THE SOCIETY OF RHEOLOGY

77TH ANNUAL MEETING
PROGRAM AND ABSTRACTS

Westin Bayshore Resort and Marina
Vancouver, B. C., Canada
October 16 - 20, 2005

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Washington University at St. Louis

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### Session Codes

- **BS** = Rheology of Biomaterials and Biological Systems
- **FS** = Non-Newtonian Fluid Mechanics and Stability
- **IP** = Interfacial Problems in Rheology
- **IR** = Industrial Rheology
- **MM** = Molecular Modeling and Simulation in Rheology
- **MR** = Microrheometry and Microfluidics
- **MS** = Dealy Symposium: Molecular Structure and Rheology
- **PL** = Plenary Lectures
- **SC** = Suspensions, Colloids, and Multiphase Fluids
- **SM** = Entangled Solutions and Melts
- **SR** = Solution Rheology
- **SS** = Viscoplasticity and Viscoelasticity of Solids and Semi-Solids
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Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Salon 1 & 2

**Modeling and simulation of dynamics of polymeric solutions: Progress and challenges**

Bamin Khomami

*Department of Chemical Engineering, Washington University, Saint Louis, MO 63130*

Quantitative understanding of the influence of physico-chemical parameters on the dynamic evolution of microstructure in polymeric solutions plays a central role in processing of wide variety of micro-structured materials. Over the past decade tremendous progress has been made in development of kinetic theory based coarse-grained micro-mechanical models for polymeric solutions as well as robust and highly accurate continuum and multi-scale simulation techniques for flow simulation of this class of fluids in complex kinematics flows. In this presentation, I will briefly review the progress made in these areas as well the remaining challenges in development of a unified approach for predicting dynamics of polymeric solutions in prototypical processing geometries. Specifically, I will address the following issues:

A detailed evaluation of various coarse-grained kinetic theory based micro-mechanical models for polymeric solutions in terms of their ability to predict detailed polymer configuration states observed via single molecule microscopy as well as measured rheological properties will be given. In addition, a new computationally tractable coarse graining approach based on "configuration sampling" is introduced and the model predictions are validated via direct comparison with experimental findings.

An overview of existing continuum and multi-scale simulation techniques for steady and dynamic simulations (including linear and nonlinear stability) of polymeric solutions in complex kinematics flows will be presented. In turn, the ability of current simulation techniques and constitutive equations/micro-mechanical models for polymeric solutions to capture the experimentally observed flow kinematics, polymeric stresses etc. in a number of complex kinematics flow geometries will be discussed. Based on these comparisons a unified approach for predicting dynamics of polymeric solutions in complex kinematics flows will be suggested.

Symposium FS
Non-Newtonian Fluid Mechanics and Stability

Organizers: Mike Graham and Satish Kumar

Monday 9:45 Oak 1 & 2

**Iterated stretching and multiple beads-on-a-string phenomena in dilute solutions of highly-extensible flexible macromolecules**

Mónica N. Oliveira and Gareth H. McKinley

*Department of Mechanical Engineering, MIT, Cambridge, MA 02139*

In the present work, the spatio-temporal dynamics of elastocapillary thinning and breakup of polymeric filaments are re-examined. The capillary necking induced by surface tension results in a strong uniaxial stretching flow which leads to large molecular elongation. The resulting large viscoelastic stresses can also lead to iterated dynamical processes that result in self-similar structures such as a 'beads on a string' morphology in which spherical fluid droplets are interconnected by thin fluid ligaments. Understanding these structures is important in numerous commercial applications including jet-breakup, fertilizer spraying, electrospinning, and inkjet printing. To eliminate external viscous and gravity effects, it is necessary to generate thin and uniform threads. This is achieved using a capillary breakup extensional rheometer together with a high molecular weight PEO solution, commonly used in drag reduction experiments. Filament thinning is examined by high-speed digital video microscopy. These elastocapillary experiments provide a means of probing the transient extensional viscosity of the fluid. At long times, the evolution of the viscoelastic thread deviates from the self-similar exponential decay and competition of elastic, capillary and inertial forces leads to the formation of a periodic array of beads connected by axially-uniform ligaments. This configuration is itself unstable and successive instabilities propagate from the necks connecting the beads and ligaments. This iterated process results in multiple generations of beads developing along the string in general agreement with predictions of Chang et al. [Phys Fluids, 11, 1717 (1999)]. However, the experiments yield a different recursion relation between successive generations of beads from that predicted theoretically. At long times, finite extensibility truncates the iterated instability and axial translation of the bead arrays along the interconnecting threads leads to progressive coalescence before the ultimate rupture of the fluid column.
Monday 10:10 Oak 1 & 2

**On the deformation and translation of multiple bubbles in a viscoelastic filament undergoing stretching**

Katerina Foteinopoulou¹, Vlasis Mavrantzas², and John Tsamopoulos³

¹Chemical Engineering, University of Patras and ICEHT/FORTH, Patras 26504, Greece; ²Chemical Engineering, University of Patras, Patras 26504, Greece

We present results concerning bubble deformation in Newtonian and viscoelastic filaments undergoing stretching. Such bubbles (or cavities) are experimentally observed to develop either in the bulk or at the interface with the substrate of a pressure sensitive adhesive, often leading to fibrillation and severely affecting its adhesion properties. In the application discussed here, the single-bubble analysis [Foteinopoulou, et al., JNNFM, 122, (2004)] is extended to the case of multiple bubbles simultaneously deforming in the stretched filament. The filament, initially having the shape of a cylinder with uniform radius, is continuously stretched by pulling the upper supporting plate along its axis with a constant velocity. A robust mesh generation scheme [Dimakopoulos, Y. & Tsamopoulos, J., J. Comp. Phys., 192, (2003)] that solves a set of partial, elliptic differential equations for the nodal points is employed. The governing equations consist of the momentum, continuity and constitutive equation and the interfacial conditions at the bubble-liquid and liquid-air interfaces. For viscoelastic liquids, described here by the PTT constitutive law, the EVVS-G technique is used to separate elastic and viscous contributions to the stress tensor, with an SUPG discretization of the constitutive equation. A finite element/Galerkin method is used to discretize the remaining equations. At each time step, the flow, mesh and constitutive equations are decoupled. Solution for the total set of unknowns is obtained using Picard iterations. Numerical results are presented concerning the dependence of bubble growth and deformation on the dimensionless numbers of the problem (De and Ca or elastocapillary), the geometry aspect ratio and the relative bubble size. The tensile force on the upper plate is also calculated and reported as a function of time.

Acknowledgement: The Project is co-funded by the European Social Fund and National Resources of Greece under the Pythagoras II program.

Monday 10:35 Oak 1 & 2

**A finite-element phase-field method for simulating interfacial dynamics in complex fluids**

Pengtao Yue¹, Chunfeng Zhou², James J. Feng¹, Carl F. Ollivier-Gooch³, and Howard H. Hu³

¹Dept. of Chem. & Biol. Engr. and Dept. of Math., University of British Columbia, Vancouver, BC V6T 1Z2, Canada; ²Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, BC, Canada; ³Department of Mechanical Engineering, University of British Columbia, Vancouver, BC, Canada; ⁴Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA

We present a novel and efficient finite-element method for treating interfacial problems involving rheologically complex fluids. Two key ingredients of the method are a phase-field representation of the interface and an adaptive meshing scheme that allows fine interfacial resolution at manageable computational cost. In the phase-field framework, the interface is seen as a thin layer across which material properties change rapidly but continuously. Thus, a set of governing equations are derived that hold for both fluids across the interface. This circumvents the cumbersome task of interface tracking. The surface tension emerges from the mixing energy at the interface, and the energy-based formalism easily incorporates complex rheology. The challenge of the method lies in resolving the interfacial layer on a fixed Eulerian grid. This is handled by adaptive meshing on a unstructured grid using the phase-field as the criterion for local refinement and coarsening. We will present several simulations on drop deformation, retraction, coalescence and breakup for Newtonian and viscoelastic liquids and nematic liquid crystals. While some of these serve as validations of our new method, the results also reveal novel physics governing the interplay between interfacial dynamics and bulk rheology.

Monday 11:00 Oak 1 & 2

**The dynamics of droplet impact on thin films of wormlike micelle solutions**

Jason Grimaldi, Ryan Lepard, Francisco Lopes, and Jonathan P. Rothstein

Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA 01003

The impact dynamics of drops on thin films of a viscoelastic wormlike micelle solutions is experimentally studied using a high speed digital video camera. The composition and thickness of the thin film is modified to investigate the effect of fluid rheology on the evolution of crown growth, the formation of satellite droplets and the formation of the Worthington jet. The experiments are performed using a series of wormlike micelle solutions composed of a surfactant, cetyltrimethylammonium bromide (CTAB), and a salt, sodium salicylate (NaSal), in deionized water. The size, velocity and composition of the impacting drops are varied to study the relative importance of Weber, Ohnesorge and Deborah numbers on the impact dynamics. The addition of elasticity to the thin film fluid is found to suppress the crown growth and the formation of satellite drops with the largest effects observed at small film thicknesses. A new form of the splashing threshold is postulated which accounts for the effects of viscoelasticity and collapses the satellite droplet data onto a single master curve dependent only on dimensionless film thickness. Additionally, a plateau is observed in the growth of the maximum height of the Worthington jet height with increasing impact velocity. It is postulated that the complex behavior of the Worthington jet growth is the result of a dissipative mechanism stemming from the scission of wormlike micelles.
Simulation of a head-on droplet collision of non-Newtonian fluids
Kerstin Wielage¹, Dieter Bothe², and Hans-Joachim Warnecke²
¹Department of Mathematics, University of British Columbia, Vancouver V6T 1Z2, Canada; ²Technische Chemie, Universität Paderborn, Paderborn 33098, Germany

In many industrial applications, e.g., powder coating production, polymeric liquids are of increasing interest. An important feature of these liquids is the fact that their viscosity changes with the shear rate. In order to understand the complexity of such an industrial process as a whole, it is necessary to gain insights into the fundamental behavior of those fluids.

The main topic of this talk will be the comparison of experiment (University Stuttgart and University Paderborn, Germany) and simulation of a head-on droplet collision using a non-Newtonian fluid. The fluid used in the experiment was selected regarding to two criteria: high shear thinning effects and low elastic effects, such that the fluid can be assumed to be of generalized Newtonian type. Accordingly, for the viscosity function in the simulation a modified Carreau model can be employed. The numerical simulation is based on the massively parallelized Volume of Fluid-code FS3D (Free Surface 3D). FS3D was originally developed at the ITLR, University Stuttgart, and has been extended to generalized Newtonian flows and adapted for the presented investigation at the University of Paderborn.

The results of the VOF-simulation and the experiment agree very well. The numerical results allow to study the viscosity and shear rate distribution inside the droplet such that the relation between viscosity and shear rate becomes visible.

These investigations can be used as a basis for the simulation of more complex applications such as the production of powder coatings by atomization of molten polymers. This technique, using an ultrasonic standing wave field to disintegrate polymers, avoids some disadvantages of other techniques. Numerical studies, e.g., of the resulting particle size distribution of this process will be also presented.

(This work was carried out in different projects at the University of Paderborn, where the author was a scientific staff member.)

Symposium SC
Suspensions, Colloids, and Multiphase Fluids
Organizers: Dan Klingenberg and Nina Shapley

Flow phase diagram and correspondence principle for linear flows of sheared magnetic suspensions
Qi Wang¹, Greg Forest², and Ruhai Zhou³
¹Mathematics, Florida State University, Tallahassee, FL 32306; ²Mathematics, UNC-Chapel Hill, 27599, NC; ³Mathematics, Old Dominion University, Norfolk, VA 23529

We study the general linear flows of sheared magnetic nematic suspensions in viscous solvent using a kinetic theory and a mesoscopic tensor model. We develop a correspondence principle between the linear flow and a simple shear and show that combined linear planar flow and external magnetic field is equivalent to a simple shear and a magnetic field imposed in the plane orthogonal to the shearing plane with a negative susceptibility. Then, the flow-phase diagram can be drawn with respect to the Peclet number and the strength of the magnetic field.

Effects of body forces on electro- and magnetorheological fluids
Daniel J. Klingenberg¹, Anthony Smith², and John Ulicny²
¹University of Wisconsin, Madison, WI; ²General Motors R&D and Planning, Warren, MI

Body forces in electro- and magnetorheological (ER and MR) suspensions are typically small compared to the magnitudes of the field-induced electric and magnetic forces. Using particle-level simulations, we show that these relatively small forces can have large effects on the structure and rheological response of these fluids in shear flow. Gravity causes the field-induced fibrous structures to collapse below a critical field strength, and causes the shear stress to decrease. The critical field strength below which the field-induced structures collapse under the force of gravity increases with increasing system size. Experiments were performed to test the simulation predictions. The effect of gravity on the structure of ER suspensions composed of barium titanate particles in mineral oil was investigated. Experimental results are consistent with the simulation predictions, where the critical field strength increases with system size. Implications of this phenomenon for ER and MR devices will be discussed.

Magnetorheological measurements in suspensions of magnetic nanoparticles
Carlos Rinaldi
Chemical Engineering, University of Puerto Rico, Mayaguez, Mayaguez 00681, Puerto Rico

Suspensions of magnetic nanoparticles, commonly referred to as ferrofluids, are a commercially relevant example of structured fluids where a magnetic body couple, resulting from non-collinear local magnetic field and magnetization vectors, produces a state of asymmetric stress. Such
stresses result in forces and torques on surfaces in contact with these suspensions, even in the absence of bulk flow. Alternatively, the internal angular momentum that enters the system due to the action of the magnetic body couple may be transformed into vorticity and result in bulk flow. These phenomena make ferrofluids attractive in applications where magnetic actuation of fluid flow is desirable. Here we report on measurements of the torque required to either rotate or restrain a polycarbonate spindle surrounded by ferrofluid in a cylindrical container and subjected to the rotating field generated by a magnetic induction motor stator, as a function of applied field amplitude and frequency, and for various values of the geometric aspect ratios of the problem. Simultaneously, ultrasonic Doppler velocimetry was used to measure the azimuthal and axial velocity profiles in the ferrofluid contained in the annular gap of our apparatus. These torque and velocity measurements are compared to an asymptotic solution of the ferrohydrodynamic flow problem in zero spin viscosity and linear magnetization limits, and to a numerical solution of the problem.

**Monday 11:00 Salon 1**

**Structure formation, dynamics and applications of MR fluids in microchannels**

Suraj S. Deshmukh, Shankar Devasenathipathy, and Gareth H. McKinley

Dept. Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

The formation and evolution of chainlike microstructures in magnetorheological fluids flowing in microchannels has been observed and analyzed. High-speed video microscopy has been used to elucidate the dynamics of chain formation and the evolution with time and flow. Particle Image Velocimetry (μPIV) techniques are used to characterize fluid velocity profiles in various channel geometries. Bulk rheological measurements under shear, creep and large amplitude oscillatory shear (LAOS) flow have also been used to characterize the plastic collapse and the structural flow response of the fluids to different magnetic fields. The response time of the particles, variation in chain length and configuration are measured as a function of the relevant dimensionless parameters including the Mason number (Mn) and λ. A force balance based on a point-dipole approximation is found to explain the chain shape profile to a good approximation. In a related investigation we use the constituent components of the MR fluid to dope and modify the properties of elastomers such as PDMS. Possible novel applications in microfluidic actuation and robotic motion are outlined.

**Monday 11:25 Salon 1**

**Graphene nanocomposites**

L. C. Brinson1, T. Ramanathan1, Ahmed A. Abdala2, S. Stankovich1, D. A. Dikin1, Margarita Herrera2, R. D. Piner1, D. H. Adamson1, J. Liu1, R. S. Ruoff1, S. T. Nguyen1, Ilhan A. Aksay2, and Robert K. Prudhomme1

1Northwestern University, Evanston, IL 60202; 2Princeton University, Princeton, NJ 08544; 3Sandia National Laboratories, Albuquerque, NM 87185

There has been considerable interest and activity in the area of nanoparticle-filled polymer composites because of the predicted enhancement in mechanical, electrical, and transport properties. Carbon nanotubes and clay nanosheets have been the most widely studied materials, but each has significant limitations. We present a new nanofiller based on completely exfoliated graphite sheets. The process for exfoliation will be described, as well as characterization of the resulting TEGO (thermally exfoliated graphite oxide). Surface areas of 1500 m2/g are obtained and aspect ratios on the order of 104 (i.e. 10 microns/1 nm) are obtained. The electrically conductive sheets show a percolation threshold between 1-2 wt % when incorporated in a polymethylmethacrylate (PMMA) polymer matrix. This is in contrast to 7.5 wt% loading of conductive carbon black that must be added to obtain conductivity. The elastic modulus versus temperature for a TEGO-filled PMMA composite shows an increase. But most significantly, the addition of 0.25 wt% TEGO increases the softening temperature (or glass transition temperature, Tg) from 95 C to 118 C. This change is unprecedented at this filler loading. The shift in Tg of the matrix polymer means that the TEGO is well enough dispersed that ”every” PMMA chain is influenced by the TEGO surface. Therefore the bulk polymer properties are modified by very low loadings of TEGO.

