significantly the self-adhesive properties and we will discuss critically the possible reasons for this discrepancy between rheology and improvement in self-adhesion.
DNA is a linear semi-rigid polyelectrolyte having a sequence that encodes the genetic information of all living organisms. The importance of the study of DNA dynamics, viscoelasticity and flow properties falls in the understanding of DNA functions, as well as cell division. Many important properties of DNA depend on polymer concentration, molar mass and stiffness and also on the external salt content. In aqueous solutions, electrostatic inter-chain and intra-chain interactions play an important role on DNA solutions behavior and have to be considered for the study of DNA interactions with other molecules. In this work, the rheological behavior of a high molecular weight DNA in aqueous solution is studied: i) at two polymer concentrations (4 and 10 mg/mL); ii) in water, and in the presence of two ionic concentrations (0.01 and 0.1M NaCl) to investigate the influence of ionic concentration on rheological behavior and on birefringence induced under flow. At the selected polymer concentrations, DNA is in the semi-dilute regime with a low degree of entanglement [1]. Rheological data are discussed, supported by small-angle X-ray scattering (SAXS) and flow birefringence visualization experiments. From rheological measurements, it is demonstrated that at the higher polymer concentration, a plateau is obtained in the s representation as soon as long-range electrostatic interactions (water and 0.01 M NaCl) are effective. At those conditions, anisotropic supramolecular texture appears. For the first time, rheological behavior indicates the presence of an electrostatic network, especially in water at 10 mg/mL DNA concentration, where electrostatic repulsions are at their maximum [2]. In addition, for all studied samples, this rheological behavior is particularly original at low flow shear rate and low dynamic frequency applied. At high shear rates, all the solutions form a homogeneous nematic phase under flow.


14:40 - 15:20

Thursday 14:40 Emerald II

PS6

Role of electrostatic interactions on supramolecular organization in calf-thymus DNA solutions under flow

Lourdes Mónica Bravo Anaya, Denis C. Roux, Armando S. Soltero, Frédéric P. Pignon, Francisco C. Carvajal Ramos, Oonagh M. Mannix, and Marguerite R. Rinaudo

1Laboratoire Rhéologie et Procédés, Université Grenoble Alpes, Grenoble, France; 2Universidad de Guadalajara, Guadalajara, Mexico; 3European Synchrotron Radiation Facility, Grenoble, France; 4Biomaterials applications, Grenoble, France

DNA is a linear semi-rigid polyelectrolyte having a sequence that encodes the genetic information of all living organisms. The importance of the study of DNA dynamics, viscoelasticity and flow properties falls in the understanding of DNA functions, as well as cell division. Many important properties of DNA depend on polymer concentration, molar mass and stiffness and also on the external salt content. In aqueous solutions, electrostatic inter-chain and intra-chain interactions play an important role on DNA solutions behavior and have to be considered for the study of DNA interactions with other molecules. In this work, the rheological behavior of a high molecular weight DNA in aqueous solution is studied: i) at two polymer concentrations (4 and 10 mg/mL); ii) in water, and in the presence of two ionic concentrations (0.01 and 0.1M NaCl) to investigate the influence of ionic concentration on rheological behavior and on birefringence induced under flow. At the selected polymer concentrations, DNA is in the semi-dilute regime with a low degree of entanglement [1]. Rheological data are discussed, supported by small-angle X-ray scattering (SAXS) and flow birefringence visualization experiments. From rheological measurements, it is demonstrated that at the higher polymer concentration, a plateau is obtained in the s representation as soon as long-range electrostatic interactions (water and 0.01 M NaCl) are effective. At those conditions, anisotropic supramolecular texture appears. For the first time, rheological behavior indicates the presence of an electrostatic network, especially in water at 10 mg/mL DNA concentration, where electrostatic repulsions are at their maximum [2]. In addition, for all studied samples, this rheological behavior is particularly original at low flow shear rate and low dynamic frequency applied. At high shear rates, all the solutions form a homogeneous nematic phase under flow.


Thursday 15:00 Emerald II

PS7

Sol-Gel transitions of modified polysaccharides under temperature and salt control

Guylaine Ducouret, Hui Guo, Mickael De Magalhaes Goncalves, and Dominique Hourdet

1Soft Matter Sciences and Engineering, CNRS-ESPCI- PSL University, PARIS 75231, France; 2Soft Matter Sciences and Engineering, Sorbonne University, PARIS 75231, France

Alginates (ALG) are natural water-soluble linear polysaccharides, widely used as a biomaterial in the field of biomedicine due to their biocompatibility and biodegradability. Alginate are easily processable in three-dimensional materials such as hydrogels, capsules, sponges as well as fibers. Alginate-based biomaterials are particularly attractive for wound healing, drug delivery, cell carriers and tissue regeneration applications. Such biopolymers have still an important role to play due to their wide potentialities. We are currently developing a platform of responsive polysaccharides able to change their properties under controlled environmental conditions like salt, pH, temperature... Recently, we showed that alginates with high mannuronic content (high-M-ALG) exhibit a reversible sol/gel transition at low temperatures in presence of potassium salts [1]. The present study focuses on new thermo-associating copolymers designed by grafting the rich mannuronic alginate backbone (high-M-ALG), mentioned above, by a thermo-responsive poly(N-isopropylacrylamide) (PNIPAM). The gelling behavior of this specific copolymer can be selectively controlled by two opposite aggregation processes driven by the LCST of PNIPAM side chains above 32°C or the UCST of mannuronic sequences located in the backbone, ensuring cold gelling in the temperature range 0-10°C, depending on the ionnic environment [2].

2. H. Guo, M. de Magalhaes Goncalves, G. Ducouret, D. Hourdet, Biomacromolecules, 19, 576-587, 2018

Thursday 15:20 Emerald II

PS8

Synthesis and rheological properties of polysaccharide hydrogels with two types of “physical” cross-links

Andrey Shibaev, Maria Smirnova, Konstantin Pashkov, and Olga Philipova

Physics department, Moscow State University, Moscow 119991, Russia

Natural polymers like polysaccharides find vast applications as thickeners, e.g. in food industry, consumer goods, oil recovery etc. One of the new and promising applications of polysaccharide gels is the production of components for soft robotics. However, the mechanical properties of the gels are usually not sufficient in order to withstand strong mechanical deformations. In order to increase their mechanical strength, several types of cross-links can be simultaneously used, which act differently during deformation - weaker “reversible” cross-links break and recombine and dissipate energy, while stronger cross-links maintain elasticity of the gel. For polysaccharides, mostly multivalent ions are used as cross-linkers, but the recovery of such cross-links after breaking is usually poor. The aim of this work is to synthesize and investigate the rheological properties of polyacrylamide and alginate gels with two types of cross-links.
of polysaccharide gels with two types of "physical" cross-links: ionic and reversible covalent bonds. As a polysaccharide, carbohymethyl hydroxypropyl guar was used in this work. Carbohymethyl groups were cross-linked by metal ions, while hydroxypropyl moieties were cross-linked by borax. It was shown that one-phase homogeneous gels with both types of cross-links are formed at the total molar concentration of cross-linkers approximately below the total number of monomer units. The mechanical properties of the dual-cross-linked gels are enhanced as compared to similar gels with each type of cross-linker taken separately: the increase of the shear and tensile elastic moduli, and the increase of dissipated energy at low deformation frequencies, where the weaker borax cross-links reversibly break and recombine, is observed. The obtained gels show self-healing properties, as well as reversible change of mechanical properties upon the change of pH due to the "labile" character of cross-links.

Acknowledgement: the work was financially supported by the Russian Science Foundation (project 18-73-10162).

Thursday 15:40 Emerald II
Rheological characterization of the sol-gel transition kinetics of K-carrageenan hydrogels
Maria Rosaria Maddaluna, Veronica Vanzanella, and Nino Grizzuti
Chemical, Materials and Industrial Production Engineering, Università degli Studi di Napoli Federico II, Napoli, NA 80125, Italy

Hydrogels find today a very wide range of applications. By appropriately playing with the chemistry, the composition and the physico-chemical properties it is possible to obtain hydrogels with completely different characteristics. Hydrogels are employed in many different bio-medical applications. In particular, thanks to their biocompatibility and their ability to host bio-instructive cell systems, they are successfully used for the production of bio-scaffolds and bio-inks. Hydrogels are made up of low-concentration, aqueous three-dimensional networks. Elements of the network can be synthetic or natural polymers, bio-molecules such as proteins and lipids, colloids or surfactants. In this work we study the rheological behaviour of a model hydrogel made of K-carrageenan (KC) extracted from red algae. Linear viscoelastic rheology has been performed on solutions of KC of varying concentration. Oscillatory shear flow during temperature ramps is used to characterize the sol/gel transition at different temperature rates of change. Isothermal oscillatory time sweeps at decreasing temperatures starting from the sol state are used to determine the sol/gel transition kinetics and its temperature dependence. Finally, the frequency response at various temperatures under equilibrium conditions is employed to determine the critical gel condition and its quantitative parameters, namely, the gel strength and the critical exponents. The results show that, contrary to the existing literature, the critical gel state is reached at a relatively high temperatures, provided a sufficiently long time is allowed to reach an equilibrium state. The critical gel is characterized by a tenuous but persistent network. The effect of KC concentration on the sol/gel kinetics and on the critical gel properties is also presented and discussed.

Thursday 16:30 Emerald II
Morphological transitions of aqueous solutions containing Pluronics
Rossana Pasquino1, Hermes Droghetti2, Salvatore Costanzo1, Nino Grizzuti1, and Daniele Marchisio2
1Chemical Materials and Industrial Production Engineering, Università degli Studi di Napoli Federico II, Naples, Italy; 2Politecnico di Torino, Torino, Italy

Pluronics are a class of polymer-based systems built up by a sequence polyethylene oxide (PEO)-polypropylene oxide (PPO)-polyethylene oxide (PEO). They have the capability, due to the existence on the same molecule of hydrophilic and hydrophobic parts, to form micelles in aqueous solutions. Pluronics differ from micelles formed by typical small-molecule surfactants in that the water-loving and water-hating groups are polymer chains while in classical surfactants the head and tail groups are small ionic, non/ionic groups. Pluronics are also analogous to the triblock polymers, with the difference of restrained molecular weights if compared to the block size of typical triblocks. By varying the number of EO and PO monomers in the Pluronics structure, it is possible to obtain various types of Pluronics, named with different labels based on the length of the repeating units. In this work, we study the diversity of structures detected in aqueous solutions of Pluronic L64 and F68 at various concentrations and temperatures by experimental rheometry and dissipative particle dynamics (DPD) simulations. Mixtures of Pluronics in water (ranging from 0% to 90%wt) have been studied in both linear and non-linear regimes by oscillatory and steady shear flow at various temperatures. The measurements allowed for the determination of a complete rheological phase diagram for both systems. Linear and non-linear regimes have been compared to equilibrium and non-equilibrium DPD bulk simulations of similar systems obtained by using the software LAMMPS. The molecular results are capable of reproducing the equilibrium structures, which are in agreement with the ones predicted through experimental linear rheology. Simulations depict also micellar microstructures at long times when a strong flow is applied. These structures are directly compared, from a qualitative point of view, with the corresponding experimental results in non linear regime and differences between equilibrium and non-equilibrium phase diagrams are highlighted.

Thursday 16:50 Emerald II
Shear-induced gelation of chitosan hydrogels under non-isothermal and isothermal conditions
Anna Ryl, Piotr Owczarz, and Marek Dziubinski
Department of Chemical Engineering, Lodz University of Technology, Lodz, Poland

Recently, the growing interest in the use of chitosan hydrogels in regenerative medicine is observed. Despite many studies on its rheological properties and their sol-gel phase transition conditions, the influence of the homogeneous shearing field on the behavior of polysaccharide chains during injection has not been discussed so far. Disentangling and ordering the chains along the shear field may consequently affect the ability to form a highly cross-linked structure and the kinetics of this process. On the other hand, determining the effect of shear on gelation of colloidal...
chitosan solutions can provide valuable information on the still-discussed mechanism of the sol-gel phase transition. The influence of shear deformation on gelation ability and conditions of phase transition was determined by oscillatory and rotational tests using rotational rheometer with a cone-plate measuring system. The value of the shear rate, corresponding to the deformation in the oscillatory tests, was determined as an equivalent function of the angular frequency and amplitude strain used in the oscillatory measurements taking into account the geometry (diameter and angle) of the used cone. It was found that the type of mechanical deformation applied has a significant impact on the gelation ability of colloidal chitosan solutions and conditions of sol-gel phase transition. Results of the rotational measurements conducted under non-isothermal conditions show that the formation of the crosslinked structure occurs at lower temperatures compared to classically performed oscillatory tests. The studies conducted at the 37 °C indicate that unidirectional shear significantly increase the rate of phase transition. Simultaneously, it was found that although the increase in applied shear rate almost does not affect the initial values of dynamic viscosity, it significantly reduces its values for the cross-linked polymer structure.

Thursday 17:10   Emerald II   PS13
Rheology of Carbopol dispersions
Priscilla R. Vargas, Camila M. Costa, Bruno S. Fonseca, Mônica F. Naccache, and Paulo R. de Souza Mendes
Department of Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Rio de Janeiro 22451900, Brazil
Rheological properties of different formulations of Carbopol® NF 980 and Carbopol® Ultrez 10 NF polymer are investigated. This polymer is usually employed in experiments as a model yield stress fluid, mainly due to its transparency and non-toxicity. We analyze the influence of the solvent type on the dispersions, using water and water/glycerol as solvents. We also investigate the effect of some important parameters in the preparation procedure, such as the mixing time and rotation velocity. Transient and steady-state experiments were performed. Considering long mixing times, for both solvent types a clearly thixotropic behavior occurs slightly above the yield stress, where the avalanche effect is observed. For larger stresses, thixotropy is always negligible. Among other findings, it is observed that, for a given Carbopol concentration, the dispersion in the more viscous solvent possesses a lower yield stress and moduli, a larger power-law index, and a longer time to reach steady state. The dispersion stability was also evaluated, and it is observed that it strongly depends on the preparation procedure.

Symposium TM

Mechanics of Time-Dependent Materials
Organizers: Mehrdad Negahban, Hongbin Lu and Alberto D’Amore

Thursday 14:40   Europe III   TM6
Resolution of the local segmental mode in amorphous polymers: Do the chain relaxation modes affect the structural relaxation?
Luigi Grassia and Alberto D’Amore
Department of Engineering, University of Campania Luigi Vanvitelli, Aversa, CE 81031, Italy
The mechanical response of amorphous polymers is completely defined once the shear and bulk viscoelastic functions are known. However, while the shear response is easily measured, the bulk properties are hardly measured as witnessed by the scarce amount of date available in literature and require the use of non-standard equipment. The shear response is often reported in terms of recoverable creep compliance and the relative master curve can be easily constructed when the time-temperature superposition (TTS) principle holds true. Usually TTS is applicable for a large number of amorphous polymers but Plazek at first, and others, found out the breakdown of TTS in polystyrene (PS), poly(vinyl acetate) (PVAc) and polybutadienes showing that, even if the time-temperature superposition of viscoelastic data allows the construction of a shear creep compliance master curve for a given temperature range, the master curves referenced to different temperatures and obtained in different temperature intervals may differ. The temperature dependence of the master curve is the signature of the failure of the TTS. Theoretical considerations and experimental observations proved that different molecular mechanisms (i.e local segmental and chain modes) contributes to the glass-rubber softening dispersion in shear. The breakdown of the thermo-rheological simplicity is, then, caused by the different temperature dependence of the retardation times of each viscoelastic mechanism. We address this issue comparing the retardation spectra of each molecular mechanism that contributes to the shear response with the retardation spectrum of the volumetric bulk response. The mechanisms overlap somehow in shear, thus each of them should be isolated before to be compared with the volumetric bulk response. We set a procedure able to isolate each mechanism contributing to the recoverable shear compliance. The procedure requires the calculation of the shear retardation spectra from the creep compliance data and, then, the fit of the shear spectra assuming that the shear creep compliance is described by the additive model. It is shown that the volumetric bulk response covers timescales up to the classical shoulder of shear relaxation spectra and suggests that a small contribution to the volume relaxation comes from the short time chain modes.
Onset of mechanical nonlineairties for amorphous polymers in their glass transition regime: experimental results and model

Aude Belguise\textsuperscript{1}, François Lequeux\textsuperscript{1}, Helene Montes\textsuperscript{1}, and Sabine Cantournet\textsuperscript{2}
\textsuperscript{1}SIMM, ESPCI, Paris, IDF 75005, France; \textsuperscript{2}Centre des Matériaux, Mines ParisTech, Corbeil-Essones, IDF 91100, France

Amorphous polymer mechanics exhibits strong non-linearities below glass transition. We focus here on their apparition in the glass transition regime, while temperature is decreasing. We compare our experimental results with a simple model that accounts for dynamical heterogeneities and Eyring-like relaxation.

We describe the effect of dynamical heterogeneities on the linear mechanical response of polymers using a stochastic continuum mechanics model that includes a local heterogeneous dynamics. Calculations are performed using a Finite Element method. In the linear regime, it leads to a quantitative description of the relaxation modulus from the glassy to the rubber state measured on various polymer systems [1-2].

We have extended our model to describe the transition from the linear to the non-linear response of polymers in the glass transition regime. In this aim, we have assumed a local Eyring stress dependence of the local relaxation times. We derive the mechanical properties and the local mechanical fields at the beginning of the non-linear regime. We show that the stress field is not spatially correlated under and after loading and follows a Gaussian distribution. The time relaxation spectrum under stress appears to be not only shifted, but is also broadened.

We show that the time stress relaxation curves measured on many polymers stretched at a constant large strain in their glass transition can be quantitatively described by our numerical approach by adjusting only one parameter i.e. the critical stress involved in the local Eyring Law. Our model can also describe recovery which occurs after relaxation.


Asymptotic impact behavior of linear viscoelastic media

George A. Gazonas
US Army Research Laboratory, Aberdeen, MD, United States

We consider several one-dimensional impact problems involving finite or semi-infinite, linear elastic flyers that collide with and adhere to a finite stationary linear viscoelastic target backed by a semi-infinite linear elastic half-space [1]. The impact generates a shock wave in the target which undergoes multiple reflections from the target boundaries. Laplace transforms with respect to time, together with impact boundary conditions derived in our previous work [2], are used to derive explicit closed-form solutions for the stress and particle velocity in the Laplace transform domain at any point in the target. For several stress relaxation functions of the Wiechert type, a modified [3, 4] Dubner-Abate-Crump (DAC) algorithm is used to numerically invert the solutions to the time domain. These solutions compare well with numerical solutions obtained using both a finite-difference method and the commercial finite element code, COMSOL Multiphysics [5]. The Final Value theorem for Laplace transforms is used to derive new explicit analytical expressions for the long-time asymptotes of the stress and particle velocity in viscoelastic targets with non-zero long-term equilibrium moduli; asymptotic behavior in such targets depends only on the elastic properties of the flyer and half-space backing material. Alternatively, viscoelastic targets in which the long-term equilibrium modulus is zero, exhibit both target length and viscosity dependent asymptotic stress; the asymptotic particle velocity is also position dependent in such targets. The analytical asymptotic expressions are useful for verification of viscoelastic impact simulations taken to long observation times.


Modeling the irreversible time-dependent rheological behavior of complex materials

Flávio H. Marchesini
Department of Materials, Textiles and Chemical Engineering, Ghent University, Ghent 9000, Belgium

A number of relevant materials undergo irreversible processes of either a chemical or physical nature and present a complex transient rheological behavior, which cannot be properly described by existing constitutive models. Two important examples are cement slurries and waxy crude oils. Cement slurries undergo solidification as a result of hydration reactions, while waxy crude oils are subjected to irreversible shear degradation under flow at low temperatures. In this talk, a recently proposed time-dependent constitutive model, which takes into account elasticity, viscoplasticity, thixotropy, and irreversible effects, is discussed in detail. The model is based on a single scalar structure parameter and composed of one differential equation describing the evolution of the material's structure, one equation relating the shear rate to the shear stress, and one equation describing the progress of the irreversible process. The predictions of the model are compared to rheometric experiments performed with a cement slurry and a gelled waxy crude oil and the parameters of the model are estimated from experimental data. Interesting phenomena are
observed and described by the model, including bifurcation, shear banding, stress overshoots, effects of chemical reactions, and irreversible shear degradation. It is argued that the ideas employed in the present model can be used to incorporate irreversible effects into other thixotropic models, giving rise to the possibility of describing the transient rheological behavior of complex materials in an unprecedented fashion.

**Symposium MN**

**Micro, Nano Fluidics & Microrheology**

Organizers: Pouyan Boukany, Manlio Tassieri and Francisco J. Galindo-Rosales

**Thursday 14:40 Europe II**

**Structurization of suspensions of soft microcapsules in confined flow, an experimental study**

Mehdi Maleki, Kaili Xie, Marc Leonetti, Hugues Bodiguel, and de Loubens Clément

1Laboratoire de Rhéologie et Procédés, Université de Grenoble Alpes, Grenoble, isère 38000, France; 2AMU, M2P2, GIERES, France; 3CNRS, Lab. Rheologie et Procédes, GIERES, France; 4Univ. Grenoble Alpes., CNRS, LRP, Grenoble 38000, France; 5CNRS, lab. Rhéologie et Procédés, Univ. Grenoble Alpes, Grenoble, isère 38000, France

Controlling the flow of suspensions of deformable particles is of prime importance in numerous industrial or biological processes. From experiments on the blood, it is expected that such suspensions can present non-linear rheological properties and strong structuration phenomena in confined flows [1]. Such phenomena could be used to develop passive cells sorting processes or new thickeners for the food industry, for example. In this work, we used soft microcapsules, that are droplets protected by a nanometric elastic membrane, as a generic model of 'soft particles' to gain insights into their rheology and structuration in confined flow according to their mechanical properties and their volume fraction. The experimental challenge is to produce microcapsules suspensions with uniform and tunable size and mechanical properties. In this regard, we have optimized a membrane emulsification process to produce monodisperse polyelectrolytes microcapsules [2] at high throughput. In this way, suspensions of microcapsules with size variation of less than 15% were produced and the diameter was varied from 50 to 200 µm via the process. The surface elasticity of the microcapsules was also tuned on several orders of magnitude and characterized by stretching the microcapsules in an extensional flow [3]. Then, we have developed a methodology based on microscopic fluorescence imaging to quantify the local volume fraction of microcapsule in a confined Poiseuille flow. We show that microcapsules concentrate in the center of the channel leaving a depletion layer near the wall. This dynamics of phase separation and its quality depends strongly on two dimensionless numbers, the Capillary number (shear stress over surface elasticity) and the confinement ratio, as well as the capsule volume fraction.