**Symposium SR**

**Solution Rheology**

Organizers: Gareth McKinley and Ravi P. Jagadeeshan

**Monday 9:45 Salon 2**

**Evolution of shear induced structures in a shear thickening micellar solution**

Vishweshwara Herle1, Benjamín M. Marin-Santibáñez2, Peter A. Fischer1, Lourdes de Vargas3, and José Pérez-González3

1Institute of Food science and Nutrition, ETH Zurich, Laboratory of Food Process Engineering, Zurich, Zurich, Switzerland; 2Postgrado en Ciencia e Ingeniería de Materiales, IIM, Universidad Nacional Autónoma de México, México D. F., México D. F. 04510, Mexico; 3Escuela Superior de Fisica y Matemáticas, Instituto Politécnico Nacional, Laboratorio de Reologia, México D. F., México D. F. 07738, Mexico

An equimolar 40 mM/l mixture of a cationic surfactant, cetylpyridinium chloride and salt sodium salicylate is used as a model to study shear induced structures (SIS). The rheological behavior of the solution was studied by using rotational and capillary rheometers under controlled shear stress conditions. In rotational rheometry the investigated solution shows a pronounced shear thickening behavior, which is coupled with
oscillations of the shear rate. Such oscillations are related with the continuous development and destruction of SIS, as confirmed by Fourier analysis. In addition, a dependence of the SIS dynamics was observed on the gap size. A similar behavior was observed in capillary flow, in which in addition, slip and a mechanical failure in the sample occur at high shear rates, due to a “solid-like” behavior of the solution when increasing its viscosity. Visualization of the contraction region in Poiseuille flow indicates pulsed unstable flow for shear rates beyond the mechanical failure.

Monday 10:10 Salon 2 SR2
**Morphology and shear banding in nematic polymer driven flows based on kinetic model simulations**
Ruhai Zhou, Greg Forest, Qi Wang, and Hong Zhou
1Mathematics, Old Dominion University,Norfolk, VA 23529; 2Mathematics, UCN-Chapel Hill, 27599, NC; 3Mathematics, Florida State University, Tallahassee, FL 32306; 4Applied Mathematics, Naval Postgraduate School, Monterey, CA 93943

We apply algorithms developed for coupled hydrodynamics and the Doi-Hess-Marrucci-Greco kinetic model for rigid rod dispersions to explore heterogeneity in the ensemble of rods and the feedback to flow through shear banding. The rod suspension is described by excluded volume, a distorsional elasticity potential with distinct elasticity constants, and anchoring conditions in a plane Couette cell. Second-moment closures are also tested for accuracy and numerical coarse-graining. We present phase diagrams of film morphology in the two-parameter space of Deborah number and Ericksen number, identifying structure phase transitions in flow profiles (shear banding and vorticity generation) and the orientational distribution of the rod ensemble.

Monday 10:35 Salon 2 SR3
**Property characterization of nematic nano-composite films: Homogenized averaging versus percolation**
Greg Forest, Xiaoyu Zheng, Ruhai Zhou, Robert Lipton, Qi Wang, and Hong Zhou
1Mathematics, UCN-Chapel Hill, 27599, NC; 2Mathematics, Old Dominion University, Norfolk, VA 23529; 3Mathematics Department, Louisiana State University, Baton Rouge, LA; 4Mathematics, Florida State University, Tallahassee, FL 32306; 5Applied Mathematics, Naval Postgraduate School, Monterey, CA 93943

We connect two critical aspects of nano-composite materials engineering. The nano-elements considered here derive from the class of high aspect ratio nematic polymers, either rod-like or platelet spheroids. First, the overall electrical properties of polymer nano-composites are well approximated by the effective electrical conductivity tensor in the low volume fraction regime of the included phase. In turn, the effective conductivity is strongly influenced by the orientation distribution of the nano-inclusions. Second, we recall results of Doi-Hess kinetic theory or mesoscopic model approximations of the orientational probability distribution, for quiescent and sheared nematic polymers, at both isotropic and ordered volume fractions. Putting the two features together, we derive the effective electrical conductivity tensor in closed form. Scaling properties of enhanced conductivity versus volume fraction and weak shear rate become explicit. While, the experimental data indicates the percolation are the dominant effect on the effective conductivity, we compute the percolation threshold consistent with Doi-Hess theory of quiscent or flowing nematic polymer.

Monday 11:00 Salon 2 SR4
**The effect of insoluble surfactants on drop deformation and breakup in simple shear flow**
Patrick D. Anderson, Ivan Bazhlekov, and Han Meijer
Eindhoven University of Technology, Eindhoven, The Netherlands

The effect of insoluble surfactants on drop deformation and breakup in simple shear flow is studied by means of a numerical method. A combination of a three-dimensional boundary-integral method and a finite-volume method is used to solve the coupled fluid dynamics and surfactant transport problem over the evolving interface,. The interfacial tension depends non-linearly on the surfactant concentration, and is described by the equation of state for the Langmuir isotherm. Results are presented over the entire range of the viscosity ratio and the surface coverage, as well as the capillary number spans from that for small deformation to values that are beyond the critical one. A convection dominated regime of surfactant transport, where the influence of the surfactant on the drop deformation is the most significant, is considered in the present study. For a better understanding of the processes the effect of surfactants on the drop dynamics is decoupled into three surfactant related mechanisms (dilution, Marangoni stress and stretching) and their influence is investigated. The dependence of the critical capillary number, known as the Grace curve, of the surface coverage is obtained and the boundaries between different modes of breakup (tip-streaming and drop fragmentation). The influence of the capillary number on the tip-streaming/dropping is also investigated.

Monday 11:25 Salon 2 SR5
**Molecular interactions between comb-like associative polymer and nonionic surfactants: Effects of surfactant mixtures and hydrophilic-lipophilic balance**
Sachin Talwar, Lauriane F. Scaru, and Saad A. Khan
Dept. of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606

The molecular interactions/rheological behavior between comb-like associative polymers and nonionic surfactants having different hydrophilic-lipophilic balance (HLB) are investigated. The effect of binary mixture of nonionic surfactants on the rheology of these systems is also examined. In this study, we use hydrophobically modified alkali-soluble emulsion (HASE) polymers and nonylphenol poly(ethylene oxide) nonionic surfactants (NP) with different degrees of ethoxylation, i.e., different HLB. In an alkaline solution, pure HASE polymers form a
network consisting of both intra- and intermolecular hydrophobic junctions. The addition of surfactant to these solutions affects its dynamics by forming free and bound micelles incorporating one or more polymer hydrophobes. Steady shear and dynamic experiments are performed and the trends of low shear viscosity, plateau modulus and longest relaxation time are discussed. Our results indicate that the surfactant HLB significantly affects the low shear viscosity trend of the associative polymer/nonionic surfactant systems. In effect, the low shear viscosity continuously increases for low HLB surfactants, exhibits a maximum for intermediate HLB surfactants, and monotonically decreases for high HLB surfactants. The different behavior patterns can be explained in terms of number and average lifetime of hydrophobic junctions, and can be related to the molecular-level interactions between associative polymer and nonionic surfactants. The results further indicate the presence of hydrophilic interactions between the polymer and surfactants with high HLB. Observations for associative polymer/binary mixture of nonionic surfactant systems suggest that the rheological behavior can be the result of either a synergistic or an additive effect of the two surfactants and their ratio.

Symposium IP

Interfacial Problems in Rheology

Organizers: Gerry Fuller and Savvas Hatzikiriakos

Monday 9:45 Seymour
Equilibrium model for capillary driven deformation of hyperelastic porous media
William H. Hartt, Richard Hamm, Paul Lipic, Rajesh Singh, Gregory Stevens, and William Worley
Corporate Engineering Technologies Lab, The Procter & Gamble Company, West Chester, OH 45069

The capillary driven volumetric strain of high porosity foams has been studied. We focus on utilization of the volume fraction concept of deformable porous media theory and the use of porosity as a thermodynamic state variable. We demonstrate experimentally and theoretically the existence of "two-phase" regions of porosity, or equivalently coexistence of regions of equal capillary pressure, but different volumetric strain. A series of elastomeric foams were produced that span from a high bulk modulus, large pore size solid foam that exhibits little deformation as a function of liquid saturation to a low bulk modulus, small pore size foam where capillary stresses collapse the structure. Foams with pore sizes that result in capillary pressures in the same range as the plateau modulus of the solid foam exhibit very complex equilibrium volumetric strain due to the nonlinearities of the capillary pressure function and volumetric stress strain curve for the solid foam. We present experimental data for these structures and a capillary-mechanical model based on previously established theoretical results using the entropy inequality. We demonstrate multiple "phase" equilibria in these systems or the coexistence of regions with different porosity.

Monday 10:10 Seymour
Diffusive coarsening of foam
Andrew M. Kraynik and Sascha Hilgenfeldt

1Sandia National Laboratories, Albuquerque, NM 87185-0834; 2Department of Engineering Sciences and Applied Mathematics, Northwestern University, Evanston, IL 60208

Computer simulations with the Surface Evolver are used to investigate the evolution of structure of three-dimensional soap froth by diffusive coarsening. The instantaneous cell growth rates are evaluated directly from the foam microstructure because the counterpart of von Neumann's law, which provides an exact relationship between cell growth rate and topology in 2D, is unavailable in 3D. Two mechanisms are responsible for topology changes in the foam: cell neighbor switching triggered by cell edges shrinking to zero length (T1 transitions) and small cells disappearing (T2 transitions). We will discuss the topological, geometric and growth-rate statistics of the foam and individual cells as the system evolves toward what is presumed to be a scaling state.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Monday 10:35 Seymour
Effect of viscoelasticity on the coalescence between a drop and a liquid-liquid interface
Xiaopeng Chen and James J. Feng

Chemical and Biological Engineering, Univ. British Columbia, Vancouver, British Columbia V6T 1Z4, Canada

Recent studies on coating flows have suggested that bulk rheology can significantly modify the dynamics of interfaces. Toward a general understanding of these effects, we report an experiment on a simple and well controlled process. A drop of fluid A rests on an interface between immiscible fluids B and A, the latter being denser and underneath. We study two interesting characteristics of the coalescence: the rest time before film rupture, and a phenomenon known as partial coalescence. Water and an oil-based solution (decane/polybutene/polyisobutylene) are used for phase A and B. The rest time depends on short-range forces and is in general stochastic. When both phases are Newtonian, the rest time varies with the drop size according to a power law with index n ∼ 2, and also increases with the phase-B viscosity. Elasticity of phase B increases the rest time, and this rheological effect can be incorporated into Newtonian film drainage models. Partial coalescence occurs when the drop does not merge into the bulk fluid A at once, but leaves a smaller drop above the interface. The process repeats with the drop size decreasing in a stepwise fashion. We use high-speed video to analyze the process for both Newtonian and viscoelastic fluids, and propose a criterion for the occurrence of partial coalescence based on a capillary instability.
Monday Morning

Coalescence, deformation and break-up in physically compatibilized blends
Ellen Van Hemelrijck¹, Peter Van Puyvelde¹, Christopher W. Macosko², and Paula Moldenaers¹
¹Department of Chemical engineering, K.U.Leuven, Leuven 3001, Belgium; ²Department of Chemical Engineering and Materials Science, University of Minnesota, MINNEAPOLIS, MN 55455

In this contribution, both the coalescence and the break-up of physically compatibilized blends have been studied, using diblock-copolymers with well-controlled molecular architectures. The mean droplet size was monitored during flow-induced coalescence by means of rheology in combination with the Palierne model. The compatibilizers were found to strongly suppress shear-induced coalescence at (relatively) high compatibilizer concentrations. At low compatibilizer concentrations, a slow relaxation process, suggestive of interfacial viscoelasticity, was observed. A possible explanation for the slow relaxation process is provided by the existence of Marangoni stresses at the interface between droplets and matrix. The deformation and breakup behaviour of the blends has also been studied, both by rheological and rheo-optical experiments. The deformation and break-up behaviour of uncompatibilized blends is rather well understood. For blends containing small amounts of compatibilizer, droplets are still deformed and broken up by the flow although a clear effect of compatibilizer concentration on breakup times is present. It has also been verified that the scaling relations that were originally developed for uncompatibilized blends can still be used to describe the rheological behaviour of the compatibilized ones. For blends containing a high concentration of block-copolymer, a peculiar behavior has been observed: under appropriate flow conditions, the droplets are no longer deformed and broken up by the flow, but display suspension-like behaviour.

Effects of flow on coupling of functional polymers at melt interfaces
Jianbin Zhang, Timothy P. Lodge, and Christopher W. Macosko
Department of Chemical Engineering and Materials Science, University of Minnesota, MINNEAPOLIS, MN 55455

The coupling reaction of functional polymers at static polymer-polymer interfaces is much slower than that at interfaces formed during mixing (see, for example, Reference 1). We have found that simple shear flow can greatly accelerate the coupling reactions at flat interfaces, even without generation of new interfacial area. For amine-terminal polystyrene (PS-NH2) / anhydride terminal poly(methyl methacrylate) (PMMA-anh), the PMMA-anh conversion under dynamic oscillation with small strain amplitude (1%) is almost five times that under static conditions, for a given temperature and duration. Under steady shear, the reaction conversion is comparable to that of batch mixing. Extensional flow also accelerates the coupling reaction. With these model flows, the effects of external flow on polymer-polymer coupling reactions are being investigated.


Symposium MM
Molecular Modeling and Simulation in Rheology
Organizers: Bamin Khomami and Antony Beris

Development of mesoscopic models for non-Newtonian flow calculations
Patrick S. Doyle and Patrick T. Underhill
Chemical Engineering, MIT, Cambridge, MA 02139

The use of mesoscopic or "molecular" models of polymers is becoming more prevalent, both in micro-macro type flow calculations and in comparisons with single molecule experiments. We have examined a new method for generating coarse-grained models of polymers. The resulting models consist of bead-spring chains with the spring force-law taken from the force-extension behavior in the constant extension ensemble. We have applied the method to the freely-jointed chain, including the case of non-equal rod lengths showing the effect of varying flexibility in the chain. The method was also used to generate a bead-spring model of F-actin, which shows how the method is not restricted to one molecular model and can even be applied to experimental data. The current limitations of the method are discussed, including the need for approximate bending potentials to model the worm-like chain with a bead-spring chain. We discuss practical issues such as using the bead-spring models in Brownian dynamics simulations and develop a simple spring force-law that can accurately represent a freely-jointed chain with only a few rods per spring. The development and use of coarse-grained models is also possible for systems that can form more complex architectures.
with the mid-point algorithm of Liu [J. Chem. Phys. 90 (1989) 5826]. Nevertheless, computations with the bead-FF-spring model are more efficient than with the bead-rod model because the former allows larger time steps. Moreover, the Brownian contribution to the stress for the bead-FF-spring model can be ignored, while Brownian stress in the bead-rod model must be included, making the bead-rod stresses harder to compute and noisier. Therefore, the bead-FF-spring model requires averaging over a smaller ensemble to achieve the same accuracy for the stress than does the bead-rod model. In addition, hydrodynamic interaction can more easily be incorporated into the bead-FF-spring model than into the bead-rod model since the metric force arising from the non-Cartesian coordinates used in bead-rod simulations is absent from bead-spring simulations. With our newly developed bead-FF-spring model, existing computer codes for the bead-spring models can trivially be converted to ones for effective bead-rod simulations merely by replacing the usual FENE or Cohen spring law with a FENE-Fraenkel law, and this convertibility provides a very convenient way to perform multi-scale BD simulations.

Modeling strong extensional flows of linear polymers

Antony N. Beris and Joydeep Mukherjee

Constitutive models for polymeric flows have been traditionally based on the Gaussian approximation assumption about the form of the distribution function dictating the conformation of polymer chains. However, although this is a fairly good approximation near equilibrium, it becomes consistently worst at high levels of extension when the chain distribution is fairly degenerate. The use of a maximum extensibility (in the form used in a traditional FENE-P like model) does not improve this situation—it actually makes it worst! Thus, as an artifact of this approximation, we have the paradox of an estimated extended free energy that becomes infinite in the limit of perfect chain extension. These observations are not limited to dilute polymer solutions but also hold for polymer melts where the role of individual chains is replaced by that of chain segments between entanglements. In fact, a new NonEquilibrium Microscopic Lattice-based Monte Carlo technique that we have recently developed within our research group has been used to develop a new, thermodynamically consistent, constitutive model correct the FENE-P expression for free energy (so called FENE-PB --- B standing for Bounded Free Energy) at high levels of extension. The model restores the consistency between the microscopic simulations and the macroscopic estimates for a dense amorphous phase (modeled by a Phan Thien and Tanner equation using the FENE-PB model to account for finite extensibility and a bounded free energy) quite a lot—up to the point where excluded volume effects are important. This new approximation can therefore be used under a variety of situations and it is expected to produce significant differences when there is a significant chain extension.

Elongational viscosity of dilute solutions of DNA molecules

P Sunthar, Duc At Nguyen, Roelf Dubbelboer, J R. Prakash, and T Sridhar

The recently introduced successive fine graining (SFG) method for refining the predictions of a bead-spring chain model of a polymer molecule, which incorporates the important non-linear phenomena of hydrodynamic interactions (HI), excluded volume (EV), and finite extensibility (Sunthar and Prakash, Macromolecules, 38, p617, 2005), is used to explore the dynamics of a dilute polymer solution subjected to uniaxial extensional flow under good solvent conditions. Predictions of stress growth in a solution containing λ-phage DNA molecules in a sugar solvent are compared with experimental measurements obtained using a filament stretching rheometer. The predicted elongational viscosity is shown to agree with experimental observations, and found to be insensitive to the microscopic model parameters associated with EV and HI. In addition, the universal evolution of elongational viscosity, which corresponds to the behaviour of an infinitely long polymer molecule, is obtained at various solvent qualities. The departure of the behaviour of finite length chains from universal behaviour is computed, and the influence of various force laws used to model the finite extensibility of chains is investigated.
Simulation of polymer chain scission using Kramers model
H.G. Sim, R. Sureshkumar, and Bamin Khomami
Washington University, Saint Louis, MO

Based on a covalent bond fracture force estimate and statistical analysis for the instantaneous tension along the chain, a new algorithm for the chain scission, based on the Kramers model, is developed. This algorithm is used to investigate the influence of the type of (flow) deformation on the evolution of chain configuration and chain breakup. For steady elongational flow, simulation results are consistent with the experimentally observed inverse square law dependence of the critical deformation rate on the molecular weight. Near the threshold flow rate for breakup, midpoint scission theory is seen to be valid. However, at elongation rates greater than the threshold value, chains can be cleaved away from the midpoint resulting in a broad distribution of shorter chains. Similar results will be presented for transient elongational as well as steady/transient shear flows. The influence of hydrodynamic interactions on chain breakup will be also discussed.
**Monday Afternoon**

**Symposium FS**

**Non-Newtonian Fluid Mechanics and Stability**

Organizers: Mike Graham and Satish Kumar

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**Monday 1:30 Oak 1 & 2 FS6**

**Droplet formation and filament breakup in roll coating**

Mohammad Pouran and David F. James

*Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario M5S3G8, Canada*

A laboratory device has been designed and built to simulate film splitting in roll coating, which occurs through filament stretching and breakup. At high speeds and for some coatings, the breakup leads to unwanted misting. In our simulator, a fluid sample is initially held between two closely-spaced small disks, and then the top disk is pulled upward at a high, constant rate of acceleration to mimic coating machine conditions. Formation and breakup of the resulting filament are observed using a high-speed video camera, and the images are analyzed by software to obtain the number and size of droplets. Tests with various Newtonian fluids, at a Weber number of 30, show that one droplet forms at low Ohnesorge numbers, and that more and smaller droplets form at Oh numbers above 0.1. Associative polymer solutions, prepared to be weakly-elastic fluids like coating liquids, produced even more and smaller droplets, but only for Ohnesorge numbers in the range of 0.01 to 0.1. Simplified coating formulations, which were both shear thinning and elastic, generated droplets that were smaller than those of equivalent Newtonian fluids but bigger than those of associative polymer solutions which were more elastic. The effects of acceleration, initial film thickness and surface tension, as well as solid content of formulations, are studied as well.

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**Monday 1:55 Oak 1 & 2 FS7**

**Imaging the velocity field of viscoelastic film splitting flows**

Melisa Y. Becerra, Luis Fernando A. Azevedo, and Marcio S. Carvalho

*Department of Mechanical Engineering, Pontificia Universidade Catolica do Rio de Janeiro, Rio de Janeiro, Rio de Janeiro 22453-900, Brazil*

At low speeds, film-splitting flow is two-dimensional and steady; as the roll speed is raised, the flow becomes unstable and is replaced by a steady three-dimensional flow with more or less regular stripes; a coating defect usually referred to as ribbing. A force balance near the free surface determines the stability of the flow. Viscoelastic behavior can drastically change the nature of the flow; when minute amounts of flexible polymer are present, the onset of the three-dimensional instability occurs at much lower speeds than in the Newtonian case. Recent theoretical predictions have shown how the stress field changes with rising liquid elasticity, leading to the formation of an elastic stress boundary layer attached to the free surface. The high stress downstream of the flow splitting stagnation point pulls liquid away from the recirculation attached to the free surface, completely changes the flow characteristic in that region and explains the mechanisms by which the liquid elasticity destabilizes the flow. In order to validate these predictions and to visualize the effect of viscoelasticity, it is important not only to visualize the streamlines of the flow, but to measure accurately the velocity field near the free surface. These measurements are extremely challenging due to the presence of the free surface, the small scale of coating flows and relative high speeds. In this work, the velocity field of film-splitting flows of dilute polymer solution is measured using the Particle Image Velocimetry (PIV) technique. Various solutions of low molecular weight polyethylene glycol (PEG) and high molecular weight polyethylene oxide (PEO) in water were used in order to evaluate the effect of mildly viscoelastic behavior on the flow. The results show the effect of the polymeric stress on the flow field near the free surface, validating the available theoretical predictions and that PIV can be successfully used to study microscale free surface flows, providing detailed information of the flow field.

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**Monday 2:20 Oak 1 & 2 FS8**

**Linear stability analysis of electrically-driven viscoelastic jets**

Colman P. Carroll and Yong L. Joo

*Department of Chemical Engineering, Cornell University, Ithaca, NY 14853*

Electrospinning is a novel process forming polymeric fibres with submicron diameter through the action of electrostatic force. The key phase in this process is the region of jet instability, where massive jet elongation occurs. In the spring meeting, we presented a model for the development of the initial stable electrosprun jet, and validated it through comparison of simulated results with experimental data from the spinning of highly elastic Boger fluids. We now expand the model to allow the introduction of axisymmetric disturbances. The stable jet model consists of a coupling of the laws of electrophydrodynamics (momentum equations and Gauss's Law) with viscoelastic polymeric constitutive equations. These coupled equations are solved numerically to establish a jet base state. Using the stable jet model as a basis, we then conduct a linear stability analysis, which allows us to predict the onset of instability including the critical wavenumber of axisymmetric disturbance modes for an
electrarily driven, viscoelastic polymer jet. Our results show the emergence of a new viscoelastic instability mode, with a critical wavenumber significantly higher than those observed for classical capillary modes. We compare predicted critical conditions at the onset of instability with experimental data from the electrospinning of polymeric solutions.

Monday 2:45 Oak 1 & 2

**Multiplicity and bifurcation in dynamic solutions of film blowing process**

Joo Sung Lee, Dong Myeong Shin, Hyun Wook Jung, and Jae Chun Hyun

*Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Republic of Korea*

The complicated system of film blowing process has been investigated focusing on the multiplicity, bifurcation and stability of the dynamic solutions of the system using both theoretical model simulations and experiments. A number of interesting findings have been revealed about the dynamics of the process including a fundamentally different behavior of the system with maximum three steady states for the non-isothermal operations in contrast to the isothermal approximation where only two steady states were predicted. These differences have been identified as stemming from the multiple values the air pressure inside the bubble can take on depending upon the values of the bifurcation parameters of the system. The stability of the three steady states also displays many different patterns dictated by the process conditions. The theoretical models of the film blowing system developed by this study produce quite accurate predictions of the bubble and film shape results both in the steady state and the transient solutions as compared with experiments. It is considered that the findings of this study can be utilized to readily enhance the stabilization and optimization of the film blowing operation.

Monday 3:35 Oak 1 & 2

**Oscillatory regimes of transition from jetting to dripping of polymeric liquids**

Jose Bico$^1$, Christian Claasen$^2$, Vladimir M. Entov$^3$, and Gareth H. McKinley$^4$

$^1$Laboratoire PMMH, ESPCI, Paris, France; $^2$Institute of Technical and Macromolecular Chemistry, Universitat Hamburg, Gamburg, Germany; $^3$Laboratory of Dynamics of Complex Fluids, Institute for Problems in Mechanics, RAS, Moscow 119526, Russia; $^4$Dept. Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

This paper discusses specific features of breakup of capillary jets of dilute polymer solutions associated with transition from dripping to jetting. Experiments monitored with a high speed camera reveal a new scenario of transition and breakup via periodic growth and detachment of large terminal drops. In this regime, thin short jet terminates with large terminal drop, much greater than the drops usually observed in the course of 'normal' jet breakup. The jet is apparently steady-state; the terminal drop experiences a regularly repeating evolution. It first grows while slowly moving upstream; then eventually it turns back, accelerates, becomes much thicker than the jet, and detaches. The phenomenon is specific for macromolecular solutions. Due to capillary instability the primary jet starts to develop the beads-on-string pattern characteristic for polymeric jets before meeting the terminal drop. Therefore, the process appears as 'gobbling' of the chain of tiny beads by a greedy terminal drop. Quantitative characteristics of 'gobbling' are determined using computer-aided processing of video images. The underlying mechanism is discussed and a basic theory of breakup is presented. The dynamics of the terminal drop growth and motion prove to be governed primarily by mass and momentum balances involving capillary, gravity and inertial forces, and the drop detachment event is controlled by kinetics of thinning of interconnecting ligaments that form between droplets. The elasto-capillary thinning process is driven by surface tension and resisted by viscoelasticity of dissolved polymer molecules. Quantitative characteristics of oscillatory regimes are derived from the above qualitative description using mass and momentum balances for the jet and the terminal drop and the theory of polymeric fluid filaments thinning under combined action of the capillary pressure and axial tensile force.

Monday 4:00 Oak 1 & 2

**Extended modeling of flow-induced crystallization and the influence on rheology**

Gerrit W. Peters and Rudi R. Steenbakkers

*Mechanical Engineering, Eindhoven University of Technology, Eindhoven 5612AZ, The Netherlands*

We present an extended phenomenological model for the effects of flow gradients on the crystallization kinetics of semicrystalline polymers. Although a lot of progress has been made in the last decennium, both experimentally and theoretically, many open issues remain and the results are very often obtained for conditions far from processing conditions. The state of modeling varies from coupling between viscoelastic stress and a global measure such as the induction time (a rather crude measure for the complicated processes that take place at different levels) to modeling of the nucleation of different crystalline structures (spherulites, shish kebabs) and the growth of these structures in time as a function of temperature and molecular state (molecular orientation and/or stretch). However experimental evidence shows that even this more extended modeling is not detailed enough to explain and describe the observed phenomena. The two most important ingredients of the extended modeling are 1) a detailed description of the coupling between the evolving crystalline structure and the non-linear viscoelastic behavior and 2) a description of the crystallization kinetics that starts from (flow-induced) precursors of different type (point, fibril) that can change into (stable) nuclei which grow into crystalline superstructures. The modeling is tested by comparing with experimental results from X-ray scattering, microscopy and rheology.
Transient and steady-state analysis of fiber spinning with flow-enhanced crystallization

William H. Kohler and Anthony J. McHugh
Chemical Engineering, Lehigh University, Bethlehem, PA 18015

Our recently modified model and algorithm for the fiber spinning of crystallizable polymers that includes flow-enhanced crystallization has been expanded to include poly lactides and polyolefin systems, in addition to nylons and PET. To account for differing viscoelastic properties of the various polymer systems, two different constitutive models are utilized for the melt phase, the Giesekus and Extended Pom-Pom (XPP) models (single- and multi-mode). Our modified algorithm enables additional insights into the relationship between thermally-induced and flow-enhanced crystallization. These steady state models have also been used to analyze the stability of the process with respect to both internal and external variable perturbations as well as the process conditions that lead to greater stable operation. Results of frequency response and full transient analyses of the fiber spinning behavior will be described.

Two-dimensional simulations of the pressure and the free surface oscillations in the stick-slip extrusion instability

Georgios Georgiou, Eleni Taliadorou, and Andreas N. Alexandrou
1. Mathematics and Statistics, University of Cyprus, Nicosia CY1678, Cyprus; 2. Mathematics and Statistics, University of Cyprus, Nicosia CY1678, Cyprus; 3. Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia CY1678, Cyprus

The time-dependent, compressible extrusion of a Carreau fluid is solved over the reservoir-die-extrudate region using finite elements in space and a fully-implicit scheme in time. A nonmonotonic slip law based on experimental data on polyethylene melts is assumed to hold along the die wall and the velocity at the entrance of the reservoir is taken to be fixed and uniform. As in the case of the extrudate-swell flow, the combination of compressibility and nonlinear slip leads to self-sustained oscillations of the pressure drop and of the mass flow rate in the unstable regime. The inclusion of the reservoir region allows the solution of the flow for compressibility numbers as low as those corresponding to real experiments. The effects of the reservoir volume and the imposed flow rate on the amplitude and frequency of the pressure and the free surface oscillations are studied and comparisons are made with experimental observations.

Capillary instability of magnetic fluid jet conducted by the applied magnetic field

Jie Ma, Ruoyu Hong, and Jun Yang
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The capillary instability of a cylindrical jet is of fundamental interest and importance in wide practical applications including ink-jet printing, fuel injectors in gas turbines and internal engines, chemical reactors, chemical separators, food processing, etc. Beside these diverse industrial applications, process of droplet formation itself is also a fascinating and formidable free boundary problem that continues to challenge experimentalists and theoreticians in recent years. A mathematical model is presented which considers capillary instability of a slender jet of magnetic fluid in an axial magnetic field. The modifications necessary to account for the controlling influence of the magnetic field are introduced into the one-dimensional long-wave theory of the slender jet. The governing equations and the constitutive equations were non-linear and strongly coupled, and hence can only be solved numerically. The best upwind scheme was used. The object-oriented-programming language C++ was used to implement the above algorithm. The computed data were processed using Tecplot. Capillary instability development and the force balance analysis are presented. The effects of the applied magnetic field are revealed. Compare to the evolution of the jet profiles in the absence of magnetic field, the application of the magnetic field has changed the breakup pattern and the neck thinning is hindered significantly at a later stage after initial development. The effects of the applied magnetic field are revealed. Firstly, it slows down the capillary jet pinch-off. Secondly, the magnetic pressure expresses a kind of elastic behavior to counteract the capillary pressure.

Symposium SC
Suspensions, Colloids, and Multiphase Fluids
Organizers: Dan Klingenberg and Nina Shapley

Structure and rheology of organically-modified clay dispersions
Jin Li and James P. Oberhauser
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Many of the desirable mechanical, optical, and mass transfer properties of polymer-clay nanocomposite materials are believed to derive from the microstructure induced by processing. To explore this hypothesis, we are working to develop model polymer-clay nanocomposite solutions upon which to base rheological studies, though the early work presented here focuses upon dispersions of clay in an organic solvent in the absence of polymer.
Superior material properties are obtained when the individual clay platelets are exfoliated from one another, creating a uniform dispersion. We use a solution-exfoliation method to disperse organically modified montmorillonite clays [Cloisite 15A (C15A) and Cloisite 20A (C20A)] from Southern Clay Products in p-xylene. These clays differ from one another only in the fraction of surfactant added relative to the cation exchange capacity of the clay. Moreover, in order to study the effect of the free surfactant on the rheology and microstructure of the dispersions, we have removed free surfactant and created surfactant extracted products that we refer to as EC15A and EC20A.