**Thursday 15:00 Europe II**

**Microrheology with optical tweezers: Peaks & troughs**

Manlio Tassieri

University of Glasgow, Glasgow, United Kingdom

Since their first appearance in the '70s, Optical Tweezers have been successfully exploited for a variety of applications throughout the natural sciences, revolutionising the field of micro-sensing.

However, when adopted for microrheology studies, there exist some 'peaks & troughs' on their modus operandi and data analysis that I wish to address and possibly iron out, providing a guide to future rheological studies from a microscopic perspective.

**Thursday 15:20 Europe II**

**Topological glass in self-entangled ring polymers**

Beatrice W. Soh, Alexander R. Klotz, and Patrick S. Doyle

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

The dynamics of entangled linear polymers is well understood in terms of the tube model. A remaining challenge in polymer physics is to fully understand the dynamics of ring polymers, which have no chain ends and lie outside the framework of the tube model. The lattice-animals model has been proposed to describe the entanglement dynamics of ring polymers and can capture the power-law stress relaxation exhibited by ring polymers, but is unable to describe the slow relaxation modes observed in the terminal relaxation regime. Recently, there have been suggestions that inter-ring threadings have an important effect on slowing down ring polymer dynamics. The main challenge in studying concentrated ring polymer solutions and melts experimentally is that even a small fraction of linear contaminants can alter the dynamics significantly. By allowing for the visualization and manipulation of individual molecules, single molecule techniques are well suited for the investigation of ring polymer dynamics. In this work, we perform single-molecule DNA experiments to investigate the dynamics of self-entangled ring polymers. We use electric fields to induce self-entanglements in circular DNA molecules, which serve as a minimal system for studying chain entanglement. Our experimental results show that self-threadings give rise to entanglements in ring polymers and can slow down polymer dynamics significantly.
We find that strongly entangled circular molecules remain kinetically arrested in a compact state for very long times, thereby providing experimental evidence for a topological glass in ring polymers.

Thursday 15:40 Europe II  
**Effects of molecular weight on drag forces of polyethyleneglycol in a flow measured by a scanning probe microscope**

Ruri Hidema, Seika Hayashi, and Hiroshi Suzuki  
*Department of Chemical Science and Engineering, Kobe University, Kobe, Japan*

Addition of a little amount of polymers to water changes fluid properties drastically. Drag reduction, elastic instability, sudden increase of extensional viscosity of polymer solution are typical examples. In such complex phenomena, polymers may interact with each other in the flow, or polymers interact with the flow. Here we call these interactions polymer-polymer interaction or polymer-fluid interaction. Such interactions in micro scales should affect fluid characteristics in macro scales.

In order to detect polymer-polymer interaction or polymer-fluid interaction, we propose a method using a scanning probe microscope (SPM) to measure drag coefficients on surface-tethered polymers on a gold coated cantilever in a shear flow field. Methoxy polyethyleneglycol thiol that is a linear PEG with a free thiol group at one end (mPEG-SH) was tethered on a gold coated cantilever by covalent bonding. The cantilever was immersed in a flow cell that was settled on a SPM sample stage. Flow rates in the flow cell were controlled by two syringe pumps. Drag coefficients of a cantilever with surface-tethered polymers were measured in water, in glycerol solution and in polyethyleneglycol (PEG) solution. Drag coefficients of an original gold cantilever were also measured in the same glycerol or PEG solution. By comparing the drag coefficients of the cantilever with or without surface-tethered polymers in each flows, we detected drag coefficients of surface-tethered polymers. The drag coefficients of surface-tethered polymers were increased in the presence of polymers in the flow channel. Effects of molecular weight of tethered-mPEG-SH on the drag coefficient were also measured. We predicted tethered polymer conformation in the flow with a stem-flower model, and confirmed the drag force due to tethered polymers.

Thursday 16:30 Europe II  
**Confinement induced gelation of Pluronic F127 in nanoporous ultrahigh molecular weight polyethylene membrane**

Wadeelada Thitisomboon, Runlai Li, and Ping Gao  
*Department of Chemical and Biological Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong*

Dynamic rheological study is widely used to characterize micellization and gel transitions of hydrogel solutions of thermo-responsive amphiphilic triblock copolymer, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide). It is widely reported that the minimum critical micellization concentration (CMC) of PEO(50)-PPO(80)-PEO(50) (Pluronic F127) in aqueous medium is 15 wt% by dynamic rheology. Here, we demonstrate that the minimum CMC can be as low as 12 wt% when nanoconfinement effect is introduced. The nanoconfinement is achieved by pore coating of Pluronic F127 to the pores of thin nanoporous ultrahigh molecular weight polyethylene (UHMWPE) membrane and the treated film was then laminated to the top surface of parallel plate fixture of rheometer. Morphology visualization by environmental scanning electron microscope of the membrane shows that Pluronic polymer crystals were retained adjacent to nanoporous structure of the membrane observed as circular imprints on the membrane surface. Further characterization by contact angle measurement demonstrated that Pluronic was permanently confined in the nanopores of the membrane. Since the low concentration Pluronic F127 solution does not undergo micellization in the absence of the membrane it can be deduced that it was the membrane and its nanoconfinement effect of Pluronic that enhanced micellization of the low concentration Pluronic F127 solution during rheology measurement. Due to nanoconfinement effect, surface property of the membrane was altered significantly as evidenced by drastic decrease in water contact angle from 121° to 30°. To better elucidate the mechanisms of interactions observed during the rheology measurements, additional characterizations were performed on the treated nanoporous UHMWPE membrane. Understanding the interactions between nanoporous UHMWPE membrane and Pluronic F127 would allow designing of advanced biocompatible material extending its applications to biomedical field including wound healing and drug delivery.

Thursday 16:50 Europe II  
**A numerical investigation of the performance of the "Extensional Viscometer Rheometer On a Chip" (e-VROC)**

Konstantinos Zografos1, William Harter2, Mark W. Hamersky2, Manuel A. Alves3, Monica S. N. Oliveira4, and Rob J. Poole1  
1School of Engineering, University of Liverpool, Liverpool, England L69 3GH, United Kingdom; 2The Procter & Gamble Co., Cincinnati, OH 45217, United States; 3Departamento de Engenharia Quimica, Faculdade de Engenharia da Universidade do Porto, Porto 4200-465, Portugal; 4Department of Mechanical and Aerospace Engineering, University of Strathclyde, Glasgow G1 1XU, United Kingdom

Constriction flows are well known for their ability to stretch fluids in a strong extensional flow and have been proposed as potential extensional rheometers [1,2]. The high deformation rates and low inertial effects associated with the microscale version of such devices made them good candidates for rheological characterisation of low elasticity fluids under extension, which is particularly challenging using standard rheological devices. Here, the performance of the first commercially available "Extensional Viscometer-Rheometer-On-a-Chip" (e-VROC) [3] is investigated. This microfluidic chip, contains a hyperbolically-shaped contraction-expansion geometry, incorporating pressure-drop measurement.
capabilities. The flow kinematics within the device are examined by performing 3D numerical simulations for Newtonian and viscoelastic fluids, under creeping flow conditions, using an in-house solver [4]. To model the viscoelastic behaviour, the simplified Phan-Thien and Tanner model and the Finitely Extensible Nonlinear Elastic model that follows the Peterlin approximation are employed. Both models are used for assessing the performance of the device in terms of increasing Weissenberg numbers and for understanding the effects of the various model parameters on the flow field. Our results show that e-VROC™ is able to generate a region of strong extensional flow and can be used for indexing fluids of interest. However, since the actual size of this region is found to be small and the flow field is mainly shear-dominated, care should be taken in the interpretation of the results. Our calculations suggest that pressure-drop measurements obtained in this device may be related to elastic first normal-stress differences that are developed via a combination of shear and extension, rather than solely due to pure extension.


Thursday 17:10 Europe II
Microfluidic rectifier for viscoelastic polymer solutions flowing through porous media
Durgesh Kawale, Jishnu Jayaraman, and Pouyan E. Boukany
Chemical Engineering, Delft University of Technology, Delft, Zuid-Holland 2629 HZ, The Netherlands

Lab-on-a-chip devices are built by integrating various components to manipulate fluids in a desired sequence. A Microfluidic rectifier is a component that allow fluids to flow in a certain direction depending on the pressure difference between two points. The flow geometry within a rectifier device that enables flow control can be classified as active or passive depending on the presence or absence of mechanically moving components. In this talk, we present a fluidic rectifier geometry for polymer solutions flowing through a porous medium and perform flow visualization while simultaneously measuring the pressure drop. This porous medium consists of a periodic array of triangular pillars. As polymer solution flows through these anisotropically-oriented triangular pillars at high Weissenberg number, various types of stationary dead-zone and time-dependent dead-zone flow instabilities are formed. At the viscoelastic Mach number (Ma) of 1, the stationary flow instability is observed and at Ma > 1 the time-dependent flow instability is observed for both flow directions. The difference in pressure drop as flow direction reverses can be qualitative related to the size of the dead-zone instability.
Order-disorder structural transitions in mazes built by evaporating drops
Pascal B. Panizza, Hugo Algaba, Marie Postic, Guillaume Raffy, Laurent Courbin, and Franck Artzner
Matière Molle, IPR, Université Rennes 1, Rennes 35000, France
Evaporation is central to many industrial and natural processes. Understanding the evaporation of liquid dispersions in porous media is important for various disciplines, e.g., soil physics and civil engineering, and diverse processes such as the underground sequestration of CO2. The key issue in most cases is to comprehend the creation, locus and morphology of the solid deposits formed during drying. For instance, this topic is crucial in civil engineering as salt weathering can cause severe damage to the built environment and in material science as evaporation can help the design of novel smart material. Yet, the development of models for drying in porous media and the proper description of the formation of deposits in such media have remained elusive as these tasks are generally challenging. Here, we study the evaporation of surfactant solutions in porous media consisting of micron-sized cylindrical posts arranged on square or rectangular lattices. Our evaporation devices are transparent and quasi two-dimensional. These two essential attributes allow us to precisely determine how and where solid deposits form during drying. We show that the evaporation of surfactant solutions confined in quasi-2D porous media creates micron-sized labyrinthine patterns composing the walls of a centimeter-sized maze. These walls are made of solid deposits formed during drying via a sequence of individual Haines jumps, resulting from an hydrodynamic instability occurring at the pore scale. We rationalize this process driven by simple iterative rules with a cellular automaton that acts as a maze generator. This model well describes the formation dynamics and final structure of an experimental maze as functions of the wettability heterogeneities of a porous medium and its geometry. Also, our findings unveil the crucial role of two geometric dimensionless quantities that control the structural order of a maze [1].

Nonlinear electrophoresis in the salt-free limit
Yasuya Nakayama
Department of Chemical Engineering, Kyushu University, Fukuoka 819-0395, Japan
Macroions, such as colloidal particles and polyelectrolytes, in a solvent move in response to an externally applied electric field, which phenomenon is called electrophoresis. The linear response regime where the electrophoretic velocity is proportional to the small external field was mainly focused in past researches and largely elucidated. In contrast, a nonlinear increase in the electrophoretic velocity at high external fields was reported, but the underlying physics of the nonlinear electrophoresis is still unclear. The response of the electric double layer which is an inhomogeneous ion distribution formed around the electrified macroion is responsible for the electrophoresis. In previous works, the increase of the electrophoretic mobility was supposed to be originated from the stripping of the counterion from the electric double layer by the strong external field. Along this line, it was believed that the electrophoretic mobility saturates when the counterions are fully stripped from the electric double layer and the electrophoretic response is determined solely by the bare charge of the macroion. However, an experimental work for the nonlinear electrophoresis in the salt-free solution showed that the electrophoretic mobility increases and then saturates with the increase of the external field, but the effective charge of the colloid is much smaller the bare charge. This suggests that the counterion stripping is not sufficient to understand the nonlinear electrophoresis. We discuss the physical mechanism of the nonlinear response of the colloid electrophoresis in the salt-free limits by using the direct numerical simulation of the electrokinetic flow of a colloid.

Effect of the nanowire aspect ratio on rheological and electrical properties of PVA/silver nanowire/silica nanoparticle suspensions
Su Yeon Kim1, Seung Hak Lee2, and Kyu Hyun3
1School of Chemical and Biomolecular Engineering, Pusan National University, Busan, Republic of Korea; 2School of Chemical and Biomolecular Engineering, Pusan National University, Busan, Republic of Korea; 3School of Chemical and Biomolecular Engineering, Pusan National University, Busan, Republic of Korea
Conductive thin film which is composed of polymer matrix and metal nanowire has been on great attention these days for their high quality of electrical conductivities, flexibility and so on. In here, we used poly vinyl alcohol (PVA) for polymer matrix due to its low surface tension protecting colloid properties. And we used silver nanowires (AgNW) as inorganic filler. They have big aspect ratio with nanoscale diameter(\text{-}nm) and microscale length(\text{-}\mu m) for good electrical properties. To understand rheological properties of PVA/AgNW suspension by varying the content and aspect ratio of AgNW, suspension was characterized via dynamic oscillatory shear (SAOS) and large amplitude oscillatory shear (LAOS) tests. In addition, when the silica nanoparticles (SiNP) were added to system as additives, the value of both rheological and electrical percolation threshold was changed. Also, surface morphology of PVA/AgNW/SiNP films was measured by using FE-SEM for investigation of the effect of shear direction during coating process.
Tuesday 18:30 Mediterranea

**PO4 Viscoelastic migration of particles and cells in a strongly shear-thinning liquid flowing in a microchannel**

Francesco Del Giudice¹, Amy Q. Shen², Shivani Sathish², and Gaetano DAvino²

¹College of Engineering, Swansea University, Fabian way, United Kingdom; ²OIST, Okinawa, Japan; ³University of Naples Federico II, Naples, Italy

Controlling the fate of particles and cells in microfluidic devices is critical in many biomedical applications, such as particle and cell alignment and separation. Recently, viscoelastic polymer solutions have been successfully used to promote transversal migration of particles and cells toward fixed positions in straight microchannels. When inertia is negligible, numerical simulations have shown that strongly shear-thinning polymer solutions (fluids with a shear viscosity that decreases with increasing flow rates) promote transversal migration of particles and cells toward the corners or toward the centerline in a straight microchannel with a square cross section, as a function of particle size, cell deformability, and channel height. However, no experimental evidence of such shifting in the positions for particles or cells suspended in strongly shear-thinning liquids has been presented so far. In this work, we demonstrate that particle positions over the channel cross section can be shifted “from the edge to the center” in a strongly shear-thinning liquid. We investigate the viscoelasticity-induced migration of both rigid particles and living cells (Jurkat cells and NIH 3T3 fibroblasts) in an aqueous 0.8 wt % hyaluronic acid solution. The combined effect of fluid elasticity, shear-thinning, geometric confinement, and cell deformability on the distribution of the particle/cell positions over the channel cross section is presented and discussed. In the same shear-thinning liquid, separation of 10 and 20 µm particles is also achieved in a straight microchannel with an abrupt expansion. Our results envisage further applications in viscoelasticity-based microfluidics, such as deformability-based cell separation and viscoelastic spacing of particles/cells.

Tuesday 18:30 Mediterranea

**PO5 Rheology and tribology of nanocellulose dispersions**

Svetlana N. Gorbacheva, Anastasia Y. Yadykova, Sergei V. Antonov, and Sergey O. Ilyin

A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow 119991, Russia

Cellulose nanoparticles are a good thickener for various polar media. Thus, they can be used for producing biodegradable greases. However, nanocellulose particles are usually crystalline, which can result in high wear of friction surfaces. So, amorphous nanocellulose particles can be advantageous as thickeners for greases. However, in spite of the fact that there are many ways for producing microcrystalline, microfibrillar, and nanocrystalline celluloses, methods of obtaining amorphous cellulose particles are practically absent.

In this research we propose a new way to prepare amorphous cellulose from its complex solution in N-methylmorpholine N-oxide by precipitation with different non-solvents. As a result dispersions of nano- or micro-sized cellulose in water and different alcohols were prepared. These dispersions are viscoplastic media (gels), the elastic modulus and yield stress of which being depended of preparation prehistory and cellulose concentration.

The medium of dispersions can be replaced with esters for producing low-temperature biodegradable grease. These greases are viscoelastic gels providing reduction of friction and wear coefficients when used in friction joints.

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Tuesday 18:30 Mediterranea

**PO6 Rheology of aqueous dispersions of Laponite and TEMPO-oxidized nanofibrillated cellulose**

Urska Šebenik¹, Matjaz Krajnc¹, Mario Grassi², and Romano Lapasin²

¹Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia; ²Engineering and Architecture Department, University of Trieste, Trieste, Italy

Both laponite and TEMPO-oxidized nanofibrillated cellulose (TEMPO-NFC) can find several applications in various fields (from industrial to biomedical one) in virtue of their peculiar features and rheological properties displayed in aqueous phases. Structural states of laponite dispersions strongly depend on concentration and ionic strength. When attractive and repulsive interparticle interactions are so effective that they lead to generate arrested states (attractive gel or repulsive glass), the rheological behavior of the dispersion undergoes a sharp transition, from quasi-Newtonian to markedly shear thinning and viscoelastic. Aqueous suspensions of TEMPO-NFC show stable gel properties at low solids content, due to the hygroscopic character of the cellulose as well as the high aspect ratio and specific surface area of nanofibrils. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) mediated oxidation pretreatment, which converts the primary alcohol groups of the cellulose D-glucose units into carboxylate groups, provides the necessary electrostatic repulsion between the fibrils to prevent agglomeration. The present work is concerned with aqueous laponite-TEMPO NFC systems and is aimed at examining how much the content and proportion of both components affect the viscoelastic and flow properties of the mixed system at different times from sample preparation. The synergistic effects produced by blending are eventually compared with those observed for pure Laponite-soluble polymer systems.

Tuesday 18:30 Mediterranea

**PO7 Thermodynamics of dense suspensions**

Vladimir V. Shelukhin

Lavrentyev Institute of Hydrodynamics, Novosibirsk, Russia

Good mathematical models for two-phase granular fluid flows are of importance in prediction of nature phenomena (landslides, avalanches etc.) and in industrial processes (foodstuff transport, etc.). Starting from the basic thermodynamic principles, we develop a new mathematical model which governs dynamics of two-phase granular fluids with non-Newtonian rheology. The first phase is a Newtonian viscous fluid. To tackle the second phase as a granular fluid, we apply the notion of the Cosserat continuum, when each fluid point is treated as a rigid body.
Such an approach is known as a theory of micropolar fluids. To meet applications, we make generalizations by passing to a non-Newtonian Cosserat-Bingham fluid which is both a micro-polar medium and a visco-plastic material. On the one hand, such a fluid exhibits micro-rotational effects and micro-rotational inertia; the fluid can support the couple stress, the body couples and the non-symmetric stress tensor. On the other hand, the fluid stiffens if its local stresses and local couple stresses do not exceed some yield stress. In that view we prove that the Einstein formula for the viscosity of dilute suspensions is due to particle rotations. We discuss sedimentation and discover that the particle lateral migration occurs if concentration flux obeys a generalized Fick law without appealing for Magnus or Saffman forces. By addressing the flows in a Hele-Show cell, we predict slow suspension flows through a porous medium.

Tuesday 18:30 Mediterraneana

**Rheological characterization of injection grouts proportioned with glass microspheres and polypropylene fibers**

Luís G. Baltazar¹, Fernando Henriques¹, João Botas¹, and Maria Teresa Cidade²

¹Dept. Civil Engineering, NOVA University of Lisbon, Almada, Setubal 2829-516, Portugal; ²Departamento de Ciência dos Materiais and CENIMAT, Faculdade de Ciências e Tecnologia, Universidade Nova de Lis, Caparica, Portugal 2829-516, Portugal

Grouting is a consolidation method intended to improve strength in old stone masonry walls. It consists of the introduction of a binding agent, in a suspension form, to fill the internal cracks and voids of stone masonry walls. It will subsequently cure and set in a durable solid form, increasing the adhesion between the constitutive masonry elements. Consequently, it improves the masonry's load bearing capacity to vertical and to horizontal actions. The suspended particles in grout system have a significant influence on the penetration performance and rheology of the grout. Several researchers have investigated the fluidity and rheology of cementitious suspensions incorporating various additives and admixtures; however few researches have endorsed the potentialities of the combined effect of glass microspheres and polypropylene fibers in natural hydraulic lime-based grouts. The present paper concerns the measurement of some relevant rheological properties for the purpose of grouting of stone masonry walls and how these properties are influenced by different dosages of glass microspheres and polypropylene fibers. The findings showed that the yield stress of all mixtures increased as the fiber volume fraction was increased in the mixture. On the other hand, the plastic viscosity strongly depended on the composition of the mixtures and dropped with increasing glass microsphere dosage. The mixtures containing fibers showed that the fiber volume fraction has higher influence on rheological parameters. Moreover, addition of fibers alone may have adverse effects on fresh properties of grout, but significantly improves the grout's durability (resistance to cracking for instance), thus it is recommended that the use of fiber will always be accompanied by the incorporation of superplasticizer.