The quiescent character of the dispersions has been characterized by XRD, TEM, and a novel wet SEM technique. Mechanical rheological data are reported for dispersions with varying concentrations (1 to 4 wt%) of C15A, EC15A, C20A and EC20A. The samples were subjected to oscillatory shear and steady shear, and classic thixotropic behavior is observed in all cases, suggesting the existence of a three-dimensional gel-like structure. Additional work aimed at probing the disorientation kinetics of flow-induced clay orientation will also be reported.

Monday 1:55 Salon 1  SC7

Microstructure-rheological behavior correlation of clay/anionic additives systems
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Different experimental measurements (rheology, granulometry, XRD) were carried out in order to study the main properties of bentonite suspensions in presence of anionic additives at different concentrations. The additives utilized were: Sodium Dodecyl Sulfate (SDS) as surfactant, a flexible polymer (Sodium Carboxy Methyl Cellulose, CMC) and a semi-rigid polymer (Xanthan gum). It has been showed that the structural nature of anionic additive influences directly the mixtures viscoelastic and flow behavior. The steric effect of the surfactant modifies the Face-Edge interactions and yields changes of the mixtures rheological behavior at low deformation rates. Polymers act by coating each clay particle and prevent their agglomeration. Therefore, bentonite has no direct effect on the rheological behavior of the mixtures : the additives are responsible for the mechanisms of destructuration and structure reorganization as well as the mixtures viscous and viscoelastic behavior.

Monday 2:20 Salon 1  SC8

Linear and non-linear rheology for clay nanocomposites characterization: Fast Fourier Transform rheology and conventional rheology
Christophe Mobuchon, Pierre J. Carreau, and Marie-Claude Heuzey
Center for Applied Research on Polymers and Composites, École Polytechnique de Montréal, Montreal, QC, Canada

The properties of polymer/clay nanocomposites are closely related to the intercalation, exfoliation, dispersion and orientation of the nanoparticles in the polymer matrix. The development of a simple rheological method to investigate the nanostructure remains a main challenge. In this study, we have compared the sensibility of the linear and non linear rheology for the characterization of polyamide6/clay nanocomposites. The nanocomposites of different nanostructures were prepared by melt compounding using a twin screw extruder. Small amplitude oscillatory shear (SAOS) and non linear data from stress growth experiments and from large amplitude oscillatory experiments (LAOS) using fast Fourier-transform rheology (FFTR) are reported. In addition, 2D X-ray diffraction and transmission electron microscopy were used to determine the nanostructure after blending and during non linear rheological measurements. SAOS and stress growth data appear insufficient to clearly distinguish the different polyamide6/clay nanocomposites while FFTR appears to be suitable for the characterization of nanostructure.

Monday 2:45 Salon 1  SC9

Large scale structures in polymer-clay hydrogels
Elena Loizou1, Lionel Porcar2, Paul D. Butler2, and Gudrun Schmidt1
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The shear orientation of a series of polymer-clay gels has been investigated by means of rheology and small angle neutron scattering (SANS) under shear. The gels have the same polymer and clay concentrations but different polymer molecular weight. The polymer chains are strongly adsorbed to the clay particles and the concentration of excess polymer chains in the gel (that are not adsorbed) is above the overlap concentration of a pure reference polymer solution. The resulting structure is fractal-like with network-type clay rich areas and polymer rich water pockets with clay poor areas. While long polymer chains can interconnect several platelets which act as multifunctional cross-links, single shorter polymer chains cannot interconnect platelets. The polymer chain length and cross linking between clay platelets strongly influence their shear orientation which leads to anisotropy in SANS. Our data suggest that the flow is strong enough to enhance and maintain a continuous increase in the shear orientation of the polymer clay gels only when individual polymer chains are long enough to interconnect or strongly entangle between platelets.

Monday 3:35 Salon 1  SC10

Melt intercalation dynamics of polystyrene and nanoclay in air and inert environments
David J. Frankowski, Richard J. Spontak, and Saad A. Khan
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695-7905

Polymer nanocomposites constitute an exciting class of materials wherein physical, mechanical, electrical and transport properties can be controllably altered via judicious control of composition, as well as the size, shape, dispersity and surface chemistry of the nanoscale additive. In
the present study, we avoid the need for organic solvents by using melt intercalation to prepare nanocomposites of polystyrene modified with organically-modified montmorillonite clay. The dynamics of clay intercalation under a variety of conditions have been monitored by dynamic oscillatory shear, and the accompanying effects of shear on molecular integrity and the extent of intercalation have likewise been investigated by size exclusion chromatography (SEC) and x-ray diffraction (XRD). An unexpected result to be presented is that the initial intercalation rate discerned from the time evolution of the elastic modulus is more than an order of magnitude faster in air than in nitrogen. Moreover, specimens exposed to air are found to attain a more highly intercalated and possibly exfoliated morphology, as evidenced by a higher modulus plateau and corresponding XRD patterns. Complementary results from SEC confirm that clay intercalation is related to chain scission in an oxygen-rich environment. Shortened chains, benefiting from a reduced entropic penalty, more readily squeeze between adjacent galleries of the clay particles than their long-chain analogs. The practical implication of this observation is that organically-modified clays may be amenable to melt intercalation in polydisperse polymer matrices containing short chains that effectively serve as dispersants. While enhancing chain diffusivity, extended annealing of the nanocomposites in different inert environments (including vacuum and supercritical carbon dioxide) appears to have little effect on rheology and microstructure development.

Monday 4:00 Salon 1

Polycaprolactone/organoclay nanocomposites: Structure, rheology, and crystallization

Ștefan Acierno\textsuperscript{1}, Ernesto Di Maio\textsuperscript{2}, Salvatore Ianname\textsuperscript{3}, and Nino Grizzuti\textsuperscript{1}

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During the last years, polymer nanocomposites are receiving great attention thanks to their dramatically improved mechanical and heat resistance properties achieved at very low loading of silicate (in the range of few %) compared to traditional filled polymers (which require some tens % of filler to obtain similar properties.) The achievement of exfoliation of the silicates in the polymer matrix is a fundamental requisite for the attainment of the increased properties characteristic of nanocomposites. Recently, polymer nanocomposites have been prepared via melt mixing thus making the use of these materials more attractive. When semicrystalline thermoplastics are used, the final properties are influenced by structure, morphology, and amount of the crystalline phase. The understanding of rheological and crystallization properties of polymer silicate nanocomposites is a fundamental prerequisite for the processing of these materials and is the aim of this work.

Nanocomposites based on polycaprolactone and organically modified silicates are prepared by melt mixing. Two different types of organoclay are used, the difference is in the organic modifier. While for the one clay it is possible to produce exfoliated structures for silicate loadings up to 5 wt\% and intercalated/exfoliated structures for higher loadings; the other clay shows an almost unchanged structure after the mixing (i.e., polymer and silicate remain phase-separated.) The rheological and crystallization properties of the different nanocomposites are investigated and they seem to be strictly interrelated. In particular, the rheological (and crystallization) properties depend on the filler-polymer interaction and on the amount of filler (in a non-monotonic fashion!) As an example, the exfoliated system has on the one hand a minimum in the viscosity as a function of the clay concentration and, on the other hand, the crystallization kinetics have a maximum as a function of the clay loading.

Monday 4:25 Salon 1

A re-entrant glass transition in laponite dispersions

Hossein Baghdadi and Surita R. Bhatta

Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, MA 01003-9303

We present rheology, dynamic light scattering, and ultra-small-angle neutron scattering (USANS) on aqueous dispersions of the synthetic clay laponite with added poly(ethylene oxide). Neat solutions of laponite at high pH with no added salt are known to form a colloidal glass at concentrations greater than roughly 2 wt\% clay. When low molecular weight poly(ethylene oxide) is added, free polymer chains in solution cause a weak depletion attraction. This results in a decrease in the elastic modulus and viscosity, and in some cases a complete melting of the glass phase. Similar behavior has been observed in other colloidal glasses with added polymer. We compare the dynamics of our system, measured via DLS, with previous results on weakly attractive colloidal glasses. We believe that, in our system, this weak attraction also leads to the formation of clusters of laponite particles, which can be confirmed with USANS. The addition of higher molecular weight poly(ethylene oxide) causes formation of an elastic gel, presumably due to interparticle bridges, which lead to a much stronger interparticle attraction.

Monday 4:50 Salon 1

Thermal hardening behavior in dispersions of anisotropic clay particles

Nitin Kumar\textsuperscript{1}, Chanjoong Kim\textsuperscript{2}, David Weitz\textsuperscript{2}, and Gareth H. McKinley\textsuperscript{2}

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Most of the known materials undergo a solid to a fluid-like transition on heating and become softer on heating. In this work, we present very unusual rheological properties of dispersions of disc-shaped nano-particles of Laponite clay in non-aqueous polar solvents. The high boiling point of solvent allows us to measure macroscopic rheological properties to temperatures as high as 140 °C. At room temperature, these dispersions are in a gel-like state. On heating, the storage modulus (G) increases by as much as 1000 fold within a temperature range of 10-20 °C. A similar increase in loss modulus is also observed. Shear viscosity under constant shear rate also increases by almost 100 fold on heating. These macroscopic rheological measurements are also confirmed by measuring micro scale rheological measurements using diffused wave light
spectroscopy (DWLS). The scaling $G'$ with Laponite weight fraction at low temperature and at high temperatures suggests that the dispersions undergo from a gel state to glass state on heating. This unusual behavior is not fully understood.

Monday 5:15 Salon 1  SC14

**Effects of nano-particles on the rheology of polymer melts**
Donald G. Baird, David W. Litchfield, and Wade S. DePolo
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The effects of nano-particles on the linear and non-linear viscoelastic properties of two polymer melts(polypropylene and a PBT/PC blend) are investigated. It is observed that at low shear rates the nano-particles enhance the viscosity and storage and loss moduli, but at high shear rates they suppress these properties. Furthermore, in capillary flow the entrance pressure is enhanced, but the over all pressure drop can be suppressed at high shear rates. In stress growth and relaxation, a noticeable increase in the time to reach equilibrium conditions (i.e. steady state or zero stress conditions, respectively) is delayed significantly. The normal stresses are also enhanced at low shear rates but are suppressed at higher shear rates. The effect of particle size is considered in an effort to sort out the origin of the observed behavior.

**Symposium SR**
**Solution Rheology**
Organizers: Gareth McKinley and Ravi P. Jagadeeshan

Monday 1:30 Salon 2  SR6

**The scaling of zero-shear viscosities of semidilute polymer solutions with concentration**
Youngsuk Heo$^1$ and Ronald G. Larson$^2$
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To test the universality of the dependence of zero-shear viscosity on concentration for both flexible and semiflexible polymers, we collected multiple literature data sets and measured the zero shear viscosity of λ-phage DNA over a range of semidilute concentrations. We found that all experimental data fall on a single empirical curve given by $\frac{\eta_p}{\eta_{Rouse}} = 45 (c/c_e)^{2.95}$ and this scaling law is in good agreement with the theoretical one, $\eta_p/\eta_{Rouse}=c(c/c_e)^{2(3v-1)}$ with $v$ the excluded volume exponent, $\eta_{Rouse}$ the polymer contribution to the zero-shear-viscosity of the solution with $\eta_p$ the zero-shear viscosity and $\eta_s$ the solvent viscosity, $\eta_{Rouse}$ the hypothetical Rouse polymer viscosity, and $c_e$ the entanglement concentration of the polymer solution. This scaling law provides a basis for estimating viscosities for arbitrary semi-dilute polymer solutions with a knowledge of the entanglement molecular weight in the melt and the excluded volume exponent. [Menezes and Graessley, *J. Polym. Sci. Part B-Polym. Phys. Ed.* **20**, 1817 (1982), Raspaud et al. *Macromolecules*, **28**, 927 (1995), Osaki et al. *J. Polym. Sci. Part B-Polym. Phys. Ed.* **39**, 1704 (2001)]

Monday 1:55 Salon 2  SR7

**Shear and extensional rheology of polymer solutions: Brownian dynamics simulations at finite concentrations**
Christopher Stoltz, Juan J. de Pablo, and Michael D. Graham
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We consider the effects of concentration on the structural and rheological properties of dilute polymer solutions via the use of Brownian dynamics simulations. The model used here is that of Jendrejack et. al. for stained 21 μm λ-phage DNA under good solvent conditions, which has been shown to quantitatively predict the non-equilibrium behavior of the molecule in the dilute limit. Of particular interest in this study are the changes in chain structure and rheology stemming from the influence of both excluded volume interactions and hydrodynamic interactions, the latter of which is accounted for through the use of the periodic Rotne-Prager interaction tensor. Our work covers the entire dilute regime, with selected investigations into the semidilute regime, as well as by spanning multiple decades of both shear and extensional flow rates. Simulation results are compared with available experimental results and theoretical predictions and are presented both in terms of the applicable flow rate and as a function of the Weissenberg number. Our results indicate significant increases in both chain size and viscosity at moderate flow rates in both simple shear and planar elongational flow as concentration increases, with the latter flow type exhibiting much larger concentration effects. In simple shear flow, we observe as much as a 30-50% increase in both the chain extension and polymer viscosity at the overlap concentration as compared to the infinitely dilute case, whereas 400-600% increases in the same quantities are observed in elongational flow. Finally, these effects are greatly enhanced by the inclusion of hydrodynamic interactions as compared to freely-draining systems.
Shear thinning in semidilute unentangled solutions of flexible polymers
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Materials Science and Engineering, Penn State University, University Park, PA 16802; Research Laboratories, Eastman Kodak Company, Rochester, NY 14650

Solutions of flexible polymers that are high enough concentration to overlap each other (above their overlap concentration $C^*$) but low enough concentration that they are not yet entangled (below their entanglement concentration $C_e$) are semidilute and unentangled. We show that the relaxation time and viscosity of such solutions obey the Rouse model. Yet these solutions exhibit shear thinning that is not anticipated by the Rouse model. We present a simple calculation based on the Rouse model for the dependence of the apparent viscosity on shear rate in steady shear. The derived power law with slope 1/2 applies to all polymer solutions that are semidilute but not entangled. We show some evidence for this power law shear thinning in solutions of high molecular weight neutral polymers (for which $C_e/C^* = 10$). However, semidilute unentangled polyelectrolyte solutions (for which $C_e/C^* = 1000$) show much stronger evidence for the universality of the predicted power law shear thinning.

Influence of configuration-dependent drag on the capillary thinning of filaments of dilute polymer solutions
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In a seminal paper, Entov and Hinch (J. Non-Newtonian Fluid Mech., 72: 37-53, 1997) predicted that surface tension causes the diameter of a thin filament of a dilute polymer solution to decrease exponentially in time, before break up. Their model showed that the resulting extensional strain rate corresponds to a Weissenberg ($Wi$) number of 2/3. Subsequent experimental observations by Anna and McKinley (J. Rheol., 45: 115-138, 2001) of an exponential decrease in the mid-filament diameter, suggested that the measured strain rate could be used with the $Wi = 2/3$ formula to extract the characteristic large-scale relaxation time of the polymer molecule. Recent studies (Clasen et al., Proc. XIVth Intl. Cong. Rheol. 2004) however show that the relaxation time calculated in this manner displays a curious concentration dependence. We demonstrate in this paper that this anomalous behaviour is due in part to the neglect of the configuration dependence of intramolecular hydrodynamic interactions. We use a set of improved constitutive models for the polymer stress in dilute solutions at the theta state, which account for the influence of configurational anisotropy and fluctuations in hydrodynamic interactions. The predictions obtained for homogeneous simple shear and uniaxial extensional flows are shown to be in good agreement with results of Brownian dynamics simulations of isolated chains with hydrodynamic interactions. Using the simple one-dimensional stress balance proposed by Entov and Hinch, we show that the $Wi = 2/3$ formula is not generally valid, and leads to an erroneous concentration dependence. Further, incorporating configuration-dependent drag leads to an improved description of the evolution of the mid-filament diameter for some solutions. In other cases, our results indicate that the self-concentrating effect of extensional flows may cause theory to deviate from experiment.