Tuesday 18:30 Mediterraneana

**Manufacture and rheological characterization of ethylcellulose based thermochromic microspheres**

Isaac Y. Miranda, Martín E. Reyes-Melo, Carlos A. Camarillo, and Beatriz C. López-Walle
Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, Monterrey, Nuevo León 64455, Mexico

Formation of polymeric microspheres (PMS) for dispersion and protection of active materials is a technique used mainly in the food and pharmaceutical industries. The application of PMS depends on the polymeric matrix from which microspheres are made. Natural polymers, such as ethylcellulose (EC), can be dissolved in a variety of solvents; they were found to provide the opportunity of manufacturing PMS with biocompatibility, controlled size, and chemical resistance through the emulsion solvent process. The chemical resistance offered by these polymers is key to protect thermochromic materials (TCM) from degradation due to environmental conditions. By incorporating a TCM with a unique thermochromic transition temperature (TTT) in PMS, it is possible to obtain thermochromic microspheres (TMS) that can be incorporated in every day products such as insulators and clothing. The research conducted that TMS with color transition between red and dark navy blue, can be dispersed in various solvents and have obtained thermochromic transition temperature (TTT) in the range of 30°C to 40°C. The physical and chemical properties of TMS were investigated by using instruments such as scanning electron microscopy (SEM), thermo-stimulated direct currents (TSDC), dynamic mechanical analysis (DMA) to confirm the successful incorporation of TCM with color transition temperatures (TTT) in the range of 30°C to 40°C.

Tuesday 18:30 Mediterraneana

**Self-diffusiophoresis in viscoelastic fluids**

Shabab Saad and Giovanniantonio Natale
University of Calgary, Calgary, Alberta T2N1N4, Canada

Self-propelling active colloids provide insights in the behavior of non-equilibrium systems by producing enhanced diffusive motion within fluid media. Our model system consists of synthetic Janus (PtSi) microspheres undergoing self-diffusiophoresis (via a local concentration gradient) in presence of H2O2. In this study, we aim to address for the first time what is the single-particle dynamics of these Janus particles in viscoelastic fluid. Experimentally, Janus particles were dispersed in a dilute polyvinylpyrrolidone (PVP) water solution and in a poly acrylamide (PAM) water solution in semi-dilute and semi-dilute entangled regime. The two systems were chosen to probe different relaxation times from relatively short (~ 3 ms) for PVP to large (~ 30 ms) for PAM. Within this regime, we attempt to investigate the coupling between the solute concentration field and the phoretic particle's motility (mean square displacement, velocity and diffusivity analyzed via multiple particle tracking) because of the viscoelasticity of the medium. These findings are the foundations to understand collective motion of ACs in complex media and to study the interplay between particle organization and fuel concentration in the limit of low Péclet number.

Poster Session

**Rheological characterization of injection grouts proportioned with glass microspheres and polypropylene fibers**

**Manufacture and rheological characterization of ethylcellulose based thermochromic microspheres**

**Self-diffusiophoresis in viscoelastic fluids**
Viscoelastic properties of kudzu starch-galactomannan pastes
Bertrand Jozwiak, Marek Dzubiński, and Magdalena Orczykowska
Department of Chemical Engineering, Lodz University of Technology, Lodz, Poland

Kudzu is a popular Asian plant widely used in traditional Chinese medicine. Starch extracted from kudzu is unique because of a content of bioactive daidzein. As a result, kudzu starch is an effective remedy for: flu, fever, migraine, diseases of upper respiratory tract, problems with stomach-intestinal ailments, and addictions to alcohol or nicotine. Viscoelastic properties of kudzu starch can be modified using galactomannans (hydrocolloid polysaccharides derived from leguminous seeds) as additives. Among them 4 main compounds can be distinguished, depending on the galactose-to-mannose ratio (so-called substitution degree) in the molecule: fenugreek gum, guar gum, tara gum, and locust bean gum.

The aim of the study was a comprehensive description of the impact of 4 basic galactomannans on viscoelastic properties of kudzu starch pastes. Kudzu starch suspensions (3% w/v) with various galactomannan additives (0.05–0.3% w/v) were pasted at 95°C for 30 min. The obtained pastes were subjected to oscillatory tests within the range of linear viscoelasticity, using rotary rheometer Physica MCR 301 (Anton Paar, Austria) with plate-plate system. The experimental data in the form of storage G’ and loss moduli G” were described by the proposed generalized fractional Kelvin-Voigt model with two springpots connected in parallel, created on the basis of differential calculus of fractional order. Fourier transform, and Rayleigh method of dimensional analysis. Calculated parameters of the model provided a comprehensive description of viscoelastic properties of kudzu starch-galactomannan mixtures. It is particularly important for materials engineers. Conducted basic research may provide a starting point for applied research in food, pharmaceutical and cosmetics industries. Its use in economic practice may concern mainly people suffering from: celiac disease, lactose intolerance and alcohol or nicotine addiction.

Electrorheological behaviour of a starch-oil system
Carlos Alberto Gracia Fernández1, López Beceiro Jorge2, Artiaga Díaz Ramón2, Álvarez García Ana2, and Gómez Barreiro Silvia3
1TA Instruments, Madrid, Madrid 28049, Spain; 2Department of Naval and Industrial Engineering, Higher Polytechnic University College, Universidade da Coruña, A Coruña, A Coruña 15010, Spain; 3CESUGA, A Coruña, A Coruña 15190, Spain

A simple system consisting of a suspension of 10 wt % of starch in silicone oil was subjected to electrorheological testing. The system exhibits a complex behaviour depending on the electrical field. On one hand, the application of an external electric field induced the formation of a linear structure, aligned with the electric field. The formation of that structure was studied by several rheological methods. The rate of modifying the electric field intensity resulted to be related to the electric field value at which percolation is observed. On the other hand, master curves for the structure formation and breakdown in squeeze experiments were obtained.

Effect of welan gum on the rheological behaviour of aqueous sepiolite gels
José A. Carmona1, Pablo Ramírez1, Rafa del Valle-Pinto1, and José Muñoz2
1Ingeniería Química, Universidad de Sevilla, Sevilla, Sevilla 41012, Spain; 2Departamento de Ingeniería Química. Facultad de Química, Universidad de Sevilla, Sevilla, Spain

Rheological measurements and cryo-scanning electron microscopy (Cryo-SEM) were used to study the influence of welan gum concentration (0.1, 0.3 and 0.5% (m/m)) on aqueous sepiolite suspension (3% m/m). Welan gum/sepiolite systems can find interesting applications as new stabilisers of aqueous based dispersions for agricultural pesticide and fertilizer formulations and for building materials. Steady shear flow curves were obtained by a stepwise protocol and the viscoelastic properties were determined by oscillatory shear and creep-recovery tests. Sepiolite aqueous suspensions exhibited marked very shear thinning flow behaviour with an apparent yield stress, whereas welan gum solutions showed shear thinning behaviour. The incorporation of welan gum yielded a decrease in zero shear viscosity and a change of flow behaviour if compared to sepiolite gel. As a consequence of the addition of welan gum, sepiolite/welan systems presented a less sharp drop of viscosity with shear stress. All the sepiolite/welan systems studied exhibited weak gel viscoelastic behaviour with G’ and G” values increasing with welan gum concentration. From creep-recovery tests an increase in the Jmax (maximum compliance of creep step) and Je0 (steady state compliance) with the gum concentration was observed. The Cryo-SEM images showed a more compact microstructure, where welan gum fill the holes observed for the sepiolite gels studied.

Evaluation of fresh state parameters of Portland cement suspensions using different rheological models
Roberto Cesar de O. Romano, José Augusto F. S. Mesquita, Marcel H. Maciel, and Rafael G. Pileggi
Civil Construction Engineering, University of São Paulo, São Paulo, Brazil

The use of supplementary cementitious materials (SCM) is growing up in the recent years in the civil construction sector, either partially added to Portland cement during the production of different kind of binders or separately to the mortars/concretes in the mixing process. However, due to the wide range of materials with potential use as SCM, it is necessary a preliminary study for its application, because each mineral addition presents a distinct interaction with the cementitious material, as consequence of its different physical, chemical and mineralogical properties. Although the fresh state properties this kind of materials to be poorly investigated, it is known that have great influence on the performance of the final products. The studied rheological parameters vary according to the interaction between the particles, and can to be described by some rheological models, which the most common Herschel-Bulkley, Power law, Casson, Bingham. However, in many cases, the applied models did not illustrate the real data obtained and they are not suitable for the reality of many applications. In this
work, the impact of use SCM in partial substitution of Portland cement was evaluated using rotational rheometry, in order to obtain the rheological behavior, thixotropy profile, yield stress and viscosity. The results obtained were fitted by different rheological models and it was possible to conclude that: i. these kinds of single models did not correctly represent the rheological profile and parameters of suspensions, mainly in the extremes shear rates, and ii. the adequate choice of rheological model was dependent on the kind of SCM. In addition, the prediction of yield stress and viscosity was made using the concepts of modified Yodel and Natural Interference models, respectively, illustrating a good correlation between the real and modeled data.

Tuesday 18:30 Mediterranean

The fracture of yield stress fluid jet in a viscous liquid

Diana Broboana1, Eugen Chiriac2, and Corneliu Balan1

1Hydraulics, REOROM, University Politehnica of Bucharest, Bucharest, Romania; 2National Institute Microtechnologies, Bucharest, Romania

The paper is concerned with the experimental investigations and numerical modeling of the dynamics of a yield stress fluid jet in an immersed fluid. A cream jet is generated through a nozzle in a bath filled with a Newtonian pure viscous liquid by a syringe pump. The pressure is measured up-stream the exit of the cream from the nozzle. The goal of the study is to establish the location of the jet fracture, as function of the imposed flow rate. The dynamics of the up-stream pressure during the fracture is recorded. The process is also simulated in a 3D configuration, the used rheological model being a Carreau relation with non-monotonic steady flow curve. The visualization of the jet flow is performed with a high speed camera and the experimental fracture length is compared with the numerical simulations.

Tuesday 18:30 Mediterranean

Onset of flow in a vibrated thin viscoplastic layer: The Faraday problem

Jan A. Frigaard1 and Cherif Nouar2

1University of British Columbia, Vancouver, British Columbia V6T1Z4, Canada; 2LEMTA, CNRS & Universite de Lorraine,, Nancy, France

The onset of flow in vibrated layer of viscoplastic fluid is investigated theoretically, using a lubrication approximation. The rheological behavior of the fluid is described by the Herschel-Bulkley model. The equation describing the evolution of the free surface is derived. Four different regimes are found depending on the ratio of the gravitational acceleration to the acceleration of vibration and the ratio of the yield stress to the shear-stress at the vibrated wall. Furthermore, a necessary condition for instability is derived. The different regimes are illustrated in the case of a 1D problem. We then discuss some of the limitations of our work, in treating the fluid layer as a simple yield stress fluid and how these might be overcome with different treatments of the sub-yield behaviour and what the consequences might be.

Tuesday 18:30 Mediterranean

A new approach for simulation viscoelastic flows at high Weissenberg number

Sajjad Pashazadeh and Azadeh Jafari

School of Mechanical Engineering, College of Engineering, University of Tehran, Tehran, Iran

The challenge for computational rheologists is to develop efficient and stable numerical schemes in order to obtain accurate numerical solutions for the governing equations at values of practical interest of the Weissenberg numbers. It is well known that the conformation tensor should, in principle, remain symmetric positive definite (SPD) as it evolves in time. In fact, this property is crucial for the well-posedness of its evolution equation. In practice this property is violated in many numerical simulations. Most likely, this is caused by the accumulation of spatial discretization errors that arises from numerical integration of the governing equations. This gives rise to spurious negative eigenvalues, causing the conformation tensor to lose its SPD property and Hadamard instabilities to grow. This was an obstacle to early attempts to numerically simulate viscoelastic fluids. In this study, we address the outstanding problem affecting the numerical simulation of viscoelastic flows at a critical value of the Weissenberg number beyond which no numerical solution can be obtained. This study presents a new approach so-called hyperbolic tangent to preserve both symmetric positive definite of the conformation tensors and also bound the magnitude of eigenvalues [1]. The aim of this study is the development of a mathematical model to preserve both the SPD of the conformation tensor and also to bound the magnitude of the eigenvalues. The hyperbolic tangent formulation of the constitutive equation removes some of the stiffness associated with the standard form of the constitutive equation. We demonstrate that this has the effect of increasing the critical Weissenberg number, thereby delaying the so-called high Weissenberg number problem. The flow of FENE-P fluid through a 2D channel and 3D pipe is selected as a test problem. Discrete solutions are obtained by spectral/hp element methods.

[1] Jafari et al., Theoretical and Computational Fluid Dynamics, 32,6, 789-803

Tuesday 18:30 Mediterranean

Cylinder rotation in a power-law fluid in a long channel

Pooja Thakur, Naveen Tiwari, and Rajendra P. Chhabra

Department of Chemical Engineering, Indian Institute of Technology, Kanpur, Kanpur, Uttar Pradesh 208016, India

Flow of non-Newtonian fluids across a rotating cylinder has many applications such as calendering process in paper making and polymer processing in chemical industries etc. Inevitably in these applications the flow becomes asymmetric due to the rotation of the cylinder. The confinement of the cylinder and its location inside the channel present important parameters to affect the flow. In this work, the momentum and heat transfer from an isothermal, rotating cylinder immersed in a power-law fluid, confined symmetrically and asymmetrically between two parallel walls are considered. The governing equations are solved numerically for a two dimensional, steady and incompressible flow of a power-law fluid in the laminar flow region. The values for the rotational Reynolds number (10-3= Re = 40), Prandtl number (1 = Pr = 100), power-law index (0.02 = n = 1), blockage ratio (10-3 = b = 0.9999) and asymmetry ratio (10-4 = ? = 1) have been chosen to elucidate the role
of these parameters on the momentum and heat transfer characteristics. The flow field is visualized by plotting the streamlines. Further the hydrodynamic forces and torque acting on the rotating cylinder are computed. The results are supplemented by a lubrication approximation analysis relevant to the large values of \( \delta \) i.e., highly confined cylinder. In this case, the asymptotic scaling of the torque for a Newtonian fluid is given by \( -1/2 \) where \( \epsilon = (1-\delta)/\delta \), which also represents the cylinder confinement. In heat transfer, apart from the Reynolds number and Prandtl number, the rate of heat transfer can also be augmented up to 30 % by the increase in the confinement and the degree of asymmetry (low values of \( \beta \)). While the shear-thinning behaviour decreases the rate of heat transfer above the corresponding value in Newtonian fluids, the exact dependence of these parameters on the rate of heat transfer are consolidated by fitting them in the form of a predictive correlation for the average Nusselt number.

**Tuesday 18:30 Mediterranea**

**Instability of Saffman-Taylor for yield stress fluids in Hele Shaw cell**

Fadoul Oumar Abdoulaye and Philippe Coussot

*Laboratoire Navier, Université Paris-Est, Champs-sur-Marne 77420, France*

Our interest is in the instability of Saffman-Taylor for yield stress fluids in porous medium. One studies here the possible viscous digitation of circular samples moved radially in a Hele Shaw cell (which consists of two plexiglass plates whose spacing between the two is weak in front of other dimensions). This flow is the analogue (two-dimensional) of a flow in a porous medium (Saffman and Taylor, 1958; Homsy, 1987). For a Newtonian fluid one knows that the instability occurs beyond some velocity of the interface. Below this speed the interface remains circular. As expected, by injecting air at controlled flow rate in the center of the cell initially filled with a yield stress fluids, the air-liquid interface moves towards outside. Two modes of flow are however then observed: beyond a critical velocity the air penetrates in the form of fingers through the material; the fluid leaves traces on the walls, indicating that in these zones it is sheared; this first mode resembles the instability of Saffman-Taylor for yield stress fluids (cf Coussot JFM 1999). Below this critical velocity the air region grows bigger regularly but the interface is still unstable, deformations resembling fractures are observed at various points of the interface. Moreover in this second mode the fluid does not leave tracks on the walls, indicating that it slips, except around the points of fracture. This new phenomenon resembles a phenomenon of fracture in a solid material (cf. e.g. Griffiths analysis). In fact this mode is particular: taking into account the slip to the walls one should obtain an elongation 2D material; the fact that we systematically get such fractures, whatever the speed, suggests that the elongation 2D of a yield stress fluids is unstable.

Keywords: yield stress fluids; Viscous digitation; Cell Hele Shaw

Références,

**Tuesday 18:30 Mediterranea**

**Reasons of missing high harmonics in LOAS of particle-filled elastomers**

Xiaorong Wang

*School of Chemical Science and Engineering, Tongji University, Shanghai, China*

A very unusual aspect of the viscoelastic nonlinearity of filled rubbers compared with other types of viscoelastic nonlinearities is that despite the reduction of modulus as the strain is increased, the response of a filled rubber to the forced oscillatory shear is still sinusoidal and essentially absent of any higher harmonics. This "linear-nonlinear dichotomy" feature ensures that the standard deconvolution of experimental torque and phase offset in terms of the \( G' \) and \( G'' \) will be still appropriate. Despite the technological significance, the cause for this peculiar "dichotomy" behavior of filled rubbers has been a long-term puzzle. Recently, it is determined that particle-filled polymer melts of widely varied molecular weights exhibit a rheological transition as the molecular weight of the matrix, \( M_n \) approaches and passes through a characteristic molecular weight \( M_c^* \). Below \( M_c^* \), the system shows typically the classic nonlinearity, where the storage modulus \( G' \) decreases as the strain amplitude increases and the resulting stress waveforms are distorted from sinusoidal waves. Above \( M_c^* \), the system displays an anomalous nonlinearity, where the stress responses at any given strain amplitude remain surprisingly sinusoidal regardless the drop of modulus \( G' \). The critical point \( M_c^* \) is found to be a few times of the entanglement molecular weight \( M_e \). The degree of entanglements in polymer chains seems to play a key role in the linear-nonlinear dichotomy rheology. Further study indicates that the time scale for topological rearrangements of entangled polymer chains that affect particle motion in the matrix is the crucial factor, and this depends on polymer molecular weight, concentration and temperature. Because of missing high harmonics, the measured dynamical properties of filled rubbers can be separated into a linear viscoelastic frequency-dependent part and a nonlinear strain-dependent part. Such a separability principle has a wide range of validity in industrial applications.

**Tuesday 18:30 Mediterranea**

**Dependence of waxy oil flow curve not only on shear rate but also on shear history**

Amanda Legnani1, Taian G. Santos1, Diogo V. Andrade2, and Cezar O. Negriao1

1CERNN, Federal University of Technology- Parana, Curitiba, PR 81280340, Brazil; 2Laboratoire Navier, IFSTTAR, Université Paris-Est, Champ-sur-Marne, Ile-de-France 77420, France

Waxy crude oil is a complex mixture of hydrocarbons that includes paraffins, aromatics, naphthenes, asphaltenes and resins. During production, the oil at high temperature in the reservoir loses heat to the surrounding and the paraffins crystalize within the oil matrix. These solid crystals suspended in the material provide a non-Newtonian behaviour to the fluid that depends on several parameters. Recent papers have showed, for instance, that the equilibrium flow curve of a gelled oil is not only a function of the thermal and shear histories but also on
the highest shear rate imposed to the sample [1, 2]. In the current work, the effect of the shear history in the flow curve of a model waxy oil is revisited by carrying out controlled shear rate experiments in a rotational rheometer. In order to impose the same thermal history, the following pre-tests were always performed: the oil was inserted in the rheometer at high temperature, cooled down statically to the test temperature and then aged for one hour. The experiments themselves consisted of imposing different shear rate plateaus to the material during different times. Differently from prior works, it was observed that the final equilibrium depends on a combination of the shear rate and on the time this shear rate is imposed - the higher the shear rate the faster the structural equilibrium is reached. By analysing the results as a function of the total strain, one can then conclude that equilibrium depends not only on the shear rate but also on the total shear strain.


Tuesday 18:30 Mediterranea

PO23
Model comb polystyrenes: from synthesis to rheology and correlated foaming properties
Lorenz Faust, Mahdi Abbasi, and Manfred Wilhelm
Karlsruhe Institute of Technology, Karlsruhe 76131, Germany

The rheology of branched polymer melts is of special interest to academia and industry. Especially in foaming process, the strain hardening and dynamic dilution effects of the branches have a distinct influence on the foaming behavior and final properties of the product. Investigating the rheological and foaming properties and correlating it to molecular topological parameters like the degree of branching requires controlled synthesized and well characterized polymers with model structure. A series of comb-PS from loosely grafted to bottlebrush-like structures were synthesized by the combination of anionic polymerization and grafting-onto method. These well-characterized comb PS had the same backbone, similar branch length but different branching density. Shear rheological and extensional properties of these combs were investigated and correlated with the molecular structure. Additionally, the samples were foamed using a batch foaming setup with supercritical CO2 as the blowing agent. Shear and extensional rheological data in the framework of the zero shear viscosity (ZSV) and strain hardening factor (SHF) as a function of number of side chains was used to define a rheological fingerprint and correlate them to foam characteristics of well-defined model polymers. This research revealed that all comb-PS with the same length of sidechains had similar cell density and cell size. However, there was an optimum number of branches per backbone resulted in a maximum volume expansion ratio (VER) at minimum zero shear viscosity with a maximum SHF > 200 for Hencky strains below 4. Such a high strain hardening shows of great fundamental and technical importance in extensional processes and could be directly correlated to the foaming results. This allows a better understanding of the important parameters of molecular dynamics during the foaming process and synthetic optimization of the topological structure towards microporous foams.

Abbasi, M.; Faust, L; Riazi, K. & Wilhelm, M. Macromolecules, 2017, 50, 5964

Tuesday 18:30 Mediterranea

PO24
Slip-link simulations of entangled linear polymer melts under fast flows: effect of the stretch/orientation-induced reduction of friction
Takeshi Satô and Takashi Taniguchi
Department of Chemical Engineering, Kyoto University, Kyoto, Japan

Macroscopic flows of entangled polymer melts are tightly related to the microscopic polymer chain dynamics. From a simulation perspective, although a Molecular Dynamics (MD) simulation is a straightforward method to understand the relationship between rheological properties and microscopic structure of polymer chains, it is difficult to perform a MD simulation of a highly entangled polymer melt until its terminal relaxation time due to the high computational cost. One possible method to tackle this problem could be obtained with a MultiScale Simulation (MSS) method, where a microscopic coarse-grained model is combined with a macroscopic continuum model. To develop the MSS method that can address polymer processing conditions, we need to construct a microscopic model that can properly predict rheological properties under fast flows. In this study, we focus on the slip-link (SL) model developed by Doi and Takimoto [Doi et al., 2003] (DT model). The DT model can successfully predict non-linear rheological properties for a moderate strain rate region where polymer chains are oriented without significant stretching. However, the rheological properties obtained by the DT model for fast flows with chain stretch deviate from experimental data especially of steady-state entanglement viscosities. Yaota et al. have introduced the concept of the stretch/orientation-induced reduction of molecular friction (SORF) to their SL model and found that SORF can improve the predictions of rheological properties under fast uniaxial entanglemental flows [Yaota et al., 2012]. In this study, we have investigated the effect of SORF on the DT model. As a result, we have found that SORF can improve the rheological properties obtained from the DT model especially under uniaxial entanglemental flows. This result will help us to develop the MSS method for fast entangled polymer melt flows.

This work was supported by JSPS KAKENHI Grant No. 1810643.

Tuesday 18:30 Mediterranea

PO25
Keratin and coconut fibres from mexican industrial wastes as flame retardant agents on thermoplastic starch biocomposites
Guadalupe Sanchez-Olivares1, Sebastian Rabe2, Ricardo Pérez1, and Bernhard Schartel1
1Materials research, CIATEC, A. C., León, Guanajuato 37545, Mexico; 2Technical Properties of Polymeric Materials, Bundesanstalt für Materialforschung und -prüfung, Berlin, Berlin 12205, Germany

Natural fibres have been thoroughly investigated in polymer composites science since many years ago. However, in the last years the researches have been focus on new applications, such as flame retardant materials. In this work keratin and coconut fibres, recovered from Mexican industries wastes were investigated as multifunctional agents: mechanical reinforcement and flame retardants. A specific treatment was applied to fibres in order to obtain biopolymer composites base on biodegradable thermoplastic starch (TPS). Biocomposites were
compounded by extrusion process. The effect of keratin and coconut fibre content and the joint action of fibres in combination with ammonium polyphosphate (APP) as fire retardant additive for TPS was studied by thermogravimetric, flame retardant, forced flaming combustion, mechanical and rheological analysis. It was found that when keratin or coconut fibres are added in combination with APP to TPS, a synergistic effect leads to replace part of APP using 20% of keratin or coconut fibers. Keratin fibres and APP showed the same flame retardant properties. Coconut fibres and APP exhibited lower heat release rate than only APP at high content (20%). According to rheological measurements, flow behavior depends on the composition of biocomposites, complex viscosity increases when keratin fibres are added in combination with APP with respect to biocomposites using high fibre content. Nevertheless, the combination of coconut fibres with APP showed a decrease on complex viscosity favoring the processing of these materials. This finding represents a promising alternative to produce ecological flame retardants and to reduce high waste from the Mexican industry. This work has a great value on technological develop of the Mexican plastic industry due to several flame retardant plastic materials are imported, they are not produced in Mexico. Rheological results contribute to set processing parameters in the plastic industry.

Tuesday 18:30 Mediterranea

PO26

Role of viscosity during radical polymerization process

Vera Penkavova, Petr Stavarek, Anna Spalova, and Petr Kluson

Institute of Chemical Process Fundamentals of the CAS, v.v.i, Prague, Czech Republic

Polymerization is a widely utilized process for production of most of commercial coatings or paintings. The specifics of this chemical reaction is the significant viscosity increase by few orders of magnitude depending on the monomer conversion degree. The viscosity increase might cause a problem in a batch reactor since the higher input power is necessary to maintain the proper mixing intensity. The sufficient reaction heat removal is also important because the reaction is highly exothermic. Nevertheless, the elevated temperature is beneficial for the reaction rate as well as for the viscosity decrease of reaction mixture, so the selection of optimal reaction conditions should take into the account both of these aspects. This contribution therefore deals with determination of viscosity of reaction mixture during polymerization reaction at different monomer conversion degrees. Rheopexy behavior is estimated on basis of polymerization kinetic measurements in the batch reactor.

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Tuesday 18:30 Mediterranea

PO27

Rheological and electrical properties of polystyrene nanocomposites incorporated with polymer-coated CNTs

Sung Ho Choi, Song Hee Lee, Tae Gon Kim, and Seong Jae Lee

Department of Polymer Engineering, The University of Suwon, Hwaseong, Gyeonggi 18323, Republic of Korea

Due to their outstanding electrical properties and thermal stability, carbon nanotubes (CNTs) are used as conducting nanofillers to enhance the electrical performance of polymers. However, it is very difficult to disperse CNTs in a polymer matrix due to large van der Waals forces between them. Here, we prepared electrically conductive polystyrene (PS) nanocomposites by incorporating non-covalently surface-modified carbon nanotubes (CNTs) with hydrophilic polymers such as polydopamine (PDA) and poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS). In addition, ethylene glycol (EG) was introduced as a second dopant to further improve electrical properties. All the conductive polymer nanocomposites were prepared through latex technology. The morphology, rheological and electrical properties of the nanocomposites were investigated. Rheological properties of all the nanocomposites were substantially increased with small addition of the CNTs. The electrical conductivity of the nanocomposite with PEDOT:PSS-wrapped CNTs was higher than that of the nanocomposite with PDA-coated CNTs because the conductive polymer PEDOT:PSS helped to form the electrical network. Furthermore, the secondary doping of PEDOT:PSS with EG resulted in a higher PEDOT-to-PSS ratio and a structural change in PEDOT, which contributed to the formation of electrical pathways, increasing the electrical conductivity.

Tuesday 18:30 Mediterranea

PO28

Effect of different polyols as plasticizers in soy-protein based bioplastics

Jose M. Aguilar, Eva Perez-Dorado, Carlos Bengoechea, and Antonio Guerrero

Department of Chemical Engineering, Universidad de Sevilla, Sevilla, Spain

Bioplastics are ecofriendly polymeric materials able to potentially replace conventional plastics, thus contributing to reduce the associated environmental pollution which has a relevant societal impact. The selection of the plasticizer is essential in the formulation of plastic materials to achieve adequate physical and thermomechanical properties depending on the application. Polyols have been extensively used as plasticizers in many bioplastics, specially glycerol (GLY). The objective of this contribution was to assess the influence of the plasticizer on the physical and mechanical properties of injection moulded bioplastics based on a soy protein isolate (SPI). Four different polyols, namely glycerol (GLY), ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG), were evaluated. SPI was blended with the plasticizer, using a constant 55/45 (w/w) ratio of SPI/polyol, and then injection moulded at 120 °C. TGA analysis of both bioplastic blends and probes pointed out a general decrease of glass transition temperature (Tg) after the injection moulding. Furthermore, Tg values showed a clear dependence on the molecular weight of the plasticizer. Dynamic mechanical thermal analysis (DMTA) and tensile tests of bioplastic probes were performed by means of an RSA 3 rheometer. All of them exhibited a predominant elastic response in the range -30 to 120 °C, being able to relate lower molecular sizes of plasticizer to stronger interactions with SPI. Water absorption tests and colorimetric measurements of bioplastic probes were also evaluated. Thus, bioplastics containing TEG were opaque and brittle, also showing higher water uptake capacity (WUC) values, whereas bioplastics containing EG were more ductile and translucent, absorbing much less water when probes were immersed in water. In this regard, the replacement of GLY by DEG or TEG as a plasticizer in bioplastic formulations might be useful depending on their specific industrial applications.
A micro-rheological model to predict the morphology development in immiscible blends of polyolefins
Ilhem Boujebelene Charfeddine, Christian Carrot, Jean Charles Majeste, and Olivier Lhoste
1Polymer Materials Engineering UMR 5223, University of Jean Monnet Saint-Étienne, Saint-Étienne 42023, France; 2Total Research Center Felay, Felay, Belgium

Recently, the control of the evolution of polymer blend morphology during processing has received attention because of its great impact on the mechanical, barrier or electrical properties. In general polymer blend morphologies can be divided into two groups: dispersed and co-continuous. In the literature, several papers illustrate that the blend morphology depends on the composition, the rheological behavior of each component, the mixing conditions and the interfacial tension. The models proposed by Veenstra and Yu were used to understand the evolution of co-continuous morphology.

In this study, a prediction model of dispersed and co-continuous morphology has been established. Blends of HDPE/sPP, LDPE/iPP, at various PE to PP weight ratios (90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80 and 10:90) prepared by twin-screw extruder were characterized. The interfacial tension was measured by the Palierne model. The shear rate in the extruder was determined using the Ludovic software. Rheological studies were conducted in an Ares rheometer using parallel plate geometry. The experimental results on the various blends show a good correlation between the interfacial area and the melt elasticity measured at low frequency. The PE/iPP blends were observed by scanning electron microscopy (SEM) using staining agent to enhance electron density contrast. The characteristic dimension of dispersed (R) and co-continuous morphology (lc) were measured from SEM observations to obtain the interface areas as a function of the composition. The results were compared to the interface areas obtained using the predictive model. The model was partially validated and showed that the breakup mechanism was dominated by Rayleigh disturbances.

The effect of surfactants on droplet deformation in a microfluidic shear flow
Rosa D’Apolito, Valentina Preziosi, Giovanna Tomaiuolo, and Stefano Guido
Department of Chemical, Materials and Production Engineering, University of Napoli Federico II, Napoli, Italy

Droplet deformation in shear flow has been widely investigated, both theoretically and experimentally, starting from the pioneering work of Taylor [1-4]. However, in nature and in most applications, interfaces are rarely clean and surfactants are often present at the droplet surface. Here, we present an experimental investigation of droplet deformation at low viscosity ratio in presence of surfactants by using microcapillary flow [5]. Our approach allows to measure interfacial tension of a water-in-oil emulsion at different surfactant concentrations from a quantitative analysis of droplet deformation in shear flow. Our results have been previously compared with experimental measurements obtained by the classical techniques such as pendant drop and a very good agreement is found [5]. Such microfluidic device has overcome the limits of the classical techniques allowing to measure the interfacial tension of systems at high surfactant concentration. In addition, we found that droplet deformation is dramatically affected by the presence of surfactant, deviating from classical theories at very large shear rates and for surfactant concentrations higher than the critical micellar one.

Self-healing and recovery of amine functionalized poly(cyclooctenes) with tunable rheological properties
Tanja Tomkovic, Damon J. Gilmour, Laurel L. Schafer, and Savvas G. Hatzikiriakos
1Chemical and Biological Engineering, The University of British Columbia, Vancouver, Canada; 2Chemistry, The University of British Columbia, Vancouver, Canada

A new class of secondary amine-containing poly(cyclooctenes) were synthesized by combining hydroaminationalkylation reaction and ring-opening metathesis polymerization. The resulting polymers of systematically different molecular weights (nearly monodisperse) were rheologically studied. A plethora of distinctively different rheological behavior was obtained by varying the molecular weight, revealing an evident transition from liquid- to solid-like behavior through gel formation. These materials have found to exhibit strong self-healing and fast recovery in ambient and aqueous environments without applying any external stimuli. The amine functionalized poly(cyclooctenes) possess multivalent hydrogen bonds, which form a robust, strong network that is responsible for the self-recovery, significantly faster than any previously reported self-healing material.

Reducing viscosity of heavy oil by surfactants and polymer additives
Kirill Zueva, Marianna Arinina, Alexander Malkin, and Valery Kulichikhin
Laboratory of Polymer Rheology, A.V. Topchiev Institute of Petrochemical Synthesis, TIPS RAS, Moscow 119991, Russia

Oil is the one of the most important source of energy and raw materials for chemical industry. However an increase in exploitation of highly viscous heavy oil leads to search for methods of reducing its viscosity to 200–400 mPa·s (in accordance with the existing technological requirements). One of the most promising and ecologically attractive concepts is the formation of oil/water (o/w) emulsions by using suitable surfactants.
This study showed that the nature of different additives and conditions of emulsification radically changes the rheological properties of heavy oil: the transition from Newtonian behavior, typical for heavy oils, to viscoplastic flows inherent for concentrated emulsions takes place. The minimum values of the apparent viscosity (below 200 mPa·s at 25 °C) and the yield stress (approx. 1 Pa) were reached for emulsions with 25 vol % of water stabilized by mixtures of non-ionic and anionic surfactants (synergetic effect).

Emulsions with the share of water higher than 25 vol % can exist only with polymer stabilizers, e.g., hydroxyethyl cellulose, which slightly increases the viscosity. Thus the minimum value of the apparent viscosity (50-90 mPa·s at 25 °C) was reached for emulsions containing 50 vol % of water. With decreasing temperature the effect of emulsification increases. The maximum result at 0 °C (decreasing the viscosity by 3 times in comparison with crude oil at 40 °C) was obtained for emulsions stabilized by the mixture of non-ionic surfactant and stabilizing agent. Nevertheless, the minimum viscosity of the obtained emulsions was below the necessary level (< 200 mPa·s at high shear stresses), which is acceptable for tube transportation of oil.

This work was carried out within the State Program of TIPS RAS. Detailed results of this study were published in *Energy & Fuels* (DOI: 10.1021/acs.energyfuels.8b02925).

**Tuesday 18:30 Mediterranea**

**PO33**

**Rheology and structure of heavy crude oil asphaltenes**

Sergey O. Ilvin, Viktoria Yi. Ignatenko, Anna V. Kostyuk, and Sergeii V. Antonov

A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow 119991, Russia

Nowadays, the problem of heavy crude oil transportation and refining has attracted global interest. Deasphalting is a process of removing high-molecular-weight compounds - the asphaltenes - from heavy crude oil or bitumen. This method consists in the addition of solvent to petroleum that dissolves light part of oil and precipitates the heavy one. This method makes it possible to achieve the greatest yield of asphaltenes, and it is the best method for viscosity reduction of heavy crude oil for its transportation.

The yield and structure of asphaltenes are determined by the solvent nature and by the ratio of solvent to crude oil. The asphaltenes were obtained from Ashalchinskaya heavy crude oil by precipitation with the use of hexamethyldisiloxane which was found to be a more efficient precipitating agent than heptane traditionally used for this purpose. The oil-to-precipitant ratio (that was varied from 1:5 to 1:30) allows producing asphaltenes with different structure and properties. Rheology, thermophysics, and structure of asphaltenes were considered. Asphaltenes are glass-forming liquids with glass transition temperature of about 60°C. Depending on their prehistory and test temperature, they can be viscoplastic media or viscoelastic shear-thinning fluids. The structure of asphaltenes was evaluated using elemental analysis, X-Ray diffraction, and IR-spectroscopy methods.

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**Tuesday 18:30 Mediterranea**

**PO34**

**Interfacial instabilities of a concentric core annular flow of viscoelastic-Newtonian fluids**

Said Shahpouri and Azadeh Jafari

Mechanical Engineering, College of Engineering, University of Tehran, Tehran, Iran

Nowadays, multi-layer flows play an important role in industries such as co-extrusions, film coating and lubricated processes. Simulation of multi-layer flows is an important tool in the quest to better understand the interfacial instabilities between two layers with different rheological characteristics. In this study, the interfacial instabilities of concentric core annular flow of Viscoelastic-Newtonian fluids in a two dimensional channel have been investigated in the context of spectral/hp element methods. The core fluid is described by Oldroyd-B fluids, which is surrounded by Newtonian fluid as a lubricant flow. The third-order Adams-Bashforth method is employed for the time discretization and velocity correction splitting scheme method has been applied for the pressure velocity decoupling algorithms. On the interface of two fluids, the interfacial instability is caused by sudden jump in the first normal stress difference across the fluid interface. Indeed, the polymeric stresses fade from its maximum absolute value to zero on the interface of two fluids. This discontinuous behaviour of polymeric stresses on the interfacial boundaries makes the numerical simulation, specifically with high-order numerical methods due to low dissipation and dispersion errors, very challenging. To resolve this numerical issue, we proposed a new stabilization function for polymeric stresses on the interface of two fluids. This new formulation, gradually decreases the polymeric stress from its maximum value on the interface both to zero on the interface of two fluids. This discontinuous behaviour of polymeric stresses on the interfacial boundaries makes the numerical simulation, specifically with high-order numerical methods due to low dissipation and dispersion errors, very challenging. To resolve this numerical issue, we proposed a new stabilization function for polymeric stresses on the interface of two fluids. This new formulation, gradually decreases the polymeric stress from its maximum value on the interface both to zero on the wall. Increasing the Weissenberg and Reynolds numbers, intensely limit the flow rate. In addition, the effects of volume ratio and viscosity ratio are also discussed in this study. All simulations of this study have been done with the C++ toolbox, Nektar++ (https://www.nektar.info/), which is an open source software library currently being developed for non-Newtonian fluids in our research group.

**Tuesday 18:30 Mediterranea**

**PO35**

**Reinforcement of emulsion elasticity by bubbles**

Maxime Schneider1, Olivier Pitois2, Sandrine Mariot1, Giuseppe Foffi1, and Annina Salonen1

1Laboratoire de Physique des Solides, Orsay, France; 2Laboratoire Navier, UMR 8205, CNRS - ENPC, Champs sur Marne, France

The elasticity of aerated materials depends on both gas inclusions (bubbles) and matrix elastic properties. It has been shown that the elasticity can decrease as a function of gas volume fraction because of the presence of soft inclusions (soft as compared to the continuous media) or increase if the inclusions are stiffer [1].

In this study, we measure the shear elastic modulus of aerated soft materials, where the matrix is a concentrated oil-in-water emulsion which behaves as a weakly elastic attractive gel. The elastic moduli are found to be higher than the matrix taken alone and in some cases even greater than the one predicted by models [1].
We elucidate this effect by resorting to solid particles in order to probe carefully the influence of the inclusion size. We measure that the elastic modulus increases even further when the size of the particles is decreased to values comparable with the size of the oil droplets. The experiments are compared to simulations, and our results suggest that this effect originates from the matrix restructuration induced by the small inclusions within the loose packing of oil droplets. This effect is not accounted for in classical theory of inclusions in elastic media.


Tuesday 18:30 Mediterranean PO36

Morphology-rheology relationship in ternary polymer blends obtained from recyclable milk bottles

Leire Sangroniz1, Jose L. Ruiz1, Ainara Sangroniz1, Mercedes Fernández1, Agustin Etxeberria1, Alejandro J. Müller2, and Antxon Santamaria1

1Polymer Science and Technology department, POLYMAT, University of the Basque Country, San Sebastian, Gipuzkoa 20018, Spain; 2Polymer Science and Technology Department, POLYMAT, IKERBASQUE, University of the Basque Country, San Sebastian, Gipuzkoa, Spain

Polymers containing titanium dioxide TiO2 have been introduced in the market to obtain white bottles, suitable for milk packaging. However, these bottles offer certain difficulties to be recycled using standard procedures. Actually, the easiest way is to recycle the bottles with their caps, that is to say, PET (bottle)/polyolefin(cap)/TiO2 ternary blends. These blends can be injection moulded to obtain products that can be used in the automotive industry. Therefore, it is necessary to study the morphology of the blends and their rheological properties in similar conditions to that of industrial processing. As observed by SEM, the blends show a droplet/matrix morphology at the compositions studied in this work and the addition of TiO2 leads to a reduction of the diameter of the droplets. TEM images reveal that the particles are located mainly at the interface, so, therefore, the diameter reduction can be attributed to the barrier effect of the particles, as well as to changes in the interfacial tension or in the viscosity. The analysis of the viscosity measured in an extrusion rheometer, covering a wide range of shear rates, allows establishing the most favourable processing methods and conditions of the blends. Small Amplitude Oscillatory Shear (SAOS) and extrusion continuous flow measurements were also carried out. Interestingly enough, some of the blends show a viscoplastic behaviour, which can aid to avoid sagging in calendaring process. The results reveal the relationship between the morphology and the viscoplastic behaviour: only for particular morphological features viscoplasticity is observed. Indeed, to obtain a viscoplastic behaviour it is necessary to have an emulsion like system, the presence of titanium dioxide, and an adequate size of the dispersed droplets.


Tuesday 18:30 Mediterranean PO37

Formation and stability of oil foams

Hoai-Phuong Tran, François Lequeux, and Laurence Talini

SIMM, ESPCI, Paris, ID, 75005, France

Foam stability, in the case of aqueous systems, is controlled by the disjunction pressure which is created by the adsorption of surfactants on liquid-gas interfaces. When exceeding the pressure generated by the channels or Plateau borders, this repulsive pressure stabilizes a film to a finite thickness, assuming responsibility for the existence of a foam. On the other hand, in the case of oil systems that do not contain surfactants, the mechanisms of formation and stability remain poorly understood. In the present study, we investigate experimentally the foamability of toluene/alkane binary mixtures in a vertical glass column in which nitrogen is injected. We observe that the mixtures of toluene and alkane form foams and that there is a proportion of the mixture for which the foamability is maximum. We suggest that foam stability results from Marangoni flows induced by the dependence of the surface tension within the thickness of a liquid mixtures. We thus show that foaming measurements can be connected to surface tension measurements of the mixtures. Our description can be generalized to any liquid mixture in which surface tension does not vary linearly with mixture proportion.