Effects of block length, pH, and ionic strength on diblock polyelectrolyte solution rheology
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We present rheological studies of the weak diblock polyelectrolyte poly(styrene-b-acrylic acid) (PS-PAA) in aqueous solutions. The amphiphilic nature of PS-PAA allows for the formation of micelles and is potentially useful for inks and coatings, oil recovery, personal care products, and biomaterials. Aqueous solutions with 1.0 wt% PS-PAA have a pH of 3, unsuitable for most applications. However, the addition of sodium hydroxide to increase solution pH leads to gelling of the solution due to PAA chain repulsion. We demonstrate the PS-PAA solutions can be tuned to acquire desired rheological properties by changing the PS and PAA block lengths, and solution pH and ionic strength. The block molecular weights range from 600 to 4300 g/mol for PS, and 19,500 to 40,200 g/mol for PAA. The 1.0 wt% aqueous solutions at various pH and sodium chloride concentrations of 0.001 to 0.1 M have been studied. In steady shear, most solutions exhibit shear-thinning behavior over the entire range of measurable shear rates. Oscillatory measurements show that these solutions have elastic character, with $G' > G''$ for most formulations in the frequency range examined. All solutions have a low critical strain, indicating they are weak physical gels. The rheological behavior appears to be dominated by the state of the PAA block. Viscosity and elastic modulus were found to increase with pH due to chain repulsion. When sodium chloride is added to the solution, the chains collapse and a decrease in viscosity and elasticity is observed.

A rheological study of structural transitions in triblock copolymers swollen with nematic liquid crystal solvent
Rafael Verduzco, Neal R. Scruggs, Mike D. Kempe, and Julia A. Kornfield
Chemical Engineering MC 210-41, California Institute of Technology, Pasadena, CA 91125

Liquid crystalline networks possess fascinating properties that arise from a mobile director field coupled to a highly deformable polymer network, including shape changes with temperature, deformations in response to electric fields, and movements in response to light. To investigate the relationship between network structure and properties, we use self-assembly to create uniform, well-defined nematic gels. These self-assembled gels are prepared by swelling a high molecular weight ABA block copolymer with the small-molecule nematic liquid crystal (LC) solvent 4-pentyl-4'-cyanobiphenyl (5CB). The "B" midblock is a side-group liquid crystal polymer designed to be soluble in 5CB, but the
"A" endblocks, composed of polystyrene, are LC-phobic and microphase separate to produce a physically cross-linked, thermoreversible, macroscopic polymer network. Small-angle neutron scattering experiments provide direct evidence of discontinuous network changes at the isotropization point. Rheology of the nematic gels reflects this dramatic change in network structure that occurs over small temperature windows (as little as 1 °C) due to the rapidly changing LC order near the isotropization point. At sufficiently low polymer concentrations, a plateau modulus in the nematic phase, characteristic of a gel, abruptly transitions to terminal behavior when the gel is heated into its isotropic phase. In more concentrated gels, endblock aggregates persist into the isotropic phase up to a microphase separation temperature. We describe the role of molecular structure - relative and overall length of the blocks and side-on vs. end-on mesogen attachment - in governing structure formation and viscoelastic properties.

Monday 4:25  Salon 2
Rheology of self-assembled block copolypeptide hydrogels
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Amphiphilic block copolypeptides were prepared through transition-metal-mediated polymerization of amino acid N-carboxyanhydrides. In aqueous solution these materials form strong hydrogels at low concentrations. The self-assembly process that is responsible for gelation was investigated by measuring the rheological properties of the gels for a variety of molecular architectures: poly-L-lysine-b-poly-L-leucine diblock and poly-L-lysine-b-poly-L-leucine-b-poly-L-lysine triblock copolypeptides. Experiments showed that the helical secondary structure of the enantiomerically pure poly-L-leucine blocks was instrumental for gelation at polypeptide concentrations as low as 0.25 wt %. The hydrophilic polyelectrolyte segments have stretched coil configurations and stabilize the twisted fibril assemblies by forming a corona around the hydrophobic core.

The self-assembly process is a delicate balance between repulsive and attractive intermolecular forces. Tuning the molecular architecture and mixing of different block copolypeptides in solution was used to control and optimize hydrogel properties. Rheological data will be presented to elucidate the role and relative importance of the key intermolecular interactions in the self-assembled structures, and to provide insight about the nature of these structure.

With potential applications in tissue scaffolding and drug delivery in mind, we have designed molecular architectures which form uniquely stable hydrogels in deionized water as well as various ionic media (salt solutions, buffer solutions, and cell growth media).

Monday 4:50  Salon 2
A multicomponent model for the non-Arrhenian viscosity of natural silicate melts
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The prediction of viscosity in silicate melts over the range of conditions found in Nature remains one of the most challenging goals in Earth Sciences. Early models for silicate melt viscosity used an Arrhenian temperature (T) dependence and were limited by their experimental data which comprised mainly high-T measurements on a relatively small range of melt compositions. The large number and quality of recently published melt viscosities suggest the possibility of new models.

We present a multicomponent model for the compositional and T dependence of silicate melt viscosity based on data spanning a wide range of anhydrous melt compositions. Experimental data include micropenetration and concentric cylinder measurements covering a viscosity range of 10⁷ to 12 Pa s and a T-range from 700 - 1650 °C. These published data provide a high-quality database comprising ~ 800 experimental data on 44 melt compositions. Our model uses the Adam-Gibbs equation to capture T-dependence:

\[ \log \eta = A + B/T \log(T/C) \]

where A, B, and C are parameters that vary for different melt compositions. We assume that all silicate melts converge to a common, but unknown, high-T limit (e.g., A) and that all compositional dependence is accommodated for by B and C. We adopt a linear compositional dependence for B and C:

\[ B = \Sigma_i x_i \beta_i; \quad C = \Sigma_i x_i \gamma_i \]

where \( x_i \)'s are the mole fractions of oxides (n=8) and the \( \beta_i \)'s and \( \gamma_i \)'s are adjustable parameters. The model comprises 2*n+1 fit parameters including a common value of A and compositional coefficients for B and C. The model reproduces the original data to within experimental error and can predict melt viscosity across the full range of conditions found in Nature.
Thermorheological properties near the glass transition temperature of oligomeric methyl methacrylate containing polyhedral silsesquioxane nanocages
Edward T. Kopesky¹, Stephen G. Boyes², Neil D. Trear², Robert E. Cohen¹, and Gareth H. McKinley³
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Miscible blends consisting of two oligomeric components of similar size and chemical functionality but disparate shape, one a linear methyl methacrylate (MMA) chain (Mₐ = 2190 g/mol, Rₜ ~ 1.1 nm) and the other a methacryl polyhedral oligomeric silsesquioxane (methacryl-POSS) nanocage (Mₐ = 2029 g/mol, Rₜ ~ 1.0 nm), were subjected to thermal and viscometric tests to determine the thermorheological properties of these blends over the temperature range Tₕ < T < Tₔ + 100°C. The glass transition temperature of the pure MMA oligomer (Tₔ = -42°C) is slightly higher than that of the methacryl-POSS (Tₔ = -57°C), and the glass transition temperatures of the blends decrease monotonically in a concave upward fashion with increasing POSS content. The zero shear rate viscosity of the blends at T = 20°C displays a similar trend with increasing POSS content. Regression of the viscosity-temperature data to the Vogel-Fulcher-Tamman (VFT) equation [log η(T) ~ B/(T-T₀)], shows that the methacryl-POSS is a much more fragile glass-forming liquid than the linear MMA oligomer, where fragility is a measure of the degree of non-Arrhenian behavior as the liquid approaches the glass transition temperature. The WLF equation [log η(T) ~ B/(T-T₀)], the fractional free volume at the glass transition Tₕ, and the glass transition temperatures of the blends decrease monotonically in a concave upward fashion with increasing POSS content. The zero shear rate viscosity of the blends at T = 20°C displays a similar trend with increasing POSS content. Regression of the viscosity-temperature data to the Vogel-Fulcher-Tamman (VFT) equation [log η(T) ~ B/(T-T₀)], shows that the methacryl-POSS is a much more fragile glass-forming liquid than the linear MMA oligomer, where fragility is a measure of the degree of non-Arrhenian behavior as the liquid approaches the glass transition temperature. The WLF equation [log η(T) ~ B/(T-T₀)], the fractional free volume at the glass transition Tₕ, is seen to increase significantly as the POSS content is increased. The highly fragile nature of the POSS combined with its high value of ψₕ is consistent with simulations of glassy transitions in ensembles of polydisperse spheres and experimental results on hyperbranched molecules.

Symposium IP
Interfacial Problems in Rheology
Organizers: Gerry Fuller and Savvas Hatzikiriakos

Interfacial stick-slip transition in simple shear of entangled melts
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We report the first observation [1] of a discontinuous interfacial stick-slip transition in simple shear flow of monodisperse entangled 1,4-polybutadiene melts of different molecular weights. A new constant-force sliding rheometer was designed and employed to accomplish the rheological and rheo-optical study. The magnitude of the transition is found to be determined by the level of chain entanglement. The interfacial nature of the flow behavior is explicitly demonstrated by surface treatment of the shearing plates and dependence of the abrupt jump in the plate velocity on the gap distance, between which the samples were sheared. Both flow birefringence and particle tracking observations were made to elucidate the interfacial nature of the observed flow behavior. These explicit results, valuable in their own right, also refute the recent idea [2] that the previously observed stick-slip transition was related to the instrument system instability of the pressure-driven capillary flow.[1] A brief report has been submitted to Phys. Rev. Lett. for publication. [2] J. M. Dealy, presented at IUPAC World Polymer Congress MACRO 2004 and published at http://www.e-polymers.org/paris/data/L590.pdf; F. Smilo, M.S. Thesis, "Wall slip and spurt of molten polymer", McGill University (2004).

Rheology of particle-laden interfaces
Hui G. Xu¹ and Gerald G. Fuller²
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Colloidal particles are often employed at fluid/fluid interfaces to assist in the stabilization of foams and emulsions. The basis for this stabilization relies on the non-Newtonian rheology of particle-laden interfaces and this paper explores those properties. This is accomplished by examining the collapse of sessile and pendant droplets that are covered with particles. During the process of collapse, these interfaces undergo a fluid-to-solid transition as the particles ultimately jam together to form a solid shell. The onset of this transition is signaled by shape transitions and buckling of the interface. By measuring the internal pressure of the droplets, it is possible to measure the Young's modulus and bending modulus of these interfaces.
Non-amphiphilic particles can adsorb at the interface between two fluids and act as interfacial modifiers. Emulsions whose drops have such adsorbed particles on them are called Pickering emulsions; the particles prevent drop coalescence, thereby stabilizing the emulsion. It was shown recently that under some circumstances, interfacially-adsorbed particles can glue together drops[1]. This raises the possibility that drops in a Pickering emulsion may stick to each other without coalescing, and thus form a network structure. We attempted to test this hypothesis rheologically.

Experiments were conducted on Pickering emulsions composed of polyisobutylene (PIB) polydimethylsiloxane (PDMS) fluids, and fumed silica particles. Vermant et al. have demonstrated that such particles can indeed adsorb at the PIB/PDMS interface[2]. We found that PIB/PDMS blends with up to 1% particles showed large increases in low-frequency moduli and complex viscosity, suggesting that a network structure is indeed present. However, unlike Vermant et al. the rheology was highly sensitive to the blend-preparation procedure and it was difficult to obtain reproducible results. Furthermore, the particles were not only interfacial modifiers, but also affected the rheology of the bulk phases: blends of particles with just one of the homopolymers (i.e. suspensions of the particles), also showed enhanced moduli at low frequency. Such gel-like behavior of fumed silica suspensions has been well-studied previously. Therefore, the low-frequency behavior of these Pickering emulsions does not lend itself to clean interpretation.

We conclude that while Pickering emulsions based on fumed silicas may prove commercially-important, they may not be ideal model systems. Instead, preliminary experiments demonstrate that spherical, monodisperse silicas are more convenient for careful experimentation.


**Monday 2:20 Seymour
Rheology of polymer blends with interfacially-active particles**
Prachi Thareja and Sachin Velankar
*Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261*

Non-amphiphilic particles can adsorb at the interface between two fluids and act as interfacial modifiers. Emulsions whose drops have such adsorbed particles on them are called Pickering emulsions; the particles prevent drop coalescence, thereby stabilizing the emulsion. It was shown recently that under some circumstances, interfacially-adsorbed particles can glue together drops[1]. This raises the possibility that drops in a Pickering emulsion may stick to each other without coalescing, and thus form a network structure. We attempted to test this hypothesis rheologically.

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**Monday 2:45 Seymour
Compression of colloidal monolayers containing ellipsoidal particles**
J. Vermant¹, M. G. Basavaraj², and Gerald G. Fuller²

*¹K. U. Leuven, Leuven, Belgium; ²Chemical Engineering, Stanford University, Stanford, CA 94305-5025*

The behaviour of dense monolayers of prolate ellipsoidal monolayers at the air-water interface is investigated. Ellipsoidal particles were prepared by embedding polystyrene spheres in a polyvinylalcohol film. Heating the film above the glass transition of the latex and stretching the film, the particles are forced to deform affinely, and after thorough cleaning of the particles, ellipsoids with controlled aspect ratios (of 2, 6 and 8) can be obtained. The latter is an important parameter, as the maximum packing of ellipsoids depends in a non-monotonic manner on the aspect ratio. The particles were dispersed at a water interface in a Langmuir trough and are subsequently compressed. Upon reaching maximum compression, the monolayers made of particles with larger aspect ratios showed the appearance of smectic-like regions. Upon further compression, selected ellipsoids were observed to flip out of the plane, arriving at a perpendicular orientation to the interface. Finally, the interface buckles out, as has been observed for monolayer of spherical particles. Upon expansion of the monolayer, it cracked irreversibly. Microstructural observations will be compared to measurements of the pressure -area isotherms recorded during compression and the elastic nature of the interface will be discussed.

**Monday 3:35 Seymour
Single-molecule analysis of a virus particle attachment to a living cell**
Melissa I. Chang, Porntula Panorchan, Terrence Dobrowsky, and Denis Wirtz

*Department of Chemical and Biomolecular Engineering, The Johns Hopkins University, Baltimore, MD 21218*

The overall goal of this research is to establish the biophysical and biochemical principles that govern the attachment of human immunodeficiency virus type 1 (HIV-1) to its host cell, in living cells and at the single molecule level. Because viral replication is never completely controlled, current molecular strategies for the design of HIV/AIDS therapies are focusing on effectively inhibiting the interactions between HIV-1 and the target cell rather than inhibiting virus replication. Therefore a detailed understanding of how HIV-1 interacts with its host cells is essential to the design of HIV entry inhibitors. While a structure-based picture of the sequence of binding events that occur between HIV-1 and the host cell is beginning to emerge, it is unclear if cell receptors are organized at the cell/virus interface and how many linkages and which molecules are required to produce a functional cell-virus junction. Here, we develop a comprehensive single- and multiple-molecule analysis complemented by theoretical and computational modeling of the HIV-1/host-cell binding interface. Our single-molecule approach does not require the use of soluble proteins or protein labeling, accommodates living cells and viral particles, and can unambiguously distinguish single-molecule binding events (i.e. affinity) from multiple-molecule adhesion (i.e. avidity). Our results establish directly the hierarchy of molecular binding events that begin with virus attachment and culminate in the fusion of the viral membrane to the plasma membrane before HIV entry into cytoplasm. This research also determines directly the number and identity of the receptor molecules that actively participate in the formation of the host-cell-virus interface as a function of applied force. The combined experimental and theoretical approach developed here enhances our basic understanding of cell-virus interaction and may serve as a general framework to analyze mechanisms of receptor-mediated cell-cell and cell-virus fusion.
When a solution of polymer molecules is confined to a two-dimensional space, its structural and flow properties become very different from those usual in the bulk. The mechanical properties of a range of polymer monolayers are investigated, including films of the protein $\beta$-lactoglobulin that are relevant in food science. A new method enables the measurement of the response to both compressional and shear deformations. While at low concentrations it is clear that the layers are in thermodynamic equilibrium, we find the emergence at higher surface concentration and to the equilibrium osmotic pressure. In $\beta$-lactoglobulin spread monolayers, a shear modulus develops at a critical concentration, indicating a transition from a fluid to a solid. We interpret this behavior as evidence of a dynamical arrest transition and provide an argument based on the statistical physics of polymer chains to estimate this critical concentration. Results show that at this same concentration the system becomes trapped in a non-equilibrium phase. Finally protein monolayer rheology is compared with other polymer monolayers and with monolayers of solid particles, pointing to various universal properties.