Tuesday 18:30 Mediterranean PO38

Structure and biodegradability of PLA and PBSA blend

Seung Joon Park

Korea Polytechnic University, Shihueung, Republic of Korea

Due to the problem of environmental pollution caused by the disposal of general-purpose plastics, there has recently been a growing interest in biodegradable. Among various types of degradable plastics, aliphatic polyesters drew huge attention due to its excellent biodegradability. Poly[lactic acid] (PLA) and poly[(butylene succinate-co-adipate)] (PBSA) have been widely used various products. Limiting factors for a broader use of synthetic aliphatic polyesters are their poor mechanical properties. Synthesis of aliphatic polyesters was performed following the two-stage melt polycondensation method (esterification and polycondensation). Controlling the molecular weight of aliphatic polyesters is necessary to improve their mechanical properties. We have optimized the reaction parameters of PBSA such as temperature of esterification and polycondensation. The reaction rate tends to rise as the reaction temperature increases within the range that does not cause the loss of the raw materials. As for a catalyst, titanium(?) tetrabutoxide showed a good reaction rate, and the most effective reaction occurred when a catalyst loading of 0.002mol% compared to diacid was applied. We have measured the biodegradability of aliphatic polyesters. For PBSA homopolymer, the ratios of succinic acid (SA) to adipic acid (AA) were controlled to examine the effect of AA contents on the biodegradability. In the case of the PLA and PBSA blend, the blending ratios and the contents of organoclay were varied. The biodegradability of PBSA increased with increasing AA contents because of the decrease of the crystallinity of PBSA. The biodegradability of PLA/PBSA/organoclay composites for various blending ratios could be controlled by the contents of organoclay.
Rheology of two-phase flow in porous media: Dependence on saturation and system disorder
Subhadeep Roy¹, Alex Hansen², and Santanu Sinha³
¹PoreLab, Department of Physics, Norwegian University of Science and Technology, Trondheim, Trondheim 7491, Norway; ²Physics Department, PoreLab, Norwegian University of Science and Technology, Trondheim, Norway; ³Beijing Computational Science Research Center, Beijing, Haidian District 100193, China

When two immiscible fluids flow in porous media the flow does not obey linear Darcy law in the regime where the capillary forces are comparable to the viscous forces. The flow rate was observed experimentally to scale in a quadratic manner with the pressure gradient for two dimensional Hele-Shaw cells [1] constructed with glass bids. The disorder in capillary barriers at pores effectively create a yield threshold, making the fluids reminiscent of a Bingham fluid in the porous medium, introducing an overall threshold pressure Pₘ in the system [2]. Due to disorder in capillary barriers, increasing number of connecting paths appear in the system while increasing the pressure gradient (ΔP), enhancing the increase of overall flow rate Q more faster than the linear dependence. This leads to a quadratic dependence of Q on the excess pressure drop (ΔP-Pₘ) at the capillary dominated regime and a linear dependence at sufficiently high flow rate when all pores open up [2,3]. The disorder in the capillary barriers at the pore level appears due to the fluctuation in pore sizes as well as from interface configurations between the two fluids inside a pore. When the saturation of the fluid approaches to zero or one, the two-phase flow reduces to single-phase flow governed by a linear Darcy law. In this work, we will present a detailed study of a two-phase flow with a continuous variation of above two system disorders. A study of the complex phase space of the rheology as a function of saturation and disorder in pore sizes can offer further insights to the existing observations.

References:

Rheology of medium-light crude oil mixtures and viscosity reduction for resolving transportation issues
Jelena Stevanovic and Marija Madzarevic
NTC NIS-NAFTAGAS d.o.o, NIS A.D, Novi Sad 21000, Serbia and Montenegro

The objective of this study was to investigate the rheological properties of medium to heavy crude oils from "Is" oilfield and their mixtures with light crude oils from another two Serbian oilfields: "Mk" and "Kg". This research was conducted in order to obtain more knowledge about the flow of these oils through pipelines, which will enable an efficient transportation from the fluid collection system to the refinery. The oil field "Is" is a recently discovered and very promising oilfield, located in the northern Banat, Serbia. Seven wells in total have been drilled so far and the crude oils from these wells were investigated in terms of their physicochemical and rheological properties. Their density at 15 °C varies from 852.3 to 873.2 kg/m³, which corresponds to medium oil. The paraffin content ranges from 6.5 to 13.2 mass%, which classifies them into highly paraffinic crude. The pour point is in the range 22-29°C, and the average asphaltene content is ca. 1.5 mass%.

The exception is oil from "Is" Well-X-007, which shows extremely high paraffin content compared to the oils from other wells (over 20%). This has resulted in a change of numerous physical and chemical characteristics of this oil: an increase in density, pour point (42°C) and viscosity. On the other hand, crude oils from "Mk" and "Kg" oilfields are classified as light oils, with low paraffin content (2-4%), low pour point (12-18°C) and good flowability characteristics.

The rheological properties (dynamic viscosity vs. temperature, wax appearance temperature and pour point) of medium-light crude oil mixtures have been investigated using an Anton Paar rheometer MCR 302. Several factors, such as shear rate, temperature, light oil concentration and the influence of two different paraffin inhibitors, and three types of oil mixtures have been studied:

Blend of "Is" oils,
Mixture "Is" blend : oil from "Mk" : oil from "Kg" = 20% : 30% : 50%,
Mixture "Is" blend: oil from "Mk" : oil from "Kg" = 30% : 30% : 40%.

All three mixtures were tested in the 45-0 °C temperature range at a constant shear rate and a linear decrease of temperature of 1°C/min. The viscosity of "Is" oil blend was lower than all the viscosities of individual oils. It was observed that blending the medium crude oil with a limited amount of lighter crude oil worked well, thus lowering the viscosity up to 50% and the pour point up to 6°C. A significant viscosity reduction for all the mixtures was achieved in the presence of one of the paraffin inhibitors, especially at lower temperatures, producing viscosity values required for the pumping of medium crude oil through the pipelines. Additionally, the effect of the paraffin inhibitors was separately tested on oil from Well-X-007; however, the viscosity reduction was not accomplished.

The obtained results indicate that the rheological properties of crude oils from "Is" oilfield are significantly influenced by light oil content, the selected paraffin inhibitor, and nature of crude oil.
Tuesday 18:30 Mediterranean

**Rheological and textural analysis of cosmetic emulsions: A combined approach for the assessment of the applicative and sensory properties**

Giovanni Tafuro¹, Alessia Costantini², Gianni Baratto³, Laura Busata³, and Alessandra Semenzato¹

¹Department of Pharmaceutical and Pharmacological Sciences, University of Padua, Padua 35131, Italy; ²Unired S.r.l., Padua 35131, Italy; ³Scientific Area, Unifarco S.p.A., Santa Giustina, Belluno 32035, Italy

Fulfilling consumers’ expectations has become imperative in the personal care industry. Sensory profiling of cosmetic products is undoubtedly a powerful tool, but manufacturers increasingly require more objective, time and money-saving approaches, which could adequately describe sensory properties. In this work, we used rheology and texture analysis to determine the physical and mechanical properties of 26 commercial skin-care emulsions, formulated with definite combinations of emulsifiers, oils and polymers (EOP(t)). The rheological analyses were conducted both in continuous and oscillatory flow conditions, while the texture analysis method used was an immersion/de-immersion test with a spherical probe. The results obtained were statistically analysed and compared to the parameters of three hydrophilic gels, which represent three different textural and rheological behaviour. R1, composed by an acrylic polymer, showed a solid-like behaviour and a weak-gel pattern; R3, a dispersion of hyaluronic acid in water, showed a liquid-like behaviour and a rheological viscoelastic profile; R2 had intermediate characteristics between R1 and R3. Statistical analysis also evidenced a significant correlation between rheological and textural parameters: viscosity correlates with firmness, while storage (G’) and loss (G”) moduli with adhesiveness and stringiness. Data suggest that the combined use of these techniques is useful to evaluate the influence of the vehicle composition on spreading properties and could provide a scientific support for cosmetic industries, when creating marketing and product targeting strategies.

Tuesday 18:30 Mediterranean

**PIV measurements of rising oil droplets in viscoelastic outer fluids**

Claudiu Patrascu¹, Titus Sava¹, Miheea-Claudiu Stoica², and Corneliu Balan¹

¹Hydraulics, REOROM, University Politehnica of Bucharest, Bucharest, Romania; ²REOROM, University Politehnica of Bucharest, Bucharest, Romania

The study is focused on the experimental determination of the velocity field around a rising droplet of oil in a viscoelastic liquid. The viscoelastic fluid is a polyacrylamide mixture which is immiscible with the Newtonian oil droplets. The field is determined by Particle Image Velocimetry (PIV) techniques having as seeding particles glass hollow spheres, in a concentration which does not alter the material properties of the external medium. Computations of the streamline patterns and vorticity are presented. One of the main objectives of the study is to identify the “negative wake” behind the rising droplet and to determine its dynamics and topology. PIV measurements reveal the time evolution of this process. The present analysis is compared with the rise of an oil droplet in a Newtonian outer immiscible fluid, emphasizing the role of elasticity during the process.

Tuesday 18:30 Mediterranean

**Spreadability of structured oil systems: A fractional derivatives approach**

Bruno de Cindio¹, Noemi Baldino², Francesca R. Lupi², Olga Mileti², and Oraldo F. Paleologo¹

¹University of Calabria, Rende, Italy; ²DIMES, University of Calabria, Rende, CS 87036, Italy

It is well known that structured systems show peculiar rheological characteristics with a behaviour ranging from solid to liquid. This has pushed researchers to interpret rheological data in terms of viscoelasticity theories assuming the existence of a molecular network. Unfortunately, often these models do not fit enough well sensorial and technological properties, that on the contrary are more interesting for industrial application. Recently, some success has been reached by abandoning the idea of viscoelasticity and turning to a new class of materials defined by quasi-properties and fractional derivatives, because of the better agreement with food data, particularly when structured systems are considered. In such a way also the old question of network or jam behaviour can be better understood. An olive oil structured by different amounts of monoglycerides of fatty acids has been investigated by bulk rheology, both at equilibrium and during transient conditions, to determine the quasi property and the material parameters, with the aim to defined spreadability. Dynamic frequency test between 0.1 and 10 Hz, time cure at 1 Hz and transient creep in the linear region are presented in a large range of concentrations and temperatures. The data have been interpreted in terms of a two springpot mechanical model, in order to quantify the material parameters. It is proposed to measure spreadability by taking into account the initial compliance, the value of final compliance at a characteristic time, and the slope of the following recovery. By this new method, once the rheological measurable properties are experimentally determined and modeled by means of quasi properties, it is possible to properly design structured oils in terms of the desired spreadability.

Tuesday 18:30 Mediterranean

**The taste of rheology: Investigating the mechanical properties of foodstuff**

Cornelia Kuechenmeister-Lehrheuer, Fabian Meyer, and Klaus Oldoerp

Material Characterization, Thermo Fisher Scientific, Karlsruhe 76227, Germany

Since foodstuff comes in such a vast variety of structures and textures, the tally of rheological methods used to characterize its mechanical properties is even bigger. From production to consumption, rheological properties play an important role during the entire life cycle of liquid or semi-solid food formulations. Starting with simple single point viscosity measurements in original containers for batch release in production, over the determination of classical rheological parameters like shear viscosity or yield point for quality control purposes, it reaches a certain level of complexity with comprehensive rheological investigations for the development of new formulations in the research and development department. While some methods rely on classic rheometer geometries like parallel plates, cone & plate or coaxial cylinders, some other methods try to emulate a certain application by utilizing special rotors and/or fixtures. The texture of food products has to match the customer's expectations. With specially designed probes a rotational rheometer can test various food specific properties such as softness,
stickiness or spreadability, and can even be utilized for performing tribological tests. Other rheometer accessories and extensions such as microscopes or spectrometers enable a better understanding of what causes a certain rheological behavior on a microscopic or even molecular level. This can be useful for instance when investigating the complex crystallization behavior of fats during phase transition. In this contribution selected rheometer accessories and measurement results of various food products will be presented. This includes the ‘classical’ rheometer capabilities as well as customized setups and hyphenated techniques for a comprehensive investigation of food formulations.

Tuesday 18:30 Mediterranea

Rheological properties of food Pickering emulsions based on edible oils and starch nanocrystals as stabilizing agent

Joanna Kruk, Paweł Ptaszek, Kacper Kaczmarsczyk, and Karolina Kijowska
Faculty of Food Technology, University of Agriculture in Cracow, Kraków 30-149, Poland

Stabilization of food emulsions, type oil-in-water, using solid particles - starch nanocrystals was studied. First step of research procedure was obtaining starch nanocrystals using hydrolysis with sulfuric(VI) acid, and their characterization with dynamic light scattering. Second step was emulsions production with different viscosity edible oils. Homogenization was carried out with high-speed homogenizer. The last step was rheological characterization of obtain emulsions using analysis of changes storage (G') and loss (G'') moduli depending on strain value (?). Analysis of dynamic light scattering measurements indicated that the average size of starch nanocrystals was 180 nm. All studied systems had only short range of linear viscoelasticity. Depending on starch nanocrystals concentration the transition from linear to nonlinear viscoelasticity region occurred at strain values between 0.2 to 0.5. It can be found that emulsions are systems, which rheological behavior is similar to soft glassy materials. Finding and examination of new stabilizing agents produced using cheap and easy available raw materials, during environmentally-friendly process, can have significant impact for further development of greener approach in food additives' production.

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Tuesday 18:30 Mediterranea

The application of locust bean gum to shaping of rheological properties of vegan ice-creams based on soya milk and different plant fats

Anna Ptaszek, Paweł Ptaszek, Kacper Kaczmarsczyk, and Justyna Poniewierka
1Faculty of Food Technology, University of Agriculture in Cracow, Kraków 30-149, Poland

A new approach for development of ice-cream production from vegan components was explored. This work focused on tests of rheological properties of the three phase systems (foam-O/W emulsion) based on soya milk and selected plant fats stabilized with the help of locust bean gum (E410). This hydrocolloid can be classified not only as surface-active agent but as viscosity-shaping biopolymer. The experiment plan involved the study of viscoelastic properties and normal forces of fresh foams and three phase systems at selected temperatures. Large Amplitude Oscillatory Shear (LAOS) was used to study the nonlinear viscoelastic properties. It allowed to demonstrate that all tested systems exhibited viscoelastic properties, the linear region was limited to deformation value dependent on temperature and fat concentration. After passing that value, a transition into nonlinear viscosity range was observed. Some three phase systems exhibited the intersection of storage and loss moduli in the range of deformation from 0.1 to 1.0. To investigate nonlinear rheological properties Fourier transformation analysis was done. During this analysis higher harmonics were observed. The changes in yield stress values and dissipation coefficient were also observed. Moreover, the changes of normal force generated during shearing were determined and correlated with viscoelastic properties and fat content. This rheological study allowed to point the main factors determining rheological properties of ice-creams and showed the future direction of industrial application.

Tuesday 18:30 Mediterranea

Selection of the gelifying system for the development of snacks with nutritional and health claims

Margarida Pina1, Sónia Oliveira2, Mayumi Mayumi3, Sofia Dinis3, Tiago Oliveira4, Marlos Silva4, Catarina Prista1, Isabel Sousa1, and Anabela Raymundo1
1LEAF, Instituto Superior de Agronomia - University of Lisbom, Lisbon 1349-017, Portugal; 2LEAF, Instituto Superior de Agronomia - University of Lisbon, Lisbou, Portugal; 3Modelo Continente Hipermercados S.A., Lisboa, Portugal; 4Sonae Center Serviços II S.A., Lisboa, Portugal

There is a shift in the paradigm of food focused on health and well-being. Consumers are increasingly aware of the impact of healthy eating and of the scientific knowledge pointing to the benefits of consuming vegetables. Chronic diseases such as diabetes, hypertension and obesity are associated to a poor and careless diet. The consumer sensitivity to well-being competes with the lifestyles and routines of individuals in modern societies, advocating that a diet should be nutritious and delicious but also convenient. The present work is part of a larger project SnackFresh, a partnership of ISA and SONAE, aiming to produce sustainable healthy snacks with nutritional and health claims. The products to be developed would meet these new requirements of the consumers, having a balanced nutritional composition, with specific health benefits, being easy, convenient consumption and leading to a sensorial innovative experience. It is a gelled product obtained from a hydrocolloid formulation with vegetables, optimized to achieve sensory and nutritional characteristics, with health impact, defined as starting requirements. The selection of the most appropriate hydrocolloid system was the aim of the present study. Few ready to use commercial blends were tested with some other hydrocolloid mixtures. To sum up, we highlight two systems: i) gellan high (HA) and low (LA) acylation level; ii) k-carrageenan / locust bean gum (LBG). The impact of the addition of salt and pH was studied, and it was verified that in both cases the addition of salt strengthens the gel structure. Texture variations were reduced in the pH range of commercial application. Gels rheology was evaluated using a controlled stress rheometer, monitoring the gels on cooling and setting, followed by the mechanical spectra. It has been found that the systems under study show rapid maturation, namely gellan gels, and that the gels obtained have a high degree of structuring.
Impact of fermented whey addition on the rheological behavior of bread

Christine Macedo, Cristiana Nunes, Isabel Sousa, and AnaBela Raymundo
LEAF Research Center, Instituto Superior de Agronomia, University of Lisbon, Lisboa 1349-017, Portugal

Whey is the by-product of cheese production, containing protein and lactose. Considering its nutritional value, it is an excellent raw material for the development of other food products, in line with the concept of circular economy. The controlled lactic fermentation of the whey (FW), generates bioactive compounds that can be explored as an added value functional ingredient, when incorporated into a staple food, such as bread. In a previous work, the whey fermentation conditions were optimised to promote the anti-inflammatory and anti-carcinogenic potential of whey. The present work is part of a project which aims to develop a sustainable and integrated alternative to the cheese production and baking industries, generating value for both sectors. The impact of the FW addition to dough has implications in its rheological behaviour, as well as in the texture and sensory properties of bread. This work aims to evaluate the impact of the replacement of water by FW, on preparation of bread. The effect of this replacement on the rheology of the dough, evaluated by empirical (microdoughLab and alveograph) and fundamental methods (controlled stress rheometer), was performed. The impact on dough texture was also analyzed. A reinforcement of the dough structure by the presence of the whey proteins, was observed by the increase of the viscoelastic functions (G’ and G″) as well as by the puncture test. In addition, an increase in the shelf life of the whey bread, compared to the normal bread with water, was also observed, followed by the increase on firmness (staling) over time. These results suggest the great potential of the use of FW for the development of bioactive bread formulations, obtaining a product with texture and sensory enhanced properties, with a positive impact on health and with excellent technological properties.

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Extensional investigation of dough like model systems with resistant starch and vegetable proteins: Effect of transglutaminase

Noemi Baldino, Ilaria Carnevale, Francesca R. Lupi, and Domenico Gabriele
Department of Informatics, Modeling, Electronics and Systems, University of Calabria, Rende, Italy

Nowadays, there is an increasing interest, in producing mixtures of flours, towards non-traditional ingredients, like lupine, chia and so on, to replace wheat or to enrich the traditional wheat-based foods with different vegetable proteins or other ingredients that could have positive health effects, such as dietary fibres. In fact, the incorporation of proteins rich in particular essential amino acids, like lysine, could help to reduce some metabolic syndromes and increase the food quality. In addition, it provides further health benefits such as the reduction of the risk of coronary heart disease, osteoporosis, menopausal and postmenopausal women symptoms and helps in cancer prevention. Moreover, according to dietary guidelines and diabetes prevention, a diet with low glycaemic index foods, i.e. rich in slowly digested carbohydrates, is recommended in people affected by coeliac disease. This result can be obtained by using resistant starch (RS) that is the fraction of starch not hydrolyzable in the gastrointestinal tract, but which ferments in the colon. For this reason RS can be considered as a dietary fibre even if, traditionally, the term dietary fibre refers to non-starch polysaccharides. In comparison with traditional dietary fibre, RS has more advantages. In fact, it does not affect in a relevant way the sensory properties of the final products and provides many technological properties, such as better appearance, texture, and mouthfeel than conventional fibres. In this work model doughs, based on RS and different vegetal proteins, were studied with and without transglutaminase using extensional and shear rheology (dynamic temperature ramp tests). Particularly, lubricated squeezing flow tests were performed, at different crosshead speeds, to obtain more information about the possibility to develop a resistant viscoelastic network able to mimic the gluten network.

Rheological comparison of hyaluronic acid and proteoglycan in well-defined shear flow fields

Hye-Jin Ahn and Ki-Won Song
Department of Organic Material Science and Engineering, Pusan National University, Busan 46241, Republic of Korea

Hyaluronic acid (HA), also called Hyaluronan, is one of the filler materials satisfying the biocompatibility factors, which has glucosaminoglycan structure with linear polysaccharides consisting of repeating units of D-glucuronic acid and N-acetylglucosamine. Due to the HA exists in the dermis, the skin is possible to retain moisture, prevent wrinkles, activate skin cell to recover injuries caused by pimple or burn. Haigh ratio of HA, especially, acts like a cushion to protect intercellular matrix and to give proper volume. In addition, Proteoglycan (PG) is one of the glycosylated proteins, which has a core protein with covalently attached glycosaminoglycan (GAG) chains containing repeated disaccharide units. Diverse species of proteoglycan are existed in extracellular matrices. Based on their characteristic complex structures, these proteoglycans can generate hydration and swelling pressure enabling to withstand compressional forces. Becoming an aging society, interests in health care and cosmetics are getting bigger in order to regain youthfulness. The functions/abilities of HA and PG (such as holding/maintaining the water or viscoelasticity in the skin or cartilage) can be assessed as being optimized for filler substance in medical and cosmetic industries. Especially, it will be the most popular raw material used for the medical injection products. The main objective of present research is to systematically investigate the rheological behavior of proteoglycan as well as HA fillers according to the extent of crosslinking using a stress-controlled rotational rheometry system in various well-defined shear flow fields including steady, oscillatory, and transient shear flow conditions.
Snails can selectively secrete several different types of mucus, depending on the environment in which they are placed. Snail mucus is a complex biological compound consisting of glycoproteins, mucopolysaccharides, allatoin, glycolic acid, and enzymes. By regulating the ratio of these mucus components, each secreted mucus has different physical and bio-chemical properties. Glycoproteins are major macromolecular constituents of the mucus, which lead to significant viscoelastic moduli by forming cross-linkage with surrounding matters. Along with this, glycosaminoglycans (GAGs) contribute to viscoelastic properties of mucus by forming numerous hydro-bonding between water and its negatively charged sugar chain ends. Based on the characteristics of these components, the snails enable to protect their skin from the conditions such as moisture evaporation and oxidation. It is especially noteworthy that the snails self-regenerate their cells to cure wounds on the deep (or superficial) skin. Because of these benefits of SSF, several trials have been carried out to reveal the benefits of snail secretion to human skin. In these days, with increasing consumption of pharmaceutical and cosmetic products to regain their youthfulness, it has led to re-evaluate and develop the products which is based on the snail mucus (or snail secrete filtrate). And, knowledge of the rheological properties of snail secretion filtrate becomes a necessary key to improve processing efficiency as well as to develop consumer-acceptable final products. The main objective of present study is to systematically characterize and compare the rheological properties of snail secretion filtrate on different pH values using a strain-controlled rotational rheometry system in steady shear and periodically small/large amplitude oscillatory shear flow fields. To provide optimum information on the effects of pH values, all samples were treated with the buffer solutions of pH value 6-8, which is the range that human skin can have in casual daily life.

Dietary fibers are assuming an important role in everyday diet owing to their beneficial effect for human health to reduce pathologies such as hypercholesterolemia, diabetes, gastro-intestinal diseases. In addition to their health effect, they contribute to modify rheological properties of aqueous phases, improving their structuration degree and consistency according to fibers content and to process conditions. Therefore, fibers can promote an increase of the nutritional level of foods, allowing the texture of materials to be properly tuned according to the desired final consistency. Because of the fat content (mainly coming from oil and eggs or their derivatives), some commercial product like dressing or mayonnaise are generally considered as high-fat and high-caloric foods. The aim of this work is addressed to the design of new products characterized by textural properties comparable to those of commercial ones (thanks to fibres addition), but with a lower content of fats and calories. The effect of citrus fibres on the texture of oil in water emulsions was investigated in order to design low-fat dressings as replacements of the already available and commercialized dressings rich in fats. Emulsions were prepared using a rotor-stator system (Ultra Turrax) by modifying the energy and/or the power of mixing to investigate the influence of the operating conditions on their rheological characteristics. Oil phase concentration and fibre content were modified to investigate the stability and the rheological properties of emulsions in comparison with commercial dressings. The change in fibre concentration and operating conditions allow the production of different final product with specific application (dressing, mayonnaise, etc.).

The Poisson’s ratio describes the lateral contraction of a material when stressing the material in axial direction [1]. For viscoelastic materials, like polymers, this parameter is a function of time (frequency) and temperature. It is an important parameter for structural mechanics simulations of viscoelastic materials and has, for example, to be considered as critical parameter regarding the quality of adhesion between different components in multicomponent materials [1,2]. Several methods are described to determine the Poisson’s ratio. The methods can be classified in direct methods which directly measure the change of the dimensions of the specimen and indirect methods from which the measurement of two moduli like shear modulus and Young’s modulus seems to be the most effective [3]. The contribution highlights a new testing procedure using a combined torsional-axial dynamic mechanical analyzer (MCR 702 MultiDrive) and different clamping fixtures for cylindrical as well as rectangular specimens in order to determine the viscoelastic Poisson’s ratio. Both the complex Young’s modulus $|E^*|$ as well as the complex shear modulus $|G^*|$ are obtained in one single measurement run, following the protocol proposed by Tschoegl et al. [2]. This approach enables, a quick and reliable determination of the viscoelastic moduli and Poisson’s ratio in a single experiment. The obtained experimental data were used to determine the viscoelastic Poisson’s ratio of several thermoplastic polymers. The suitability of the method is further examined and discussed by comparing the results with literature data.

Combined rheo – spectroscopy methods to monitor the transient kinetics of early cement paste hydration

Nonkululeko W. Radebe, Christopher O. Klein, and Manfred Wilhelm
Institut für Technische Chemie und Polymerchemie, Karlsruher Institut für Technologie, Karlsruhe, Baden-Württemberg 76131, Germany

The combination of rheological measurements with a spectroscopic method is addressed in order to gain simultaneous information about the molecular dynamics and the structure of time-dependent phenomena on cement paste. Two such spectroscopic techniques are 1H nuclear magnetic resonance (NMR) relaxometry and Fourier Transform Infrared Spectroscopy (FTIR). These are powerful tools to study molecular mobility and molecular chemistry. In this project, these techniques are used to study cement hydration kinetics and cement product formation during the early hydration I phase. Cement hydration begins immediately upon contact of cement powder with water. The hydration products begin to form while the cement paste undergoes structural build up in the first few hours. After mixing an increase in the storage modulus, G', at rest, is observed. 1H protons are mobile and this mobility is dependent on the environment in which they are in (i.e bulk water, gel pore, interlayer pore). Simultaneous interpretation of the transient rheological behaviour of cement paste and molecular dynamics or chemistry are not readily available. Here, we will show the relationship between the spin-spin relaxation rate as per low - field 1HNMR relaxometry and the G' via the Rheo - NMR combined technique. In addition, we introduce a Rheo - IR coupled technique used to study the structuration and chemistry relationship of early cement hydration. In this set - up the IR beam is directly focused on the ATR crystal geometry with the help of two parabolic mirrors. A nitrogen cooled, highly sensitive, mercury cadmium telluride (MCT) detector is used for detection. The host instrument is a strain - controlled (ARES G2) rheometer. These combined techniques will enable the analysis of the interaction of reactive (hydrating) particles on the molecular length scale. This includes quantifying the effects of additives, temperature, and time. This will subsequently aid in the development of well-defined cement for construction.

Improved tack characterization of transdermal therapeutic systems (TTS)

Michael Meurer1, Maike Unkelbach1, Sarah Klaas1, Bernhard Möginger2, and Berenika Hausnerova2
1Natural Sciences, University of Applied Sciences Bonn-Rhein-Sieg, Rheinbach 53559, Germany; 2Faculty of Technology, Tomas Batu University, Zlin 76001, Czech Republic

Transdermal patches are designed for drug delivery trough human skin for several disease treatments. They consist of Pressure Sensitive Adhesives (PSA) and a protective Backing Layer (BL). Excellent short-term and long-term adhesion of the PSA to skin during application time is essential for patient's compliance. A challenge within TTS development is to choose suitable PSA mixtures and appropriate BL to meet all requirements. Currently short time adhesion of TTS is measured by the Probe Tack according to ASTM D2979. In the Probe Tack experiment the maximum force due to initial adhesion is determined with a stainless steel stamp Ø = 5 mm after a contact time of 1 s. However, the "real" adhesion behavior of the TTS due to effects of different adhesive mixtures and BL is characterized by a force-time-curve. It allows for to evaluate the maximum force as well as the cohesive energy and the maximal detach rate. Therefore, the Haake MARS III rheometer in normal stress mode was used to measure force-time curves of these patches. This method is named "Rheo-Tack". In this study, the short-term adhesion behavior of five types of silicone based adhesives (55% - 60% resin) on two different BL (19 µm PET; 52 µm PET/EVA) is determined using both the Probe Tack Tester and Rheo-Tack. First results show increasing cohesive energies with decreasing resin contents and increasing layer thicknesses of the PSAs. Furthermore, the maximal detach rate given by the minimal slope of the force-time-curve after reaching the maximum force increases with decreasing resin contents, and the maximum force values correspond to the Probe Tack values. The Rheo-Tack method provides considerably more information about the patch behavior for optimization purposes of TTS without loosing the standardized Probe-Tack values.

Multifractal analysis of the failure patterns of thin sheet type of Dried Laver (Porphyra) at different humidity circumstances

Hwabin Jung and Won Byong Yoon
Food Science and Biotechnology, Kangwon National University, CHUNCHEON, Gangwon-do 24341, Republic of Korea

The effect of water activity (aw) or the relative humidity (RH) on the tensile rupture properties of dried laver (DL) associated with structures formed with phycocolloids was investigated. The morphological characteristics of tensile ruptured DL samples at various relative humidities were evaluated by multifractal analysis. The RH of the microclimate was controlled from 10 to 90% at 25 °C using supersaturated salt solutions. The sorption isotherm of DL was experimentally obtained and quantitatively analyzed using mathematical models. The monolayer moisture contents from the GAB (Guggenheim-Anderson-de Boer) model was 5.92% (w.b.). An increase in the RH resulted in increasing ring tensile stress and maintaining constant ring tensile strain up to 58% -75% RH, whereas the ring tensile stress and the ring tensile strain rapidly decreased and increased, respectively, when the RH was higher than 75%. The general fractal dimensions and the multifractal spectra f(a) manifested that the patterns of the lowest and the highest moisture content of dried laver showed high irregularity. The different multifractal parameters obtained from the DL at various RHs well-represented the transient moment of the structures from the monolayer moisture to texture changes associated with RH. Overall, the ring tensile test and the multifractal analysis were useful tools to analyze the change of crispness of DL from its structural characteristics. In addition, the results of this study revealed that the integration and disintegration properties of DL occurred through the networks of phycocolloids at various moisture contents. This research demonstrated that the tensile test and the image analysis are useful tools to evaluate the quality of dried laver products.
Effect of shear deformation on rheological properties of chitosan colloidal systems studied by rheological measurements coupled with light scattering

Patryk Ziolkowski, Piotr Owczarz, and Marek Dziubinski
Department of Chemical Engineering, Lodz University of Technology, Lodz, Poland

Chitosan as a natural biopolymer has found a wide application in medicine, food and cosmetics industries. In this work, we aimed to study the microstructural and macroscopic properties of chitosan colloidal systems. An analysis was conducted using rheological methods combined with a simultaneous small angle light scattering measurements.

All rheological properties were investigated using Anton Paar Physica MCR 502 rheometer. The impact of shearing deformation on the behavior of samples was specified based on the three-interval thixotropy test. The samples were deformed at three different shearing deformations: 10, 100 and 1000 1/s using cone-plate geometry. The light scattering measurements were conducted in a double-gap system of a rotational rheometer. As the light source a diode laser operating at a wavelength 658 nm was used. The viscosity was determined during equilibrium test, in which the sample was sheared for 60 s at subsequent constant shear rates of 1 ... 500 1/s.

The investigated chitosan system reveal a shear thinning behavior. Simultaneously with a viscosity decreases, a change in the shape of the scattering pattern from circular to elliptical was observed. This change represents orientations and deformations of the polymer domains. Based on the eigenvalues of the second-order tensor of the intensity distribution, the anisotropy was determined to quantify a deformation phenomenon. Based on three-interval thixotropy test, the deformation parameters were determined for a samples prepared with three different molecular weight of chitosan. A correlation between the molecular weight and the degree of deformation was found. The degree of deformation of the polymer increases with a decrease of the value of molecular weight. However, this correlation weakens or vanishes with the decrease of applied shear rate. From designing point of view of the hydrogel matrices in biomedical applications, such information is relevant to predicting the crosslinked structure and forming mechanism.

Correlation of rheological data and optically visible sample effects during measurements

Tobias Nill, Gunther Arnold, and Joerg Laeuger
Anton Paar Germany GmbH, Ostfildern 73760, Germany

Many optically visible sample effects such as edge fracture, sagging, stringing, necking degradation, slip, gap emptying and phase transitions can occur during a rheological measurement in a dynamic shear rheometer. Very often, these are undesired effects which affect the measurement results in a significant way and therefore should be avoided. On the other hand, it may also be a goal to investigate these effects in more detail in order to better understand the rheological behavior of materials. The occurrence of these effects is dependent on many influence factors like the type of measuring system and test parameters (e.g. shear rate, frequency, strain amplitude and temperature). This contribution will present a way to investigate the sample behavior and the influence factors of these effects and to help with the interpretation of measurement results by observing and recording the optically visible real-time sample behavior and by correlating it with the rheological data. It will highlight applications which show significant effects of optically visible sample behavior on rheological data. Furthermore, these optical data can add valuable information to the post-measurement analysis, validate measurement results and help to optimize the test parameters in order to avoid undesired sample behavior during the measurement. The investigation is enabled by the use of a camera setup for a high temperature oven with integrated illumination mounted on a Modular Compact Rheometer from Anton Paar. With this optical system sharp real-time pictures and videos of the sample behavior during the measurement can be recorded and correlated directly to the measuring points at which they were recorded. Optical investigations can be performed over a temperature range of -160 °C to 600 °C and with a field of view of 50 mm diameter, allowing to observe a wide sample area.

The yield stress – a rheological mystery?

Fabian Meyer, Cornelia Kuechenmeister-Lehrheuer, and Fritz Soergel
Material Characterization, Thermo Fisher Scientific, Karlsruhe, Baden-Württemberg 76227, Germany

The existence of a true yield stress was discussed controversially among rheologists for many years. This is no surprise, since its existence basically contradicts the motto of the rheological society: panta rhei - everything flows, it is just a matter of time. However, since for most materials and technical applications it is important that flow is achieved in a reasonable amount of time, the concept of an apparent yield point that separates elastic from flow behavior has been widely accepted. The yield stress has become an important parameter in research as well as in quality control to describe the 'flow' behavior of many structured fluids and semi solid. A yield stress can improve the stability of dispersed systems by preventing sedimentation, keeps a toothpaste from sinking into the brush or simply prevents a paint from running down on a vertical wall. However, the measured value of the yield stress is strongly dependent on sample handling, the chosen rheological measuring method, the data evaluation and even the utilized measuring geometry. Because of the variety of available approaches, many users of rotational rheometer face conceptual confusion when trying to extract “the” yield stress from a measured set of data. The aim of this contribution is to show the differences among the test protocols and evaluation methods commonly used for yield stress analysis. It also provides a guideline on how to set up Standard Operating Procedures (SOPs) for sample handling and presents the potential pitfalls that an inexperienced user should be aware of.
Facing new challenges like 3D-printing or complex flow simulation, it is crucial to characterize the rheological behaviour of fresh concrete on a scientific level. However, the standard construction site methods (e.g. slump- or L-Box test) and even more precise concrete rheometers (e.g. viscomat or BT) only provide researchers with relative values in contrast to absolute rheological parameters. This is mostly due to the unpredictable shear fields in these apparatuses. Conventional coaxial or torsional rheometers are only applicable to cement paste because of particle size restrictions. Therefore, a scientific grade rheological setup is necessary to measure true rheological properties. We developed a coaxial type rheometer, which not only allows the measurement of rheological parameters of fresh concrete, but is also capable of conducting in situ velocity measurements via ultrasonic image velocimetry (UVI). To prevent wall slip, it can be equipped with exchangeable 3D-printed surfaces. Thus, it is possible to adjust the rheometer to the investigated material, concerning its particle size distribution. The apparatus dimensions are scaled up to measure suspensions containing particles up to 5 mm while maintaining a particle size to gap ratio that does not influence the bulk measurement. To this end, Newtonian, non-Newtonian (e.g. shear thinning) model fluids and model suspensions were investigated. Furthermore, as described above, the implementation of an in situ velocity measurement systems will be presented. The UVI measurement allows for the investigation of wall slip and migration properties as well as the velocity field in general to monitor the system. Additionally, the direct measurement of the flow properties creates valuable input and calibration data for simulations.

Characterizing the effect of relative humidity on rheological properties

The rheology of a wide range of materials can be strongly influenced by environmental conditions including temperature and humidity. In polymeric materials, exposure to humid environments can lead to significant changes in the modulus and glass transition temperature depending on the amount of moisture absorbed - this behaviour is often attributed to the diffusion of water inside the sample, effectively acting as a plasticiser that “lubricates” the polymer chains. Such dramatic changes in the material properties can adversely affect the performance of products such as packaging materials and has important implications on the customer perception of food stuff quality and safety. Hydroscopic materials are particularly sensitive to atmospheric water content and products like silicone sealants and adhesives that make use of specific chemistries to drive the curing reaction that could be affected by humidity. Similarly, geographic variations in environmental conditions during the transportation and storage of industrial products like paints and coatings could affect its end use properties. In this study, we report data demonstrating the effect of relative humidity and temperature on the curing of paint films, adhesives, and the tensile moduli of fuel cell membranes. The results underscore the effectiveness and sensitivity of the experimental approach, using a specially designed environmental chamber capable of controlling both temperature and relative humidity, to explore the impact of environmental conditions on material properties. We also discuss the use of novel geometries that are designed to ensure rapid, uniform, and homogeneous diffusion into the sample, which is another key factor in any such studies.

Dynamic oscillatory testing and viscoelastic characterization of aqueous fluids under pressure

Characterizing viscoelastic properties of fluids at temperatures above boiling poses significant challenges, most notably the boiling of volatile ingredients resulting in changes to material composition. Various methods and apparatuses have been employed to trap solvents or suppress evaporation; these slow compositional changes at higher temperatures but are ineffective beyond the boiling point. A pressurized testing environment is the only means to characterize the rheological properties of materials under such conditions. Many commercialized rheometer pressure cells are inherently limited in torque sensitivity due to the reliance on mechanical bearings. These limit the measurable range of shear stresses and viscosities, and confine testing to steady shear protocols. Naturally, this precludes the measurement of important viscoelastic properties and alters structured fluids such as gels and suspensions, where steady shear suppresses the modulus of the fully formed structure and does not accurately represent the quiescent state properties. In this poster, we demonstrate the viscoelastic characterization of aqueous solutions through dynamic oscillatory testing using a novel flow cell that provides atmospheric pressure and temperature control in a controlled-strain shear rheometer. The absence of a mechanical bearing provides the low torque sensitivity required for dynamic testing. Evidence of functionality will be demonstrated using gelling solutions, dilute polymer solutions, and various suspensions and emulsions.
The effect of viscosity, yield stress, and surface tension on the deformation and breakup profiles of fluid filaments stretched at very high velocities
Malcolm R. Mackley¹, Rudy Valette², Elie Hatchem², Mehdi Khalloufi², Anselmo Pereira², and Simon Butler³
¹Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, Cambridge CB3 OAS, United Kingdom; ²CEMEF, MINES ParisTech, PSL - Research University., Sophia-Antipolis, Sophia-Antipolis 06904, United Kingdom; ³Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, Cambridge CB3 OAS, United Kingdom

The fast stretching of fluid filaments to form either drops or broken threads is sensitive to both fluid rheology and surface tension and in this presentation numerical tools are used to simulate the behaviour and compare simulations with experimental results. The simulation uses finite element techniques and the free surface is tracked using a level set method. By using mesh adaptation it was possible to simulate both Newtonian and yield stress fluids during rapid stretching between moving pistons and capture the deformation, breakup and final form behaviour in the ms time scales. The simulations are able to show clearly how Newtonian viscosity, surface tension and Bingham yield stress all influence the deformation in different ways. Initially, the simulations were tested against matching experimental observations for low and high viscosity Newtonian fluids and both the experimentally observed end pinching for low viscosity fluids and the longer time scale linear filament thinning for the higher viscosity fluid were successfully matched with the experimental results. A further selection of complex fluids with yield stress characteristics was also experimentally tested and the simulation matched using a Bingham and or Carreau-Yasuda constitutive equation. By suitable adjustment of the constitutive parameters to match experimental stress sweep rheological data, the filament deformation simulations were in general able to give realistic agreement with the experimental observations. The paper provides a key for understanding liquid droplet formation in general and shows clearly how both surface tension and fluid rheology influence breakup behaviour.

Normal stresses in yield stress materials
Tatiana N. Rochinha, Priscilla R. Varges, and Paulo R. de Souza Mendes
Department of Mechanical Engineering, Pontificia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Rio de Janeiro 22451900, Brazil

This work investigates the rheological properties in the normal direction of elastoviscoplastic materials. We analyze the fluid's normal stresses under shear in order to better comprehend the phenomena that surround the stress tensor of a viscoplastic material. Due to the complexity of the experiments needed to characterize this behavior, a procedure to measure the normal stresses while the fluid undergoes steady and transient rheological tests under shear was developed. Oil and air were tested to insure the validation of the transducer used. Hair gel was used for the transient and steady-state experiments. Firstly, it was observed that residual stresses in viscoplastic materials deeply affect the measurements of the normal stresses. Considering low shear rates, for a hair gel, a substantial value is found for normal stresses in comparison to the yield stress. Among other findings, it was found that the time needed to reach a steady state while measuring normal stresses is longer than that of the shear properties of yield stress materials.