Fatty alcohols are strongly amphiphilic and form stable monolayers between water and air (or oil). These are important emulsifiers and are used to enhance the stability of foams and emulsions. This paper reports on the structure and interfacial rheology of monolayers formed from mixtures of straight chain and branched chain hexadecanol. It is found that below a critical concentration of the branched material, the branched chains are "squeezed" out of the layer while the system is in the liquid expanded phase, producing a much more compliant layer. Above the transition to the liquid condensed state, the layer consists of a monolayer of the straight chains with two dimensional micelles of the branched material sitting on top. This results in a layer with the same compressibility as monolayers of pure straight chains, but the mixtures have an enhanced surface viscosity. This result suggests the possibility of using such mixtures to enhance stability in foams and emulsions.

Faraday instability measurements of the critical acceleration, $a_c$, and wavenumber, $k_c$, for standing surface waves on a tetracosanol ($C_{23}H_{46}$) melt exhibit abrupt changes at $T_s = 54^\circ C$, ~4 $^\circ C$ above the bulk freezing temperature. The measured variations of $a_c$ and $k_c$ vs. temperature and driving frequency are accounted for quantitatively by a hydrodynamic model, revealing a change from a free-slip surface flow, generic for a free liquid surface ($T > T_s$), to a surface-pinned, no-slip flow, characteristic of a flow near a wetted solid wall ($T < T_s$). The foundation of the hydrodynamic model is a vertically vibrated liquid-air interface covered by an insoluble surfactant. When the Marangoni number (ratio of surface-tension-gradient forces to viscous forces) becomes large, the contractions and expansions of the interface are suppressed and it behaves like a no-slip surface. The abrupt change in instability behavior at $T_s$ is traced to the onset of surface freezing, where the steep velocity gradient in the surface-pinned flow significantly increases the viscous dissipation near the surface. These results shed light on the hydrodynamics associated with the surface freezing phenomenon, and may find use in other areas such as foam drainage, surface rheology, and microfluidic transport. [P. Huber, V. P. Soprunkuk, J. P. Enns, C. Wagner, M. Deutsch, and S. Kumar, Phys. Rev. Lett. 94, 184504 (2005).]
spinodal regime. The general method discretizes the Euler-Lagrange nonlinear integral equation by the finite element method and uses Newton's method to solve the resulting nonlinear equations. The equilibrium solutions are characterized by combinations of bend, twist, and splay distortions in physical space. These solutions correspond to unstable intermediate states in the spinodal decomposition process. Second, the dynamic spinodal-decomposition transition is simulated by time-integrating the nonlinear, nonhomogeneous diffusion equation forward in time. A nonhomogeneous destabilizing perturbation is applied to the unstable isotropic state, and the evolution of the system from its initial distorted state to a homogeneous aligned state is tracked. The connections between the unstable, nonhomogeneous, equilibrium states and the corresponding unstable attractors in the dynamic problem are analyzed. All calculations utilize an intermolecular potential that models interaction between rods on the scale of a single rod length. Finally, wall-rod interaction calculations show the impact of hard walls on the nonhomogeneous phase behavior of the system.

Monday 1:55 Salon 3

Network modeling of entangled wormlike micellar solutions in shearing and extensional flows
Pam Cook¹, Gareth H. McKinley², and Paula Vasquez³
¹Mathematical Sciences, University of Delaware, Newark, DE 19716; ²Dept. Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

Wormlike micelles, also known as "living polymers", are characterized by their ability to break and reform in solution. In steady shear flow entangled wormlike micellar solutions exhibit a plateau in the stress/stress-rate curve and spatial inhomogeneities develop in the flow field. In particular "shear-banding" features are observed which include steep spatial variations in the local deformation rate and regions of localized intense birefringence in which the micelles are locally oriented and elongated. In transient extensional flow, wormlike micellar solutions exhibit pronounced strain-hardening at moderate strains and also a decrease in the extensional viscosity (rate-thinning) at a critical extension rate. Using a filament stretching rheometer, Rothstein [J. Rheol. 2003] examined transient extensional flow of wormlike micellar solutions and showed that at a critical Hencky strain, independent of extension rate or surfactant and salt concentration, a filament instability leads to rupture of the fluid column. The filament rupture and the associated strain softening are believed to be due to breakage of the wormlike micellar chains under high stresses.

We outline the development of constitutive models formulated to describe the behavior of entangled wormlike micellar solutions. The models, originating in nonlinear network theories, are formulated to capture the essential features of both the shear flow and the extensional flow observations; including a plateau in the steady state shear-stress/shear-rate curve, and a maximum in the steady extensional viscosity as a function of extension rate. If time permits transient predictions of the models will also be presented together with comparisons with experimental data.

Monday 2:20 Salon 3

Simulation of semidilute polymer solutions by dissipative particle dynamics
Susan Weitz¹, Guoai Pan¹, Jeffrey Potoff¹, Charles W. Manke¹, and Andrea S. Ferrante²
¹Dept. Chemical Engineering and Mat. Science, Wayne State University, Detroit, MI 48202; ²Port Sunlight Laboratories, Unilever R&D, Bebington, Merseyside CH63 3JW, United Kingdom

While there has been a great deal of progress in modeling the dynamics of dilute polymer solutions through simulation techniques such as Brownian Dynamics, there have been relatively few attempts to extend these simulations to higher concentration regimes. Dissipative Particle Dynamics (DPD), which has previously been applied to dilute polymer solutions, can easily be extended to model the dynamics of semidilute and concentrated polymer solutions. Since DPD employs a periodic simulation box in which the polymer chains and solvent are explicitly represented by DPD particles, concentrated polymer systems can, in principal, be represented simply by adding more polymer chains to the simulation box. In practice, successful modeling of concentrated polymer solutions is more complicated, because features of polymer-polymer chain interactions such as frictional interactions and entanglements must be incorporated into the DPD model to give a physically realistic representation. Here we extend the dilute solution DPD model of Pan, et al (2002), a linear bead-and-spring chain with FENE springs, to the case of semidilute polymer solutions having concentrations up to c[h] = 1.5. Viscosity in steady shear flow is evaluated as a function of polymer concentration, and a Huggins plot is constructed to determine the intrinsic viscosity and Huggins coefficient. With the standard DPD model, in which all dissipative interactions among particles are equal, the Huggins coefficient is found to be nearly zero. When dissipative interactions among polymer particles are set higher than polymer-solvent and solvent-solvent dissipation interactions, however, positive values of the Huggins coefficient emerge from the simulations. For the good solvent case, realistic values of the Huggins coefficient, in the range of 0.3 to 0.5, are obtained for polymer-polymer dissipation coefficients set 5 to 15 times higher than polymer-solvent dissipation coefficients. Similar results are obtained for near-theta solutions.

Monday 2:45 Salon 3

Mesoscopic simulation of polymer chains by DPD
Vasileios Symeonidis¹, Bruce Caswell², and George E. Karniadakis¹
¹Division of Applied Mathematics, Brown University, Providence, RI 02912; ²Division of Engineering, Brown University, Providence, RI 02912

Dissipative Particle Dynamics (DPD) is a method for simulation at mesoscopic scales between the molecular dynamics and the continuum levels. DPD efficiently simulates complex liquids and dense suspensions with but a few thousand virtual particles at speed-up factors of some hundreds.
of thousands relative to molecular dynamics. We have developed time-staggered integrators to efficiently exploit the disparate temporal resolutions required for polymer and solvent. Several bead-spring models are used to demonstrate the potential and accuracy of the method. In statics the power-law exponent of the radius of gyration is employed as an indicator of the tendency of a chain to permit phantom collisions. In steady shear flow chain extension and its autocorrelation are compared to experimental values for DNA.

Monday 3:35 Salon 3

The Consistently Unconstrained Brownian Slip-link (CUBS) model with semi-flexibility and finite extensibility

Jay D. Schieber and Thidaporn Kitkrailard

The CUBS model has shown the ability to predict nearly all rheometric data on linear entangled polymer liquids without adjustable parameters; the single phenomenological time constant is fit to linear viscoelastic data. To date the model has successfully predicted shear and normal stresses in the startup of steady shear flow, single step strains, double step strains and exponential flow. In particular, it is able to predict quantitatively the transient undershoot observed in the extinction angle. CUBS was also able to predict the transients in simple elongational flow, but showed large growth and overshoot not observed experimentally. Recent neutron scattering data taken at the DTU in Denmark showed that the chains were significantly stretched at steady state. Therefore, we have expanded the CUBS model to include finite extensibility by using a free energy expression derived from the worm-like chain model. We first compared this new form of the model to linear viscoelasticity and startup of steady shear, in order to confirm that shear predictions are not affected by finite extensibility. They aren't. Next, we compared the theory to simple elongation. Here we found two surprises. One of these surprises is that we are able to describe the steady state elongational data very well, but this has little to do with finite extensibility.

Monday 4:00 Salon 3

Dynamic Monte Carlo for rheological properties of polymer melts

John R. Dorgan

Polymeric melts exhibit very complex flow response. Features of linear and non-linear viscoelasticity include normal stresses and elastic instabilities. Very few experimental techniques can access molecular details during flow. Clearly, a viable simulation strategy for predicting rheological response would be extremely valuable for a variety of reasons. In particular, if the effects of blending varying molecular architectures on rheological properties could be understood, new and effective flow modifiers might be developed. In this work, rheological properties of polymer melts are studied using a newly developed dynamic Monte Carlo simulation technique. The iso-thermal, iso-stress ensemble is utilized in conjunction with a biasing applied to the cooperative motion algorithm of Pakula on a face centered cubic lattice. Coarse graining on a lattice allows access to the large length and time scales associated with macromolecules at moderate computational costs. In addition, rheological properties of polymer melts may be calculated from configurational properties. Stress can be calculated based on the elastic dumbbell model. It is shown that the trends in viscosity and normal stress differences can be correctly predicted. Results are in excellent agreement with well-established experimental facts; a shear thinning viscosity is obtained, the first normal stress difference increases with shear rate, and the first normal stress coefficient decreases with shear rate. The technique also enables the calculation of the second normal stresses and its coefficient - this quantity is extremely difficult to measure experimentally. Accordingly, the simulation technique provides new information into the dynamics of polymer melts under shear flow. Because the underlying Monte Carlo lattice model is well-suited can easily accommodate mixtures of chain architectures, the a priori prediction of rheological properties of arbitrary mixtures of chain architectures should now be possible.

Monday 4:25 Salon 3

Brownian dynamics simulations of polymer blend droplets

Bharad Narayanan, Victor Pryamitsyn, and Venkat Ganesan

We present the results of a multiscale simulation approach which combines Brownian dynamics simulations with polymer self-consistent field theory and continuum mechanics to study the deformation characteristics of polymer droplets. We use this approach to study the influence of the bulk rheological properties, such as viscosity and elasticity ratios, upon droplet deformation. Despite the comparatively small size of our droplets and the 2-D nature of our simulations, our results agree semi-quantitatively with the asymptotic predictions for the droplet deformations. In addition, we are able to examine the effects of the droplet and the matrix Weissenberg numbers and their effects upon the droplet deformations. We also present results elucidating the influence of block compatibilizers upon the droplet deformations. Our results suggest that even trace fractions of compatibilizers can lead to significant changes in the flow fields around the droplets and their deformation characteristics. We study the influences of the molecular weight of the block copolymer, the coverage of block copolymers upon the dynamical properties of polymer blend interfaces.
Monday Afternoon

Monday 4:50 Salon 3

**Kinetic theory for ellipsoidal suspensions and biaxial liquid crystal polymers**

Qi Wang  
*Mathematics, Florida State University, Tallahassee, FL 32306*

We present a new molecular (kinetic) theory for ellipsoidal suspensions and biaxial liquid crystal polymers. Given the potential technological application of the biaxial liquid crystals, this new theory provides the platform for ones to probe the rheological properties of the less symmetric suspensions in viscous solvent and the impact of broken symmetry on the material phase diagram. Smoluchowski equation, elastic stress and viscous stress will be derived. Phase transition and flow perturbation of the phase diagram will be discussed in details.

Monday 5:15 Salon 3

**Self-consistent Brownian dynamics simulations of ternary polymer blends**

Bharad Narayanan, Victor Pryamitsyn, and Venkat Ganesan  
*Chemical Engineering, University of Texas at Austin, Austin, TX 78712*

We present a Brownian dynamics-based simulation study of flow-induced phase transitions in the microemulsion phases of ternary polymer blends. The simulation method combines Brownian dynamics simulations with polymer self-consistent field theory to enable the predictions of flow-induced phase transitions. The results match qualitatively with the experimental observations and suggests that flow transforms the microemulsion phases into a three-phase coexistence (of a lamellar-phase coexisting with phase separated homopolymer phases) at strong shears followed by a macrophase separation of the homopolymers at even stronger shear flows. These transitions are also accompanied by a strong shear-thinning behavior in the rheological response. The results suggest significant differences between ternary polymeric systems and oil-water-surfactant systems, which we rationalize from a molecular viewpoint.
Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Salon 1 & 2 PL2
Thixotropy or «inelastic» time dependency
Jan Mewis
K. U. Leuven, Leuven, Belgium

Although thixotropy is one of the oldest known non-Newtonian phenomena, it is still poorly understood. The existence of nearly hundred models for thixotropy indicates that a good generic model is still missing. It can actually be demonstrated that some of the assumptions on which most models are based are often not satisfied by real systems. Theoretical and experimental problems encountered in thixotropy studies are discussed. The complex microstructure and the complex effects of shear history on the structure are identified as major causes of these problems, as shown by rheological and scattering experiments. Nevertheless, these materials also obey some specific scaling laws. More insight can be gained by applying fast transient measurements. Here, such data are used to analyse the physical nature of thixotropic phenomena in a model system as well as to evaluate thixotropy models.

Symposium FS
Non-Newtonian Fluid Mechanics and Stability
Organizers: Mike Graham and Satish Kumar

Tuesday 9:45 Oak 1 & 2 FS15
Direct numerical simulations of sheared mesophase pitches
Dana Grecov and Alejandro D. Rey
Mechanical Engineering Department, University of British Columbia, Vancouver, British Columbia v6t 1z4, Canada

Carbon fibers produced from mesophase pitches exhibit high stiffness and thermal conductivity and are used in satellite structures and other thermal management applications. The internal structure and therefore the final properties of mesophase-pitch-based carbon fibers are highly dependent on the flow-induced microstructure developed during the melt-spinning process. Mesophase pitches are thermotropic discotic nematic liquid crystals (DNLCs). The distinguishing features of the mechanical behavior can be summarized by stating that these materials exhibit anisotropic, non-linear, viscoelastic behaviour quite distinct from Newtonian viscous materials and from isotropic flexible-chain polymers. The remarkable rheological properties of the liquid crystals are governed by the flow-induced evolution of molecular configurations. The manufacturing of fibers based on liquid crystalline precursors usually involves complex processing flows, and hence good rheological models are needed for product optimization and control. This work uses a very well established mesoscopic model for liquid crystalline materials based on the Landau-de Gennes free energy. This model takes into account all the three major effects (short and long range order elasticity and viscous flow) and can capture general and complex phenomena of liquid crystals behavior (e.g. banded texture, defect generation and coarsening phenomena) which are not captured by the classical theories. The presented multiscale theory and simulation of hydrodynamic meso and macrotexture formation is able to provide fundamental principles for control and optimization of structures and to elucidate the relation between rheological properties and textural transformations for mesophase pitches. We characterize the relation between rheological functions growth and textural transformations of mesophase pitches subjected to shear start-up flow. The non-monotonic stress growth is consistent with experimental observations.