Flow behavior of electrode pastes for Lithium-Ion Batteries
Ronald Gordon and Norbert Willenbacher
Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, Baden Württemberg 76131, Germany

Lithium-Ion Batteries (LIB) show great potential for stationary energy storage and electric mobility. The manufacturing process of the electrode is decisive for the battery performance. Electrodes consist of metallic current collectors coated with electrode pastes. In addition to active material, these pastes contain, carbon black as a conductivity enhancer and polymers as binder. Polymeric binders may be added as a thickener to control the flow and hence the processing behavior. Furthermore, they can act as dispersing agents for active materials or carbon black particles, thus strongly determining the component distribution in dry electrodes. Therefore, the adsorption of Carboxymethylcellulose (CMC) on LiFePO₄ and carbon black particles was investigated. The resulting flow behavior of the electrode pastes as a function of CMC and solid particle concentration was thoroughly characterized using rheological measurements. Yield stress and viscosity exhibit a pronounced minimum with increasing CMC concentration, indicating that CMC acts as dispersing agent at low concentrations and as a thickener at higher concentrations when the equilibrium adsorption concentration is exceeded. Furthermore, higher solid particle concentrations shift the equilibrium adsorption concentration to higher CMC fractions due to the increased internal surface. Measurements of carbon black free pastes and carbon black slurries yield an analogue effect of CMC on the flow, suggesting that the polymeric binder acts as a dispersing agent for LiFePO₄ as well as carbon black particles. Finally, lower molecular weights result in lower CMC concentrations needed to cover the equilibrium adsorption. Accordingly, the proper selection of binder concentration and molecular weight leads to homogeneous solid particle distribution and tunable flow behavior, offering a pathway to customize paste processing properties and improve electrochemical performance of the battery.
Tuesday 18:30 Mediterranea

**Influence of compacting times and pressures on rheological properties of kaolin and sawdust ceramic powder mixtures**

Emese Kurovics\(^1\), Jamal E. Ibrahim\(^1\), and László A. Gömze\(^2\)

\(^1\)Institute of Ceramics and Polymer Engineering, University of Miskolc, Miskolc 3515, Hungary; \(^2\)IGREX Engineering Service Ltd., Igrici 3459, Hungary

In this research the compacting and rheological properties of kaolin and sawdust powder mixtures were examined depending on compacting pressures and times. On the basis of the achieved relative compaction curves as function of forming pressure and time the authors could successfully describe the changes of rheological behavior and rheological model of these powder mixtures having different particle compactions and size distributions. Increasing the compression pressure and changing the composition ratio of the kaolin and sawdust powder mixtures considerable changes of rheological properties could be observed. In this work the authors have shown how the compacting deformations of cylindrical specimen are depended on material composition, forming pressures and times. Based on their research the authors could successfully illustrate also how the rheological behaviors and models of kaolin-sawdust ceramic powder mixtures are depending on forming pressures. Keywords: ceramics, compacting, deformation, pressure, rheological model

Tuesday 18:30 Mediterranea

**Influence of compacting times and pressures on rheological properties of zeolite and alumina ceramic powder mixtures**

Jamal E. Ibrahim\(^1\), Emese Kurovics\(^1\), and László A. Gömze\(^2\)

\(^1\)Institute of Ceramics and Polymer Engineering, University of Miskolc, Miskolc 3515, Hungary; \(^2\)IGREX Engineering Service Ltd., Igrici 3459, Hungary

In this research the compacting and rheological properties of zeolite and alumina powder mixtures were examined depending on mineral compositions, compacting pressures and times. On the basis of the achieved relative compaction curves as function of forming pressure and time the authors could successfully describe the changes of rheological behavior and rheological model of these powder mixtures having different particle compactions and size distributions. Increasing the compression pressure and changing the composition ratio of the zeolite and alumina powder mixtures considerable changes of rheological properties could be observed. In this work the authors have shown how the compacting deformations of cylindrical specimen are depended on material composition, forming pressures and times. Based on their research the authors also could successfully illustrate how the rheological behaviors and models of zeolite-alumina ceramic powder mixtures are depending on forming pressures. Keywords: alumina, powders, pressures, rheological models, zeolite

Tuesday 18:30 Mediterranea

**Rheological studies of cordierite feedstocks for CIM processing**

Cristina Berges, Alberto Gallego, and Gemma Herranz

INEN-ETSI Industriales, University of Castilla-La Mancha, Ciudad Real 13071, Spain

In the recent years, the search for low-cost ceramics but showing remarkable properties to replace alumina and zirconia has been demanded from an industrial point of view. Cordierites have been suggested as a viable alternative, since they have demonstrated good mechanical and thermal properties, exhibiting superior thermal shock resistance. Therefore, this refractory and cheaper material can be attractive for aerospace, electrotechnics high temperature applications and consumer goods sectors. However, the key factor to introduce these ceramics into new markets is the development of a competitive production process of the desired components. Ceramic Injection Moulding (CIM) technology has been presented as a cost-efficient processing method to produce highly complex geometries at high-volume production scale. In this way, both issues of final component cost and new markets generation are addressed. The fabrication of appropriate feedstocks to be processed by CIM is crucial to achieve optimal ceramic parts, which implies the knowledge of its viscosity behavior and the prediction of temperature and shear rate influence.

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Tuesday 18:30 Mediterranea

**Rheological behaviour of highly-filled polymers for metal injection moulding**

Marko Bek\(^1\), Joamin Gonzalez-Gutierrez\(^2\), Lidija Slemenik Perše\(^3\), Clemens Holzer\(^2\), and Christian Kukla\(^3\)

\(^1\)Center for Experimental Mechanics, University of Ljubljana, Ljubljana 1000, Slovenia; \(^2\)Institute of Polymer Processing, Montanuniversitaet Leoben, Leoben, Styria 8700, Austria; \(^3\)Industrial Liaison, Montanuniversitaet Leoben, Leoben, Styria 8700, Austria

Metal injection moulding (MIM) is a versatile technology used for the mass production of small metallic parts with complex geometry. MIM makes use of highly-filled polymers with metal particles that can be sintered after the polymer is removed to obtain a solid metallic part. The polymeric components of the MIM feedstock serve as a processing aid to transport and shape the metallic particles in an injection moulding machine. Thus, the rheological behaviour of MIM feedstocks is critical to ensure the quality of the produced parts by the MIM process. There are many factors that affect the rheology of MIM feedstocks, including the binder composition, amount of filler particles, particle size and shape, and as it is shown in this study the chemical composition of the filler particles. Particles with the same shape and a comparable size distribution of steel, titanium and aluminium were introduced into a fixed binder system at 30, 45 and 60 vol% concentrations. Small amplitude oscillatory tests were performed on all of the materials at a constant temperature. It was observed that depending on the chemical nature of the particle the rheological properties (complex viscosity, storage and loss moduli) were affected differently as the powder content increased from 30, 45 to 60 vol% for the different metallic alloys.
Effect of SiO$_2$ nanoparticles on drying process condition on the PEO-based solid polymer electrolytes

Sun Kyung Kim and Kyu Hyun
School of Chemical and Biomolecular Engineering, Pusan National University, Pusan, Republic of Korea

Rechargeable secondary batteries are necessary in modern society. In particular, as alternatives of Liquid electrolytes, Solid Polymer Electrolytes (SPEs) are investigated due to the advantage of safety and ease of fabrication. Among the SPEs, PEO-based SPEs are widely studied but have low ionic conductivity. This is because poly (ethylene oxide) (PEO) have semi-crystalline nature. To achieve the improvement of the ionic conductivity, many researchers add additives such as plasticizer, inorganic filler and ionic liquid. In SPEs, the ionic conductivity exhibits by movement of cation by polymer segmental motion. Addition of additives decreases the crystallinity of polymer matrix, which increases the ionic conductivity by two or three orders of magnitude. SPEs need the ionic conductivity of more than 10$^{-3}$S/cm for application as secondary batteries but the effect of additives is limited. In this study, therefore, the PEO-based SPEs are prepared with sodium perchlorate as salt by solution casting method. We dissolved PEO into distilled water as alternatives of organic solvent which is toxic. In addition, 1-butyl-3-methylimidazolium thiocyanate and SiO$_2$-nanoparticle (SiNP) are added for the increase of ionic conductivity. Especially, to investigate the effects of SiNP in detail, SPEs are prepared with different size and various concentration of SiNP and analyzed by rheological and electrical property. Furthermore, for additional increase of the ionic conductivity, we changed drying process condition during the evaporation of water. The effects of the drying process condition are investigated with drying equipment which can calculate weight variation by heat flux measurement. By correlation of electrical property with rheological property and heat flux measurement data, we plan to find optimum process for SPEs preparation.

Microscopic flows of a Carbopol gel in the presence of wall slip

Eliane Younes, Cathy Castelain, and Teodor Burghlea
Laboratoire de thermique et énergie de Nantes, Nantes 44306, France

A systematic experimental study of steady microscopic flows of a Carbopol gel in wide range of flow rates is presented. By means of epifluorescent microscopy combined with a customly developed Digital Particle Image Velocimetry too we measure transversal profiles of the axial velocity and identify three distinct flow regimes: full plug, partial plug and fully yielded. Corresponding to each flow regime, the wall velocity gradients and slip velocity are obtained. Furthermore, by combining the flow field measurements with the macro-rheological measurements of the flow curves, we identify scaling laws of the slip velocity with the wall shear stress.

Comparison of the fracture characteristics of myofibrillar protein gels evaluated by punch penetration, tensile, and torsion test and digital images upon the fracture

Hyeon Woo Park and Won Byong Yoon
Food Science and Biotechnology, Kangwon National University, CHUNCHEN, Gangwon-do 24341, Republic of Korea

Fracture properties of food gel known as physical properties having a high correlation with sensory attributes were analyzed to determine the structure-failure relation. Fracture properties of surimi gels made with or without dried egg white (SG-EW), whey protein concentrate (SG-WP) and potato starch (SG-PS) were measured under penetration, tensile and torsion. The relationships of textural properties related to the hardness and deformation of surimi gel without any ingredient (SG) showed linear functions (R$^2$ > 0.90 and 0.85, respectively). However, R$^2$ values of tensile strain and shear strain of surimi gel made with egg white (SG-EW) and whey protein (SG-WP) were significantly lower than that of SG. Local strain values concentrated in surimi gels regardless of ingredient addition were estimated by digital image correlation (DIC) analysis. Local strain values concentrated in SG-EW and SG-WP were significantly higher than SG (P < 0.05). To minimize the effect of local strain concentrated at fracture, tensile strain and shear strain values were estimated. Based on the tensile strain and shear strain, the estimated textural properties of SG-EW and SG-WP were significantly higher than the actual values, but no significant difference was found for SG (P > 0.05). DIC analysis was an effective tool to estimate the characteristics of surimi gels, with and without added ingredients, upon fracture from penetration, tensile, and torsion. This study demonstrated that a simple tensile test showed a high correlation to characterize the protein gels’ failure properties.

Agarose-k-carrageenan-based hydrogel films enriched with natural extracts for wound healing applications

Lorena Anna Ditta$^1$, Fiorenza Provenzano$^1$, Radha Santonocito$^1$, Estella Rao$^1$, Maria Assunta Costa$^1$, Rosa Passantino$^1$, Maria Antonietta Sabatino$^1$, Clelia Dispenza$^2$, Pier Luigi San Biagio$^1$, Daniela Giacomazza$^1$, and Romano Lapasin$^3$
$^1$Istituto di BioFisica, Consiglio Nazionale delle Ricerche, Palermo 90146, Italy; $^2$Dipartimento dell’Innovazione Industriale e Digitale, Università degli Studi di Palermo, Palermo 90128, Italy; $^3$Engineering and Architecture Department, University of Trieste, Trieste, Italy

Hydrogels are 3D hydrophilic networks that can hold significant amounts of water within their structure, without dissolving in water. They can offer a combination of favorable properties, including high absorbency of biological fluids, biocompatibility, biodegradability, stimuli-responsiveness, high storage capacity and release ability of small and large therapeutic molecules. The hydrogel films designed for wound dressing may accomplish several functions, playing an important role in the healing processes. They can absorb and retain the wound exudates, stimulating fibroblast proliferation and keratinocyte migration and promoting re-epithelialization. Furthermore, they can incorporate and release bioactive molecules allowing a faster healing process. Materials used to make hydrogel films for wound dressing have been synthetic polymers, but more recently, collagen, hyaluronic acid and chitosan have been employed as main components of hydrogel dressings for their active involvement in the wound healing process and new tissue generation. The main components of the films here proposed are agarose...
(AGA, 2.0% w/w) and increasing amount of k-carrageenan (k-Car, 0.5, 1.0 and 1.5% w/w) mixed with two different concentrations of glycerol (Gly, 5 and 10 w/w) in order to obtain an optimal combination of softness and conformability. During preparation, the polymers were added of natural extracts obtained by Cryphea heteromallia, a bryophyte species living in the Mediterranean area and possessing a strong antioxidant machinery that makes it able to survive in unfavorable environments. All the films (AGA_k-Car_Gly) have been characterized in terms of dynamic rheological properties and ability to absorb fluids. Furthermore, their biocompatibility has been tested in vitro in NIH 3T3 cell model.

Tuesday 18:30 Mediterranean PO74

Structural, micro- and macrorheological properties of alginate solutions as bioink for 3D bioprinting
Bruna R. Maciel, Claude Oelschläger, and Norbert Willenbacher
Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany

In the last decade, interest in the field of 3D bioprinting has increased enormously. One of the most important components in bioprinting is the bioink, which is crucial for the development of tissue engineering. In this study, we have used classical rotational rheology and two microrheology methods, namely Multiple Particle Tracking (MPT) and Diffusing Wave Spectroscopy (DWS) to get new insight into structural and dynamical properties of bioinks composed of pure alginate dissolved in water, phosphate buffered saline (PBS) and DMEM cell media.

We found very good agreement between linear viscoelastic properties obtained from bulk rheology and DWS. DWS results obtained at high frequencies (up to MHz) also allow to derive directly the terminal relaxation time $\eta_0$, the plateau modulus $G_\infty$ and for the first time the persistence length $\ell_p$ of alginate solutions. Consistent values of $\ell_p$=10 nm were obtained. Additionally, the scaling exponents describing the concentration dependence of the specific viscosity $\eta_\ell$, $\ell_p$ and $G_\infty$ have been investigated in the entangled regime. In water and PBS solutions, the exponent for $\eta_\ell$ agrees well with the one predicted for neutral polymers in good solvents, whereas in DMEM it is slightly higher and agrees with the one for polymers in a theta solvent. Finally, we used the MPT technique to characterize micromechanical and microstructural properties of pure alginate solutions and alginate–pre-crosslinked with calcium chloride. Pure alginate exhibits a homogeneous structure independently of the solvent used. In contrast, the structure of crosslinked alginate shows very strong heterogeneities on the μm-scale with the formation of viscous inclusions within a highly elastic matrix in both PBS and DMEM solutions. These results will help to better understand the relationship between the bioink’s microstructure before printing and cell viability as well as 3D construct resolution after the printing process.

Tuesday 18:30 Mediterranean PO75

Texture profile analysis of hybrid chitosan scaffolds
Piotr Owczarz and Anna Ryl
Department of Chemical Engineering, Lodz University of Technology, Lodz, Poland

A low concentrated, chitosan colloidal solutions have a specific ability to undergo a sol-gel phase transition induced by an temperature increase. At room temperature, they are shear thinning fluids with low apparent viscosity and undergo a phase transition at the body temperature. This allows the injection application and formation of a gel structure (scaffold for tissue engineering) in vivo, directly in the damaged tissue. The main disadvantage of chitosan scaffolds is their low mechanical resistance to compression and stretching, which can be improved through the use of hybrid systems with collagen or calcium phosphate ceramics. The aim of the work was to determine the influence of chitosan molecular mass and the type/concentration of filling material (e.g. calcium carbonate, fish collagen) on the mechanical properties of hybrid chitosan gels. The pH value and the sol-gel phase transition temperature were controlled by the addition of β-glycerophosphate salts, disodium (Na2GP) and calcium (CaGP). The mechanical properties of the obtained hydrogels were determined by standard TPA test carried out at 37°C using a Brookfield CT3 Texture Analyzer. The determined texture parameter values indicate that the mechanical properties of the hybrid gel depend on both the molecular weight of the polymer, the type of solvent and the neutralizing substance as well as the type and concentration of the filler. It has been found that in order to obtain scaffolds with the best mechanical parameters, the commonly used Na2GP salt should be added to low molecular weight chitosan solutions, while the addition of CaGP is suggested for high molecular weight chitosan solutions. Supplementing these systems with calcium carbonate resulted in additional strengthening of the structure. Thus, such systems are a promising material as an injectable scaffolds for bone tissue engineering, due to mechanical strength of the gel phase as well as the chemical composition similar to hydroxyapatites.

Tuesday 18:30 Mediterranean PO76

Influence of rotational pre-shearing on the conditions of the sol-gel phase transition of chitosan colloidal solutions
Anna Ryl, Piotr Owczarz, and Marek Dziubinski
Department of Chemical Engineering, Lodz University of Technology, Lodz 90-924, Poland

The chitosan colloidal solutions have the ability to undergo a sol-gel phase transition, thereby forming highly cross-linked porous structures. Recently, application of chitosan in regenerative medicine as a thermosensitive hydrogels is observed. These systems, properly designed, undergo a phase transition at a temperature close to the human body and under physiological pH conditions, which creates the possibility of using them as scaffolds in tissue engineering and controlled drug release systems. However, the injection application and the unidirectional forces created during it can significantly affect the phase transition conditions. Disentangling and ordering the chains along the shear field may consequently affect the ability to form a highly cross-linked structure and the kinetics of this process. The effect of unidirectional shear on the gelation conditions of chitosan solutions was determined by short-term rotational shear, in the wide shear rate range. Next, standard oscillatory measurements at constant deformation under non-isothermal (5-60 °C) and isothermal (at 37 °C) conditions were carried out to determine the temperature and kinetic of the sol-gel phase transition, respectively. The duration of the initial shear interval was also analyzed at a constant shear rate value. Based on the conducted oscillatory measurements preceded by short-term rotational shearing, it was found that the increase in applied shear rate decelerate the kinetics of sol-gel phase transitions of colloidal chitosan solutions. Regardless of the applied heating rate, an increase in the temperature of the sol-gel phase transition with the increase of the shear rate in the pre-shearing interval was
observed. Moreover, it was found that the increase in deformation in the pre-shearing interval leads to a weakening of the formed gel structure. Simultaneously, there was no influence of the rotational pre-shearing duration on the sol-gel phase transition conditions.

**Tuesday 18:30 Mediterranean**

**Assessment of the rheological behaviour of hydrogels formulated with starch isolated from discarded potatoes**

Patrícia Fradinho¹, Anabela Raymundo¹, Isabel Sousa¹, Hermínia Dominguez², and María Dolores Torres²
¹LEAF Research Center, Instituto Superior de Agronomía, University of Lisboa, Lisboa 1349-017, Portugal; ²Department of Chemical Engineering, Universidad de Vigo, Campus Ourense, Science Faculty, Ourense 32004, Spain

An increasing demand for renewable sources to produce natural biopolymers has been observed for food and non-food applications, as they offer lower environmental costs. Potato is most used as a source for industrial starch production, since the extraction procedure is simple in comparison to cereal starches. When trading potato there is a high discarding degree, up to 30% in our region, due to undersized potatoes, which currently is primarily used for animal feed. In this context, the objective of this work was the recovery of starch from discarded local potatoes and the assessment of the mechanical properties of the corresponding hydrogels. For this purpose, three potato varieties (Kennebec, Neiker and Agria) kindly supplied by INORDE were used. After extraction, potato starch hydrogels were prepared in a broad range of starch content (10-30%) and gelling temperatures (60-90 °C). Rheological behaviour of hydrogels was assessed by SAOS (heating/cooling cycles, maturation kinetics, mechanical spectrum), as well as Texture Profile Analysis. Hydrogels exhibited comparable properties to those commercially available. Starch yield, post-harvest storage and gelling temperature played a relevant role in the final mechanical properties of the hydrogels. Depending on the processing conditions, a set of gelled matrices for a broad range of potential applications from personal care products to pharmaceuticals could be obtained. We would like to emphasize the societal value of rheology by demonstrating its importance on the characterisation of the performance of the materials for everyday life and industrial applications.

Acknowledgements: Financial support (INOU 2018) from the Diputación Provincial de Ourense, University of Vigo and Fundação para a Ciência e a Tecnologia (Portugal) through the research unit UID/AGR/04129/2013 (LEAF). P.F. acknowledges her PhD Grant (refª C0144M) from University of Lisbon. M.D. Torres thanks the Ministério de Economía, Industria y Competitividad for her postdoctoral grant (IJC-2016-27535).

**Tuesday 18:30 Mediterranean**

**Effect of pH on gelation in aqueous xanthan solutions in the presence of multivalent ions**

Andrey Shibaev¹, Dmitri Muravlev², Dmitri Mityuk², and Olga Philippova¹
¹Physics department, Moscow State University, Moscow 119991, Russia; ²Gubkin Russian State University of Oil and Gas, Moscow 119991, Russia

Natural polysaccharides are very promising for applications as thickeners, since they are available, biocompatible, biodegradable and can form gels with sufficient elastic properties at very low polymer concentrations. Gelation is usually promoted by multivalent metal ions, which can cross-link polymer chains with each other into a 3D-network. Polysaccharide gels cross-linked by metal ions find vast application in oil industry as fluids for water shut-off. However, the ability of certain types of ions to cross-link polysaccharides and the cross-link energy strongly depend on the external conditions, such as pH, which determines the degree of charge of polymer chains, as well as the equilibrium of the cross-linking reaction. Therefore, this work is aimed at the investigation of the effect of pH on cross-linking of xanthan macromolecules in aqueous solutions by Cr³⁺ and Al³⁺ ions. It was shown that pH has a different influence on xanthan cross-linking by either Cr³⁺ or Al³⁺. In the case of Cr³⁺ ions, the gelation occurs at neutral and weakly acidic pH; however, at pH lower than ~ 4.5 the gel becomes weaker and transforms into a liquid with low viscosity. It is due to the fact that at these pH values polymer chains are uncharged, and in order to form a cross-link, Cr³⁺ ions need to replace protons in acetate units, which proceeds more easily with increasing pH. When Al³⁺ is used, gel is formed only at neutral and weakly basic conditions, which indicates to the lower ability of Al³⁺ to replace protons in acetate units. Moreover, gelation time for Cr³⁺ ions is much higher than for Al³⁺ ions, but the gels formed by Cr³⁺ cross-links have much stronger mechanical properties. These data suggest that the energy of cross-link is higher for Cr³⁺ than for Al³⁺. Acknowledgement. The reported study was funded by RFBR according to the research project N 18-33-01171 mol_a.

**Tuesday 18:30 Mediterranean**

**Soft nanocomposite with natural nanoclay**

Vyacheslav Molchanov, Marina Efremova, and Olga Philippova
*Physics Department, Moscow State University, Moscow 119991, Russia*

The present study is devoted to soft nanocomposite based on network of wormlike micelles (WLMs) composed of zwitterionic and anionic surfactants with embedded plate-like bentonite nanoclay particles. It is shown that nanoparticles enhance significantly the rheological properties of WLM hydrogel acting as physical cross-links between micellar chains. It was explained by the formation of micelle-nanoparticle junctions as a result of binding of the WLMs end-caps to the layer of surfactant adsorbed on the particle surface. The networks under study possess gel-like properties. In particular, their rheological properties demonstrate plateau modulus, low values of loss factor. At the same time, under high deformation, the micellar chains are disrupted, which induces a much more pronounced drop of viscosity than the disruption of physical cross-links in polymer gels. The disrupted micellar chains were completely recovered due to restoration of non-covalent bonds between surfactant molecules within the micelle. It was demonstrated that the prepared nanocomposite hydrogels possess promising properties for injection applications and can be used as controlled release delivery systems.