Tuesday 10:10 Oak 1 & 2 FS16
Computational simulations of the behavior of a model nematic LCP in a simple shear device
D. H. Klein and L. G. Leal
Dept of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106

We consider the behavior of the Doi-Marrucci-Greco model for nematic LCPs in a simple shear device. We consider a range of Erickson and Deborah numbers from the Leslie-Erickson limit up to Deborah numbers of order O(10).The computational results show behavior that is qualitatively identical to the Erickson and Deborah number cascades that were observed experimentally by Larson and Mead. Of special interest is the formation of both disclinations. The former appear at lower Erickson / Deborah numbers. At higher Erickson / Deborah numbers, both types of disclinations occur. The disclinations form very near to the top and bottom boundaries of the flow cell, but not at the walls. The
The wormlike micellar system of cetylpyridinium chloride (CPyCl) and sodium salicylate (NaSal), at various concentrations in a constant 2:1 molar ratio, in 100mM NaCl brine water has been studied in Couette flow. Using high-speed imaging for particle-image velocimetry (PIV) measurements coupled with flow-induced birefringence (FIB) measurements, we have been able to visualize the development of structured shear bands in steady-shear flows and the startup of steady-shear experiments. Of great interest is how the development of the shear bands and structure correlate during the initial formation of the shear bands and the subsequent fluctuations. A very high spatial resolution was achieved in both the PIV and FIB measurements using a large Couette cell having a gap of 5.75mm. Our velocity profiles demonstrate the existence of shear bands exhibiting a velocity limit in the low shear rate band that is consistent with shear rates where steady rheology experiments exhibit a characteristic stress plateau, indicative of shear banding. Within the different bands, our FIB measurements show a contrast between the level of time, consistently. Steady-shear startup measurements demonstrate a slow evolution (over several relaxation times) of both shear banding and birefringence.

A common problem in multi-layer shear flows, especially from the perspective of process engineering, is the occurrence of interfacial instabilities. For purely viscous fluids these occur at both long and short wavelengths, and at low Reynolds numbers. However, multi-layer duct flows can be stabilised by using a suitable yield stress fluid as the lubricant [1,2]. We focus on the simplest practically interesting case of visco-plastically lubricated viscous shear flow: a core-annular pipe flow consisting of a central core of Newtonian fluid surrounded by a Bingham fluid. First we show how interfacial instabilities may be eliminated through the introduction of a yield-stress fluid as the lubricant and by preserving an unyielded layer adjacent to the interface. Second, we show that nonlinear stability of this type of two-layer flow can also be achieved, at significant Reynolds numbers. Finally we show the initial results of an experimental study of these flows. The ability to have stable multi-layer flows at moderate Reynolds numbers opens up new possibilities for high speed manufacture/processing of multi-layered products.


The linear stability of creeping plane Couette flow of an upper-convected Maxwell (UCM) fluid past a deformable wall is the subject of this work [V. Shankar and S. Kumar, J. Non-Newtonian Fluid Mech. 116 (2004) 371]. The wall is modeled as a linear viscoelastic solid, and the effect of wall elasticity on the stable modes of Gorodtsov and Leonov [J. Appl. Math. Mech. 31 (1967) 310] for Couette flow of a UCM fluid past a rigid wall, and the effect of fluid elasticity on the unstable modes of Kumaran et al. [J. Phys. II (France) 4 (1994) 893] for Couette flow of a Newtonian fluid past a deformable wall are analyzed. Results of our analysis show that there is only one unstable mode at finite values of the Weissenberg number (Wi). In the rigid wall limit at finite Wi, this mode becomes stable and reduces to the stable mode of Gorodtsov and Leonov. In the Newtonian fluid limit and for a deformable wall, this mode reduces to the unstable mode of Kumaran et al. In general, the flow becomes unstable when the viscous forces become sufficiently large relative to the elastic forces associated with the wall, and when the fluid relaxation time is sufficiently small relative to the wall relaxation time. Results from related flow visualization experiments will also be discussed.
Annular expansion flow of a concentrated suspension measured by NMRI

Tracey Moraczewski and Nina Shapley
Chemical Engineering, Columbia University, New York, NY 10027

We investigate the flow of a concentrated suspension through an abrupt, axisymmetric expansion, which can be encountered in such applications as materials processing or flow in the circulatory system. Although the abrupt expansion is a classic test geometry that has been employed in the characterization of many non-Newtonian materials, few experimental data and modeling calculations are available for concentrated suspensions in expansion flow. In this study, suspensions of neutrally buoyant, noncolloidal spheres in Newtonian liquids undergo steady, pressure-driven flow in an abrupt, axisymmetric 1:4 expansion. Particle concentration and velocity profiles are obtained by nuclear magnetic resonance imaging (NMRI). We aim to determine the influence of particle and flow properties (e.g. particle volume fraction, particle and flow Reynolds number, particle-tube radius ratio, inlet conditions) on the interaction between particles and recirculating flow regions such as the corner vortex. For example, in the case of a long narrow tube inlet, observed vortex lengths for suspensions are greater than for Newtonian fluids at comparable Reynolds numbers. Also, inlet conditions have a strong influence on whether particle accumulation or depletion results in the vortex region. Results from expansion flow experiments at various inlet conditions will be presented.

Rheological behavior of fiber-filled polypropylene under large amplitude oscillatory shear flow

Julien Férec¹, Marie-Claude Heuzey¹, Pierre J. Carreau¹, and Gilles Ausias²
¹Center for Applied Research on Polymers and Composites, Ecole Polytechnique de Montreal, Montreal, QC, Canada;
²Laboratoire de Génie Mécanique et Matériaux (LG2M), Université de Bretagne Sud, Lorient, France

The rheological behavior of short glass fiber-filled polypropylene melts was investigated under small and large amplitude oscillatory shear (LAOS) flow. The application of LAOS to materials results in the appearance of higher harmonics in the shear stress response. Analysis of these data via Fourier transformation (FT) can be used to quantify the non-linear behavior of the fiber-filled systems, and in particular to evaluate the contributions of the fibers to the non-linearity. Harmonic oscillating strain excitations were applied and resulting stress and normal force responses were recorded. We performed Fast Fourier-Transform (FFT) analyses and examined Lissajous figures together with FT amplitude and phase angle. It was observed that at small strain amplitude the measured responses were harmonic with the imposed signals. Under increasing deformation, higher harmonics appeared and were related to changes in the fiber microstructure and to fiber-fiber interactions. Average dissipated energies of the fiber systems evaluated over one cycle were determined and compared with that of the unfilled matrix. Our results showed that fiber-fiber interactions in concentrated suspensions contributed strongly to the dissipation of energy.

Stress dielectric response in polymeric suspensions

Yiyan Peng and Yuri M. Shkel
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Deformation-induced dielectric response of dielectric materials, called dielectrostriction, provides a new approach to study properties and structure of polymers. The dielectrostriction effect resembles the well-known birefringence phenomenon. While birefringence in polymers is described by the stress-optic relationship, a stress-dielectric relationship applies to dielectrostriction. However, dielectrostriction measurements can be performed on both transparent and opaque materials, require a much simpler data acquisition technique, are capable of local measuring stresses and can be implemented for in-line monitoring of polymer processing. In this study, a planar capacitor sensor technique has been developed to detect the dielectrostriction effect in shear flow of suspension of micro and nano inclusions in polymers. Mechanisms contributing to the similarity between the stress-dielectric and the stress-optic relationship are discussed.

Colloidal interaction forces and their relationship to the heterogeneous structure and dynamics of gels

Clare J. Dibble, Michael Kogan, and Michael J. Solomon
Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136

Particulate gels are manipulated in sol-gel ceramic processing and the production of coatings. They also can be an undesirable outcome of attempts to fabricate ordered arrays for optical materials and sensors. In both cases, control would be enhanced by elucidating the state-variable dependence of gel development and the resulting structure and dynamics. Here, we probe the dynamic and structural changes that accompany the gelation transition by visualizing single-particle motion immediately above and below the gel boundary. The gels are comprised of sterically-stabilized poly(methyl methacrylate) colloids suspended in a density-matched solvent. The colloids experience attractive forces through depletion interactions induced by non-adsorbing polymer. We use confocal laser scanning microscopy to directly visualize three-
dimensional volumes and two-dimensional time series of gel structure and dynamics. We study in particular the transition from cluster-like to gel-like single-particle dynamics. We correlate the localization of single particle dynamics on the order of the range of the depletion interaction to the emergence of a structural length scale in number density fluctuations. In addition, we investigate dynamic heterogeneity as an explanation for non-Gaussian behavior of the van Hove self-correlation function.

Tuesday 11:25 Salon 1

Consolidation of a colloidal dispersion under shear
Jeffrey F. Morris
The Levich Institute, City College of New York, New York, NY 10031

The problem of describing a colloidal dispersion undergoing consolidation (by drying or filtration) is considered by applying a two-phase flow, or suspension balance, model. Of special interest is development of a framework for simultaneous shear and consolidation. Existing models of the consolidation of a colloidal suspension, particularly in the flocculated case, and the shear flow of suspensions are shown to be derivable from the same general equations for mass and momentum transport in a mixture. In both cases, the rheology associated with the particle phase plays the key role. The bulk shear and compressional rheology are considered along with osmotic effects to develop a framework for describing the consolidation process under general flow conditions. The model is tested to describe characteristics including the evolution of solids fraction and phase velocities against published experimental data in consolidation, cross-flow filtration, and cohesive sediment transport. The potential for use of shear to optimize the consolidation process is examined.

Symposium SM

Entangled Solutions and Melts
Organizers: Lynden Archer and Jay Schieber

Tuesday 9:45 Salon 2

Hierarchical modelling of entangled polymer dynamics: the bottom up approach
Alexei Likhtman and Sathish K. Sukumaran
Applied Mathematics, University of Leeds, Leeds LS2 9JT, United Kingdom

I will present the hierarchy of models for the dynamics of polymer melts, developed in Leeds over the last few years. The traditional rheological approach to constitutive modelling is to write down the simplest possible constitutive equation and then add extra terms as required to fit experimental data. I will argue in favour of the opposite bottom up approach, in which we start from microscopic models and carefully coarse-grain them, comparing the results at each intermediate stage. To this end, we start with molecular dynamics simulations of polymer melts, a multi-chain problem. These simulations are currently possible for mildly entangled chains in the intermediate time regime. We show, however, that this is sufficient to obtain the local parameters of the "entanglement field", which can then be incorporated into the new single-chain slip-links model, developed on the basis of the Rubinstein-Panyukov network model. This model can be further coarse-grained to a tube-like model and requires new components missing in the previous tube models. Then I will demonstrate how such tube models can themselves be coarse-grained to obtain a new class of constitutive equations, applicable to linear and comb-like polymers and useful for complex flow modelling.

Tuesday 10:10 Salon 2

Primitive path identification and statistics in molecular dynamics simulations of entangled polymer melts
Qiang Zhou1 and Ronald G. Larson2
1Mechanical Engineering, University of Michigan, ann arbor, MI 48109; 2Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136

Identification of primitive paths, which are centerlines of confining tubes, is one of major challenges in linking the well established tube theory to molecular reality in entangled polymeric systems. Two leading methods, namely total quadratic energy minimization and length minimization, are explored and compared in molecular dynamic(MD) simulations of linear pearl-necklace polymer chains. Energy minimization leads to a slightly larger averaged length but much narrower contour length distribution around the average length than does length minimization. Applications of both methods to melts of linear polymers in MD simulations confirm a quadratic entropic potential governing the primitive path length distribution. However, length minimization leads to a pre-factor of around 1.5, in agreement with the classical result of Doi and Edwards, while energy minimization gives a pre-factor of around 3.0.

Tuesday 10:35 Salon 2

What are the respective contributions of contour length fluctuations and tube motions to the 3.4-power law for zero-shear viscosity?
Chen-Yang Liu, Evelyne van Ruymbeke, Adrien Leygue, Roland Keunings, and Christian Bailly
Université catholique de Louvain, Louvain-la-Neuve, Belgium

"Standard" tube models [1, 2] attribute the observed departure from the 3.0 exponent for the molecular weight (Mw) dependence of the zero-shear viscosity (\(\eta_0\)) entirely to contour-length fluctuations (CLF) effects. We had compiled data on the Mw-dependence of the experimental
plateau modulus, and found that tube models overestimate the influence of the fast dynamic process CLF on the level of stress relaxation, while at the same time providing accurate predictions for relaxation times or $\eta_0$. Results of neutron spin-echo experiments and slip-link simulations also indicated a weaker Mw-dependence of the apparent plateau modulus. This inherent contradiction between relaxation stress and relaxation time results indicates a possible overestimation of CLF by the models. As a result, actual CLF effects would not generate an additional exponent of 0.4 for $\eta_0$ over a wide range of Mw. In this work, we will clarify any possible contributions from motions of surrounding chains (tube motions) to the exponent 3.4. By widely separating the molecular weights of binary mixtures, it is possible to suppress tube motions for test chains in a high Mw matrix, which allows to isolate the contribution of tube motions from CLF in a very clear way. Reanalysis of published results and carefully designed experiments indicate that tube motions have indeed at least a partial influence on the exponent.


Tuesday 11:00 Salon 2

A study of the LAOS response of linear entangled polystyrene melts
Adrien Leygue$^1$, Chen-Yang Liu$^2$, Christian Bailly$^2$, and Roland Keunings$^1$

$^1$Universite catholique de Louvain, Louvain-la-Neuve, Belgium; $^2$Universite catholique de Louvain, Louvain-la-Neuve, Belgium

Large Amplitude Oscillatory Shear (LAOS) flows allow the study of the non-linear response of a material with a smooth flow where both the strain and the rate of strain are well controlled. As both the maximum strain and the angular frequency can be imposed independently, a Deborah number and a Weissenberg number can be defined separately. Although LAOS experimental data can be represented both in the time and spectral domains, the interpretation of the non-linear response remains a challenge.

The comparison of LAOS data with the predictions of a constitutive model might offer the only way to a non-phenomenological interpretation of the measured non-linear response.

In this work, we investigate linear entangled polystyrene melts under LAOS using the CRAFT model [1]. We first identify the linear parameters of the model from the linear response of two linear polystyrene samples. The only non-linear parameter, related to finite extensibility, is obtained from microstructural knowledge. We show that as long as the chains are not too stretched, the CRAFT model predicts quantitatively the LAOS response of mono- and poly-disperse polystyrene melts. Although the response of the samples is highly non-linear, we show that linear parameters only are required to predict the polymeric stress. Furthermore, we show that the spectral-domain is well suited to describe the differences between the experimental data and the model predictions.


Tuesday 11:25 Salon 2

Wall slip and spurt flow of polybutadiene
Fabrizio Smillo, Sung Taek Lim, and John M. Dealy
Department of Chemical Engineering, McGill University, Montreal, Quebec H3A 2B2, Canada

The analysis of flow-rate versus driving pressure data during spurt flow in a capillary rheometer is generally based on two assumptions: 1. that spurt occurs at a constant wall shear rate, and 2. that pressure does not affect the slip velocity. These assumptions have led some researchers to propose that spurt is the manifestation of a change in molecular conformation at a critical shear stress. We demonstrate that the two assumptions cited above are not correct, and this requires a reassessment of the physics underlying the spurt phenomenon. Using a sliding plate rheometer, we demonstrate that the slip velocity depends on pressure and is a non-monotone function of the shear stress. These observations lead us to the conclusion that spurt is a system instability arising from the particular combination of factors involved in capillary flow and not the manifestation of any change in the behavior of the polymer itself at a critical shear stress.

Symposium SS
Viscoelasticity and Viscoplasticity of Solids and Semi-Solids
Organizers: Ian Frigaard and Gregory B. McKenna

Tuesday 9:45 Seymour
Predicting aging phenomena in glassy polymers with the potential energy clock model
Douglas B. Adolf$^1$ and Robert S. Chambers$^2$

$^1$Materials and Process Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185-0888; $^2$Engineering Sciences Center, Sandia National Laboratories, Albuquerque, NM 87111-0893

We previously developed a thermodynamically consistent constitutive equation based on a potential energy material clock [1]. Characterization tests for defining model inputs included such simple linear viscoelastic tests as heat capacity, coefficient of thermal expansion, and shear relaxation modulus. Model predictions for enthalpy relaxation and temperature-dependent yield in both tension and compression were in good agreement with experimental data on several unfilled polymers [2]. The model also predicted physical aging as seen by an aging exponent of 0.8 for the viscoelastic shift factor and a 20% increase in the compressive yield stress as the sample was held isothermally below the glass transition.
Moreover, molecular dynamics simulations have validated the underlying assumption that the temperature and volume dependencies of polymer relaxation rates in equilibrated systems are correctly captured by the potential energy \[3\]. We will now examine more complex responses of glassy polymers presented in the literature and detail the ability of this rheologically simple model to capture these responses quantitatively.