This work was financially supported by the Russian Science Foundation (project N 17-13-01535).
**Synthesis and properties of epoxy-silica vitrimer nanocomposites**

Anna Barabanova¹, Olga Philippova², and Alexei Khokhlov³

¹Institute of organoelement compounds of RAS, Moscow 119991, Russia; ²Physics Department, Moscow State University, Moscow 119991, Russia; ³Ulm University, Ulm 89081, Germany

Epoxy-silica vitrimer nanocomposites (VNs) were processed by curing of commercial epoxy monomer 4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate ERL-4221 with 4-methylhexahydrophthalic anhydride in the presence of zinc acetylacetone as a transesterification catalyst and 10-15 nm silica nanoparticles (NPs) with phenyl and anhydride functional groups as a filler. It was demonstrated that the introduction of modified NPs did not hinder the rearrangement of the network topology, which allow to retain the most important properties of vitrimers - ability to reprocessing and remolding as well as to self-healing and welding. Moreover, the NPs strengthen the polymer matrix. Introduction of negligible quantity of modified NPs ([SiO2] ≤ 0.5 and 1.0 wt. %) leads to increase of strength of welded joint of two assemblies of VNs. The materials with anhydride-modified NPs show the highest efficiency of welding: the separation forces for VNs with 1 wt. % of phenyl- and anhydride-modified NPs were 83 and 94 N in comparison with 45 N for epoxy vitrimer. The modification of NPs surface by grafting of phenyl and anhydride functional groups providing non-covalent (Van-der-Vaals interaction) and covalent bonds with epoxy network, respectively, improves their dispersion in polymer matrix and accelerates the relaxation process.

This work was supported by Russian Foundation of Basic Research (project #18-53-76007).

**Functional hydrogels of a flexible hydrophilic polymer mixed with wormlike surfactant micelles**

Andrey Shibaev and Olga Philippova

Physics Department, Moscow State University, Moscow 119991, Russia

Surfactant molecules can self-assemble into giant cylindrical (wormlike) micelles, which are formed by weak non-covalent interactions and are "dynamic" - they can reversibly break and recombine or respond to different external stimuli. However, due to their labile structure, wormlike micellar solutions usually possess mechanical properties much weaker than "traditional" polymer gels. Rheological properties of the micellar networks can be enhanced by the addition of polymer chains, which do not break and recombine and thus strengthen the network. The aim of this work is to study hydrogels formed by wormlike surfactant micelles and a hydrophilic polymer - poly(vinyl alcohol). It was shown that the addition of polymer results in the increase of viscosity of the solutions by 2 orders of magnitude as compared to each individual component, and the appearance of a well-defined plateau at the frequency dependence of the storage modulus, which is due to the formation of entanglements between polymer and micellar chains and formation of a common polymer-micellar network. Above a certain polymer concentration, the rheological parameters become constant, which is explained by microphase separation with the formation of domains enriched by either wormlike micelles or polymer chains, due to the existence of weak repulsion between polymer and micelles. The formation of microphase separated structure was confirmed by SANS. The addition of a hydrocarbon to the polymer-surfactant network results in the decrease of viscosity by 6-7 orders of magnitude and complete loss of viscoelastic properties, which is explained by disruption of wormlike micelles. Thus, polymer-micellar networks combined enhances viscoelastic properties with functional properties, e.g. responsiveness to hydrocarbons, and are very promising for applications as thickening agents in oil industry.

Acknowledgement. The reported study was funded by RFBR according to the research project N 19-03-00879 a.

**Modelling of tape flow under roller of PEI-CF/PEEK hybrid thermoplastic composites manufactured by laser-assisted automated-tape-placement**

Gilles Ausias, Omar Baho, and Julien Férec

IRDL - UMR CNRS 6027, Université Bretagne Sud, Lorient, Bretagne 56321, France

The manufacturing time of aircraft is becoming increasingly important because of the increase in production rates of aircraft. This constraint leads the growing interest of thermoplastic composite materials by using an additive manufacturing out of autoclave such as in-situ automated fibre placement (AFP). The PEEK (poly-ether-ether-ketone) and PEI (polyetherimide) are high-tech polymers, which are characterized by high temperature resistance. The tape is made with a layer of APC2 (PEEK + carbon fibers) between two thin layers of PEI. However, the use of AFP is slow in aerospace applications due to various AFP process parameters and difficulties of processing at high temperature. Recently, the diode laser heating source being the most solution of AFP owing to its capability of focusing higher intensity at a localized point. In this process laser can be heating both incoming tape and substrate. After being heated with a laser the thermoplastic is welded with the help of a roller onto a substrate made up of layers of tapes welded onto one another. Under the roller, the thermoplastic flows and the tape reaches its final thickness. Pressure and temperature are required to achieve a good bond. In this study, a numerical simulation was performed to get the temperature field into the tape under the roller. Then, rheological modelling is carried out to simulate the polymer flow under the roller and obtain the pressure field. Finally, the consolidation level between the substrate and the tape can be calculated. The bonding achievement can be predicted using indicators as degree of intimate contact according to the roller velocity, the laser power density and the force applied by the roller.

The NHYTE project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 723309.
The process of electrospinning was applied to solutions of poly(ethylene oxide) (PEO) in distilled water. An increase of mean nanofibre diameter with polymer molecular weight (4 different PEO) and polymer concentration (concentrations chosen with respect to spinnability) was expressed by a simple relationship quantifying this dependence within an experimental error. Further, another relationship was proposed for expressing shear viscosity of the entry polymer solution through corresponding molecular weight and concentration. The results show a possibility to prepare PEO nanofibrous mats with prescribed mean nanofibre diameter. The proposed relationship provides an instruction which PEO material and at which concentration should be chosen if we want to obtain a nanofibrous mat with the required nanofibre diameter. These results were obtained for PEO solutions in water; however, it is possible to expect that similar expressions could be derived for other materials.

Acknowledgement: The authors wish to acknowledge GA CR for the financial support of Grant No. 17-26808S.

Tuesday 18:30 Mediterranea

Electrospinning - dependence of poly(ethylene oxide) mean nanofibre diameters on concentration and molecular weight

Petra Peer and Petr Filip
Institute of Hydrodynamics of the Czech Academy of Sciences, Prague, Czech Republic

The suspensions of soft microgels can be concentrated far beyond a volume fraction of random close packing. Such dense microgel suspensions (pastes) behave as soft elastic solids with finite equilibrium shear modulus (G0) below the critical stress (σc) whereas they flow like liquid above σc. The present study focuses on the effects of size- and stiffness disparities in the constituent microgels on the elastic and flow properties of the pastes. The binary blends are made by mixing the pastes with the same apparent particle volume fraction at various weight fraction of soft microgels (fSO). The G0-fSOA relations for the binary pastes is considerably affected by size-disparity. When the size-disparities are small, the relation obey the logarithmic mixing rule. When size-disparities are large, they have a wide fSOA-regime where G0 are very close to those of the single small-microgel pastes, regardless of whether the small microgels are soft or hard. This plateau region for the mixtures with large size-disparities is at G0, at which the steady-state flow behavior of the binary pastes is obtained the Herschel-Bulkley (H-B) equation and G0. In each binary paste, the characteristic time (τ) of the fast local dynamics of microgels trapped in the densely packed structures evaluated from diffuse wave spectroscopy (DWS) is close to τB. This agreement indicates that the dynamics of the position rearrangement of microgels in the steady-state flow is closely related to the fast local dynamics in the quiescent state of the pastes, independently of the size- and stiffness disparities in the constituent microgels.

Tuesday 18:30 Mediterranea

Comparing recycled and virgin poly(ethylene terephthalate) melt-spun fibers

Yijing Qin and Dirk W. Schubert
Institute of Polymer Materials, Friedrich-Alexander University Erlangen-Nuremberg, Erlangen, Germany

Five different poly(ethylene terephthalate) (PET) materials (two recycled and three virgin ones) were melt-spun into fibres using a capillary rheometer and aerodynamic stretching. In order to cover a wide range of processing parameters, two temperatures in combination with six different take-up pressures were used during the melt spinning process. The surface smoothness, diameter and mechanical properties of the PET fibres were investigated. Compared with other studies, this study provides comprehensive research on melt-spun PET fibres. One recycled PET and one virgin PET in this study showed acceptable tenacity, outstanding elongation at break and desirable fibre fineness in denier. The molecular and rheological properties of these materials were studied further and presented minor differences in weight-average molar mass and molar mass distribution as well as in their viscosity, which resulted in their similar processing behaviour. This study proved the possibility to make a fibre from bottle-grade recycled co-polymer PET with similar properties to the fibre-grade virgin homo-polymer PET, which could be a guidance for the PET melt spinning in the industry.

Tuesday 18:30 Mediterranea

Elastic and flow properties of dense microgel mixtures with size- and stiffness disparities

Saori Minami1, Ayaki Nakaishi1, Shun Oura2, Takumi Watanabe2, Daisuke Suzuki2, and Kenji Urayama1
1Kyoto institute of technology, Kyoto, Japan; 2Shinshu university, Shinshu, Japan

The suspensions of soft microgels can be concentrated far beyond a volume fraction of random close packing. Such dense microgel suspensions (pastes) behave as soft elastic solids with finite equilibrium shear modulus (G0) below the critical stress (σc) whereas they flow like liquid above σc. The present study focuses on the effects of size- and stiffness disparities in the constituent microgels on the elastic and flow properties of the pastes. The binary blends are made by mixing the pastes with the same apparent particle volume fraction at various weight fraction of soft microgels (fSO). The G0-fSOA relations for the binary pastes is considerably affected by size-disparity. When the size-disparities are small, the relation obey the logarithmic mixing rule. When size-disparities are large, they have a wide fSOA-regime where G0 are very close to those of the single small-microgel pastes, regardless of whether the small microgels are soft or hard. This plateau region for the mixtures with large size-disparities is at G0, at which the steady-state flow behavior of the binary pastes is obtained the Herschel-Bulkley (H-B) equation and G0. In each binary paste, the characteristic time (τCPE) of the fast local dynamics of microgels trapped in the densely packed structures evaluated from diffuse wave spectroscopy (DWS) is close to τB. This agreement indicates that the dynamics of the position rearrangement of microgels in the steady-state flow is closely related to the fast local dynamics in the quiescent state of the pastes, independently of the size- and stiffness disparities in the constituent microgels.

Tuesday 18:30 Mediterranea

Modelling the rheology of thixotropic elasto-visco-plastic materials

Stylianos Varchanis, Georgios Makrigiorgos, Pantelis Moschopoulos, Yannis Dimakopoulos, and John Tsamopoulos
Chemical Engineering, University of Patras, Patras, Greece

To describe the macroscopic rheological behavior of Thixotropic Elasto-Visco-Plastic materials (TEVP), phenomena that take place in their microstructure must be accounted for. To this end, we couple the tensorial constitutive model by Saramito for EVP materials with thixotropy, extending the ideas of Isotropic Hardening (IH), and with Kinematic Hardening (KH), to account for back stresses. We use a scalar variable that describes the level of structure at any instance and a modified Armstrong-Frederick KH equation, thus providing rules governing the dynamics of the apparent yield stress. The material viscosity, yield stress and back stress modulus feature a nonlinear dependence on the structural parameter, enabling the model to make accurate predictions with a single structural parameter. To avoid unphysical stress evolution in both shear and extensional flows, we propose a modified back stress constitutive equation that keeps the components of the stress tensor bounded. The predictions of the new model are compared to experimental data and predictions of previously proposed TEVP models in simple rheometric flows, including steady and step-shear tests, flow reversal, intermittent step tests, SAOS and LAOS. In most cases, the proposed model reproduces more accurately these experimental data than the other models, highlighting its predictive capabilities. Moreover, SAOS illustrates that introducing viscoplasticity via the Saramito model necessarily reduces G′ to zero in the linear strain regime. This calls
for model adjustments in the solid state. Finally, we examined the proposed model in uniaxial elongation and concluded that it is important to include this flow in the rheological characterization and modeling of such systems.

**Tuesday 18:30 Mediterranea**  
**Rheology and self-adhesion of uncrosslinked butadiene-acrylonitrile rubber**  
Valentine Hervio and Costantino Creton  
*Laboratory of Soft Matter Science and Engineering, ESPCI Paris, Paris 75005, France*

The adhesion of unvulcanized elastomers, to themselves (self-adhesion) or to other materials, is industrially very important for the manufacturing of rubbers, and in our specific case, for the fabrication process of helicopters’ fuel tanks.

We investigated the self-healing behavior of an unfilled and unvulcanized acrylonitrile-butadiene random copolymer (commonly called nitrile butadiene rubber NBR). We have shown that unlike more classical non-polar elastomers such as polyisoprene or polybutadiene, shows very poor self-adhesion properties. We suggest, supported by DSC and linear rheology experiments, that because of its polarity, our material tends to self-organize with time and form nano-clusters of polar groups. This organization can be seen as some physical crosslinking, preventing both the flow at low frequency in linear rheology, and the diffusion of the polymeric chains in the bulk and at the interface.

Different strategies were explored to disrupt these supramolecular objects knowing that when sheared at high temperature the material flows at low frequency. First, we blended NBR with small molecules (tackifiers), expecting that for polar tackifiers, the polar clusters could be disrupted. Second, we impregnate the surface of the elastomer with solvent to break and dilute the physical interactions between polar groups, and accelerate the interdiffusion of the polymer at the interface between two pieces of uncrosslinked NBR.

We find that while the rheological properties are not much affected, both strategies are efficient in improving significantly the self-adhesive properties and we will discuss critically the possible reasons for this discrepancy between rheology and improvement in self-adhesion.

**Tuesday 18:30 Mediterranea**  
**Cooperative breakup induced by drop-to-drop interactions in one-dimensional flows of drops against micro-obstacles**  
Pascal B. Panizza, Alexandre Schmit, Louis Salkin, and Laurent Courbin  
*Matière Molle, IPR, Université Rennes 1, Rennes 35000, France*

The fragmentation of drops into smaller ones, when impacting a surface, is a phenomenon which occurs in Nature as well as in Industry. Examples include splashes of drops, essential for pesticide deposition, spray painting or ink-jet printing, as well as geometrically mediated drop breakup phenomena occurring in microfluidic devices. When addressing this topic, two key issues are to understand the necessary conditions to observe fragmentation and to predict the final droplet size distribution resulting from this process. Although, the breakup of single drops has drawn much attention for over a century, the parallel problem of the fragmentation of several drops in a sequence, yet essential for various applications, has become a topic of investigation only recently. Here, we study the fragmentation of a train of monodisperse drops flowing through a narrow conduct where a post is placed and against which the successive drops may break up into two daughter droplets or not. By changing the distance separating two consecutive drops, this system offers a unique opportunity to probe the influence of hydrodynamic interactions between successive drops at the scale of an individual fragmentation event. The complexity herein lies in the fact that the possible presence of fluid/liquid interfaces in the two channels on both sides of the obstacle alters the hydrodynamic resistance of these channels. This creates time-delayed feedback effects, whereby the breakups of preceding droplets influence the behavior of the subsequent droplets reaching the obstacle. We show that such effects may lead to sequences of breakup events in which the size of the daughter drops created upon breaking mother ones becomes a periodic function of time. We demonstrate the existence of numerous bifurcations between periodic breakup regimes and we establish diagrams mapping the possible breakup dynamics as a function of the governing physical parameters.

**Tuesday 18:30 Mediterranea**  
**Dynamic mechanical analysis of wood-plastic composites with varying filler ratios and the effect of accelerated weathering**  
Jaka Gašper Pecnik, Matthew Schwarzkopf, Michael Burnard, and Andreja Kutnar  
*Department of Technology, University of Primorska, Andrej Marusic Institute, Koper, Slovenia*

Wood plastic composites (WPC) have been in use for the last 40 years. They consist of two primary components, a wooden component in form of a particle or “wood flour” and a polymer matrix (Schwarzkopf & Burnard 2016). The majority of WPCs in Europe are used in terrace flooring which competes with natural wood (Feifel et al. 2015). Previous research using Life Cycle Impact assessment (LCIA) has shown that the introduction of wood content into polymer composites positively affects the environmental impacts of the products (Feifel et al. 2015). Furthermore, the addition of wood to plastic reduces the final price of the products as wooden particles often come as a byproduct of lumbar manufacturing (Schwarzkopf & Burnard 2016). The objective of this study was to assess how the amount of wood and artificial weathering affect the dynamic mechanical performance of WPCs.

Polypropylene (PP) and wood flour (WF) composites were obtained from an industrial partner. The composites had 50% and 60% (by weight) wood, with 47% and 37% PP with 3% processing additives (respectively). Half of each sample were exposed to artificial weathering conducted in a Q-LAB accelerated weathering unit, according to European standard EN 927-6. Dynamic mechanical analyses (DMA) was performed on an ARES RSA G2 testing machine to obtain the complex modulus and tan delta. The testing geometry was a single cantilever and specimens underwent a temperature ramp from the ambient room temperature (25 °C) to 130 °C. A 0.02 % loading strain at 1 Hz frequency was used to load the specimens.
At near 75 °C, specimens from pure PP start softening and showing a significant decrease in complex modulus. Un-weathed samples with 50 % and 60 % WF exhibit more stable behavior at elevated temperatures. Weathered samples of 50 % and 60 % WF showed a negative effect on mechanical properties, which may be related to UV degradation or swelling/shrinking of specimens exposed to water spray and heat cycles that damage the adhesion between the wood flour and PP matrix. The highest performing group were the un-weathered specimens with 60 % WF.


Efficiency of passive micromixers based on vortex shedding mechanism
Ahmad Fakhari1, Francisco J. Galindo-Rosas2, and Joaquín Ortega-Casanova3
1Departamento de Ingeniería Mecánica, CEFT, Facultad de Ingeniería da Universidade do Porto, Porto, Porto 4200-465, Portugal; 2Departamento de Ingeniería Química, CEFT, Facultad de Ingeniería da Universidade do Porto, Porto, Porto 4200-465, Portugal; 3Gruppo di Mecanica dei Fluidi, Escuela de Ingenierías Industriales, Universidad de Málaga, Málaga, Málaga 29071, Spain

Enhancing mixing efficiency of passive micromixers is a current challenge due to small dimensions leading to low Re numbers and, then, laminar diffusion governs the process. The main approach in the literature for increasing their efficiency consists of modifying the geometry of the microchannel so that the surface contact between the two fluids increases; such is the case of grooved, ribbed or sinusoidal micromixers. Alternatively, it is known that by adding an obstacle the efficiency of the micromixers can be increased by triggering the vortex shedding mechanism.

In this work we have designed thorough 2D and 3D numerical and experimental study the efficiency of passive micromixers based on vortex shedding mechanism. To determine the whole map for understanding the influence of confinement, i.e. aspect ratio (AR) between the depth and the width of the channel and a wide range of Re number have been considered. Three regimes for the dynamics of the wake have been identified: symmetric, oscillatory and vortex shedding. Results have been validated experimentally by microPIV techniques. Results showed that AR is the key parameter, inhibiting oscillatory wakes at low ARs<3 and relatively high Re~200. With an BR=0.5, AR~8 and moderate Re~80, the onset of vortex shedding can be observed, and mixing fluids can take advantage of this effect.

Supported by: Fundação para a Ciência e a Tecnologia (FCT), COMPETE and FEDER, grant IF/00190/2013 and through projects POCI-01-0145-FEDER-030765 and IF/00190/2013/CP1160/CT0003; and Ministério de Ciencia, Educación y Universidades, program “Salvador de Madariaga” 2018 reference PRX18/00334.
The blood samples from people (5 ml) were transported to laboratory. We used LORCA - Laser-assisted Optical Rotational Cell Analyzer (LORCA) and spectrophotometric method with a reagent kit and the Roche Diagnostics c501 Cobas analyzer. The study was authorized by the Bioethics Committee at the Regional Medical Chamber in Krakow, license no 63/KBL/OIL/2010.

Statistical analysis: Continuous variables are presented as mean ± standard deviation (x ±SD). Statistical significance was defined as p=0.05. All calculations were performed using the Statistica 12 (StatSoft®, USA) software.

Conclusion: We found that systematic winter swimming has impact on several rheological and biochemical and immune system parameters.

Electrolytes: Observed substantial decrease in sodium and chloride levels is possibly caused by several mechanisms. The most possible explanation of this phenomenon is diuretic-urine sodium loss. Increased diuresis after swimming leads to greater electrolytes loss with the urine).

Renal function tests: Winter swimming was connected with a downward tendency in urea levels which is consistent with previous findings.

Serum proteins: In our study, an increased rate of albumin and A/G indicator, which is associated with building up winter swimmers' resistance against cold water after winter swimming.

Rheology blood: Regular immersion in cold water increases the deformability of red blood cells. The research results indicate that there is no negative impact of performing 'walrusing'.

Tuesday 18:30 Mediterranea PO94

**Rheological properties of starch pastes and their mixtures with hydrocolloids during extensional flow**

Kacper Kaczmarczyk, Joanna Kruk, Anna Ptaszek, and Pawel Ptaszek

*Faculty of Food Technology, University of Agriculture in Cracow, Kraków 30-149, Poland*

Rheological properties of starch pastes and their mixtures with hydrocolloids during shear flow are described quite well in literature. However there is significant lack of knowledge about their properties during extensional flow. To fully describe rheological properties of food (or food ingredients) during production process or during eating extensional flow has to be concerned. To produce food with specific sensory properties it behavior during stretching, biting, chewing and swallowing has to be known. Starch and hydrocolloids are widely used in many types of food. Measuring their rheological properties during extensional flow in specific range of elongation rate and compare obtained values to values obtained in the same range of shear rate is necessary to describe their properties fully.

As a research material starch pastes obtained from different types of regular and waxy starches were used. Additionally starch pastes mixes with non starch hydrocolloids were the object of research. For measuring values of extensional viscosity prototype opposite nozzle device was used. For measuring shear viscosity values rotational rheometer (RS6000, Haake) was used.

Obtained values of Trouton's ratio (extensional viscosity to shear viscosity value in the same elongation/shear rate) differed significantly depending on the starch types and hydrocolloids addition.

The work was created as a result of the research project No. 2015/17/N/ NZ9/01120 financed from the funds of the National Science Center.
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