*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Tuesday 11:00 Seymour

**A Gaussian slip-link model for cross-linked polymers**
Mahnaz Eskandari, Jay D. Schieber, and Hamid Arastoopour
Chemical Engineering and Environmental, Illinois Institute of Technology, Chicago, IL 60616

We have developed a slip-link model valid for both liquids and for cross-linked systems. Here we focus on the equilibrium properties of the slip-link model with cross-links, assuming Gaussian chains. In our slip-link model it is assumed that the positions of the cross-links are deformed affinely. Averages necessary to predict stress cannot be found analytically, so numerical simulation is required. The simulation consists of two steps: preparation and deformation. In the preparation step, cross-links and slip-links are assumed to be distributed uniformly along the chain, but with independent parameters describing their statistics: the average number of Kuhn steps between entanglements, \(N\_e\), and the average number of Kuhn steps between cross-links, \(N\_c\). The dynamic variables include the number of Kuhn steps for the slip-link strands and the slip-link strands vector. In the second step, the prepared system undergoes deformation. The variables of the preparation step become the parameters of the deformation step and the stress tensor can be found as a function of the deformation. The Mooney plot of the simulation result has been compared with the experimental data. Good agreement has been obtained for uniaxial and equibiaxial elongation deformations for cross-linked natural rubber, poly(dimethyl-siloxane), and poly(butadiene). The model is used to predict values for the Mooney plot parameters \(C\_1\) and \(C\_2\) as a function of \(N\_e\) and the average number of entanglements between cross-links \(<z>-1\). The \(C\_2/C\_1\) ratio is found to be strongly dependent on \(<z>-1\), but weakly dependent on \(N\_e\). From the experimental data for a given cross-linked polymer, this observation provides a new way of predicting the cross-link density and separating it from the entanglement density. However, for systems of known \(N\_e\) and known cross-link density, the model requires no adjustable parameters.

Tuesday 11:25 Seymour

**Viscoelastic behavior of low molecular weight sulfonated polystyrene ionomers**
Hongying Zhao\(^1\) and R. A. Weiss\(^2\)
\(^1\)Polymer Program, University of Connecticut, Storrs, CT 06269-3136; \(^2\)Chemical Engineering Department, University of Connecticut, Storrs, CT 06269-3136

The rheology of sulfonated polystyrene ionomers (SPS) was characterized using a series of ionomers prepared from a low molecular weight (4,000), narrow molecular weight distribution (1.06) polystyrene. Two sulfonation levels were examined, 2.50 and 4.78 mol%, and the metal counterions was varied across the alkali metal series of the periodic table. Dynamic and steady shear experiments were performed. For SPS with 4.78% sulfonation level, good time-temperature superposition (TTS) was obtained for KSPS, RbSPS and CsSPS, while TTS for G* failed for LiSPS and NaSPS. All TTS for G* failed for lower sulfonation level (2.50%). The steady shear viscosity increased with sulfonation level and as the size of counterion decreased for the alkali metal salts, whereas the parent polystyrene exhibited no elasticity. Shear thinning and shear thickening behavior were observed for the lower sulfonation level, not for the higher sulfonation level within the measurable range. The microstructure of the SPS ionomers was also studied using small-angle X-ray scattering (SAXS). A scattering peak and an upturn in intensity near zero angle confirmed the existence of ionic clusters.

**Symposium MM**

**Molecular Modeling and Simulation in Rheology**

Organizers: Bamin Khomami and Antony Beris

Tuesday 9:45 Salon 3

**Steady-state and transient analysis of film blowing with flow-enhanced crystallization**
Lars Henrichsen and Anthony J. McHugh
Lehigh University, Bethlehem, PA

A modified version of the two-phase Doufas-McHugh model is used to fit steady-state blown film data for both LLDPE and LDPE. Model data fits of bubble radius, temperature, and crystallinity are shown for each material. The radius and temperature predictions are excellent, while the crystallinity predictions are the least accurate, although still reasonable approximations of the experimental data. These steady-state fits are then used to explore the transient behavior of the model via dynamic frequency response. The stability of the process is examined through perturbations to both external and internal variables.
In electrospinning, electrical field is used to produce high elongational forces that result in formation of nearly one-dimensional fiber structures with fiber diameters as small as 50 nm. These nanofiber mats have attractive characteristics such as high surface area to mass ratio. Early electrospinning processes were based on polymer solutions and involved coupling of momentum, energy, and mass transfer, as well as phase transition, which made them virtually impossible to model predictively. Recently we developed a scheme for electrospinning directly from polymer melts that can be used for a variety of polymers with different crystallization behaviors including nylon, polypropylene, polyethylene terephthalate, and polylactic acid. Along with other experimental advances, this technique has renewed the interest in modeling of electrospinning. The new experiments eliminate the complications of mass transfer, in particular in development of constitutive models, thus allowing for tractable numerical simulation.

In the present study we formulate the governing equations for non-isothermal free surface flows of electrically charged viscoelastic fluids in the stable jet region. We fully couple momentum, continuity, and energy equations with Gauss’ law and the non-isothermal Giesekus constitutive model. For polymers that exhibit significant crystallinity we also add a detailed crystallization model that incorporates the overall degree of crystallinity and microstructural elements such as the number of crystals and their size distribution. The system of governing differential equations was derived based on thin filament approximation and has been numerically solved. Our results reveal that the shape of the liquid cone and the resulting jets from melts are significantly different from those from solutions. We will compare predicted results with flow visualization experiments for the above-mentioned polymeric systems. The present model forms the basis for a full-scale finite element analysis to follow.

Because of its high melt viscosity, polytetrafluoroethylene (PTFE) is usually processed by paste extrusion instead of conventional melt processing techniques. Experimentally it has been reported that the extrusion pressure varies non-monotonically with the entrance angle of the conical die attached at the bottom of a capillary extruder. SEM micrographs show the formation of submicron-diameter fibrils in between polymer particles due apparently to squeezing of neighboring particles inside the converging conical die and unwinding of mechanically locked crystallites. In the present study the mechanism of fibrillation is captured through a microscopic model for a structural parameter that accounts for the population of fibrils. The evolution of the structural parameter is described by a first-order kinetic differential equation. A constitutive equation is constructed that shows shear-thinning and shear-thickening behavior depending on the evolution of the structural parameter during extrusion. Finite element simulations have predicted variations of the extrusion pressure with the apparent shear rate and die geometry, especially the die entrance angle. The simulation results will be compared with experimental findings. Key words: PTFE paste, extrusion, conical die, fibrils, micro-structural parameter, shear thinning, shear thickening, finite element simulations.
Cyber infrastructure for polymer rheology
H H. Winter\textsuperscript{1} and Marian Mours\textsuperscript{2}
\textsuperscript{1}Chemical Engineering and Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003; \textsuperscript{2}Brussels, Belgium

We are in the process of building a global cyberinfrastructure (CI) for exploring and predicting rheological properties of complex materials. Such a CI for rheology has the potential of integrating, for the first time, the diverse knowledge of the world's experts in applied and theoretical rheology. Through such collaboration, seemingly disparate theories and experimental observations will be linked and taken to their limits, thereby leading to unexpected insights and new questions. We envision a global alliance of rheology experts who access each other's experimental results, make predictions with each other's theories and simulate with each other's computer codes. At the center of the CI is a platform operating system (IRIS code) that connects a wide range of dedicated software modules. These CI modules perform calculations and return the corresponding results to a central graphics screen. A universal data standard facilitates communication between laboratories worldwide. Several of the world's leading rheology experts have begun to write theory modules that seamlessly connect into the rheology CI; several modules are complete and more are in progress. The rheology CI helps with tasks such as materials development, polymer engineering applications, teaching of rheology, rheology research (experimental and theoretical), data communication and archiving.
Tuesday Afternoon

Symposium FS
Non-Newtonian Fluid Mechanics and Stability
Organizers: Mike Graham and Satish Kumar

Parallel shear of viscoelastic fluids as a control problem
Michael Renardy
Mathematics, Virginia Tech, Blacksburg, VA 24061-0123

We consider homogeneous parallel shear flow of a viscoelastic fluid and study the following control problem: Given an initial state of stress, can we choose a shear rate as a function of time such that the flow achieves another given state of stress at a given final time? It is clear that in general the answer is no, since, for instance, the second normal stress difference will remain zero for many constitutive models, regardless of the shear rate. For a number of popular constitutive models, we discuss how to characterize the set of stresses which can be reached.

Linear stability of shear flow in the high Weissenberg number boundary layer
Andreas Putz
Mathematics, University of British Columbia, Vancouver, B.C., Canada

The Upper Convected Maxwell model is noted for developing sharp boundary layers close to solid surfaces, which require a very fine resolution to ensure accurate numerical results. The continuous part of the spectrum of the linearized UCM equations approaches zero as the Weissenberg number increases causing numerical methods to predict instabilities [M. Renardy, JNNFM 94 (2000)]. In this work, linear stability analysis for a scaled set of boundary layer equations is presented. We show that uniform shear flow is a solution of these equations and approximate the discrete spectrum. A bound on the continuous part of the spectrum is obtained as well. In contrast to the full equations, the spectrum does not depend on the Weissenberg number and is well separated from the instability region.

Non-Newtonian effects in lubrication flow
Dana Grecov\footnote{Mechanical Engineering Department, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada;} and Jean-Robert Clermont\footnote{Laboratoire de Rheologie, Institut National Polytechnique, Grenoble 38401, Canada}

The addition of polymers to Newtonian oils for industrial purposes has resulted in shear-thinning and elastic properties of the materials, thus leading to complex behaviour in lubrication flow. The growing interest in considering materials with non-Newtonian properties in lubrication has lead to generate various numerical techniques being formulated for investigating such flows with complex constitutive equations. In this work, we have applied an original approach to simulate two-dimensional complex flows in a journal bearing geometry and investigate the influence of rheological properties on the performance of lubrication flow, using domain decomposition and local transformation functions. The analysis has permitted to compute the main flow characteristics in journal bearing geometries at significant angular speeds. To compute this flow where vortex regions are encountered, the physical domain is split up into a finite number of sub-domains that are mapped into domains where open and closed streamlines are parallel and straight by means of local mapping functions to be determined numerically. Such simplicity for the mapped streamlines makes it easy to handle time-dependent constitutive models in viscoelasticity. The study of inelastic and viscoelastic fluid flows in journal bearing conditions has led to significant differences in predictions for the kinematics and stresses, even at moderate rotating rates. Particularly, the results highlight the preponderant influence of elastic properties on the flow characteristics, when compared to shear thinning effects. The governing non-linear equations are solved by the means of an optimization algorithm. The results point the influence of non-Newtonian properties of the fluids in lubrication flow, notably the influence of elasticity. The numerical results are consistent with those in the literature. The influence of the rheological properties on the journal bearing performances is presented.
Tuesday 2:45 Oak 1 & 2 FS23

**The circular-hole pressure for non-newtonian fluids**
Bruce Caswell¹, Vasilios Symeonidis², and George E. Karniadakis¹

¹Division of Engineering, Brown University, Providence, RI 02912; ²Division of Applied Mathematics, Brown University, Providence, RI 02912

A new theorem has been proved that allows the hole pressure for 3-dimensional geometries to be determined approximately by the equilibrium(inertialless) velocity field of a Reiner-Rivlin(R-R)fluid. At low shear rates and in plane flow the theorem reduces to the Giesekus-Tanner(G-T)theorem whereby the Stokes velocity field satisfies the equilibrium problem for the secon order fluid. In plane flow G-T yields the hole pressure relative to the Newtonian value, usually neglected. In 3-dimensions the new theorem yields the hole pressure relative to the R-R value which is not negligible. This is the motivation for the simulation of R-R flow, a purely 3-dimensional problem. The flow geometry is a plane channel(gap H) with a long tube(diameter d) mounted transversely on one wall. The finite element implementation has been verified with Kearsley’s(Trans.Soc.Rheol.17,617,1973) analytical result for the channel with a parallel slot. For small holes (d/H:1/10) the numerical results agree with the Higatshitami-Pritchard formula, but not so for large holes(d/H:1/1).

The calculated disturbance pressures for large holes for Newtonian fluids is shown to be in good agreement with experiment.

Tuesday 3:35 Oak 1 & 2 FS24

**Investigation of maxwellian fluid flow in the capillary tubes and studying the effective parameter: Theoretical parameter: Theoretical approach**
Majid Soltani

Mechanical Engineering department, K.N.T University of Technology, Tehran, Iran

The analytic solution of capillary tube is valuable for theoretical analysis and engineering calculation and is helpful to have an insight into the flow characteristics. In this study we investigate the flow of the maxwellian fluid in the capillary tube. First the fundamental equations of conservation of mass, momentum and energy of the fluid were derived. And then these correlations were generalized to the capillary tubes. Due to the particular geometry of capillary tubes, the governing equations were reduced and then these correlations were solved analytically. Finally influences of geometrical parameters (inner diameter and length) and inlet operating parameters (pressure, subcooling or quality) on the mass flow rate through an adiabatic capillary tube have been studied in this work. And it was seen that flow fluid can be affected by polymeric additives. This result can be useful in the heat transfer rate or pressure drop in line heat exchangers.

Tuesday 4:00 Oak 1 & 2 FS25

**Universality in rheology**
Kyung H. Ahn and Seung J. Lee

School of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea

Complex fluids and flows are all around us, and it is always challenging to find a simple principle that actually governs the complex-looking phenomena. Sometimes we call it as a universal or scaling behavior. Time-temperature superposition is an example. Though not completely understood from the molecular basis, it works fairly well to wide variety of polymeric systems, and provides us useful informations. Weakly aggregating colloidal particle systems also show a universal scaling behavior. In this talk, we will show more examples in which a simple principle governs the complex-looking phenomena. They include linear viscoelastic properties, flow behavior in planar contraction geometry, and the response of nanocomposites to the electric field.

Tuesday 4:25 Oak 1 & 2 FS26

**Hydrodynamic theory of polymeric liquids: Comparison to experiments**
Oliver Mueller¹, Mario Liu¹, Harald Pleiner², and Helmut R. Brand³

¹Theor. Phys., University Tuebingen, Tuebingen 72076, Germany; ²Max Planck Institute for Polymer Research, Mainz 55021, Germany; ³Theor. Physics, University Bayreuth, Bayreuth 95440, Germany

The hydrodynamic theory on visco-elasticity derived previously [see Phys. Rev. Lett. 84, 3228 (2000), Rheol. Acta 39, 560 (2000)] is applied to typical experiments in polymer rheology. Because the theory is cogently derived from general principles including both the energy and momentum conservation, without the need or possibility for trial and error, we expect it to competently account for most aspects of polymer behavior even if heavy-handedly simplified. The set of equations we employ contains only four parameters: The relaxation time of the strain, two elastic coefficients (that enter the expression for the energy), and less importantly, the constant shear viscosity, to be measured at infinite shear. And the results we find, mostly analytic solutions, are quite gratifying: Starting with (1) stationary shear, the total viscosity and the normal stress differences are calculated as a function of the shear rate, recovering shear thinning and the usual values for normal stresses, unless the parameters are given atypical values. Next, (2) the rod climbing (or Weissenberg) effect is considered at small rotation rates, yielding a typically observed surface profile. (3) For a sudden onset of shear flows, the shear stress and the normal stress differences are obtained as functions of time, displaying overshoot and oscillation at large shear rates. (4) Small-amplitude shear oscillation is studied, and the result is used to recover empirical relations such as the Cox-Merz rule and the Gleissle mirror relation. (5) For uniaxial elongational flows, we confirm that stationary solutions exist only for a limited range of elongation rates. Also, viscosity is found to grow monotonically with the rate for uniaxial
flows, and traverse a minimum for biaxial flows. (6) Finally, at the onset of elongational flows, the viscosity is seen to converge into the stationary value if it exists, and display diverging strain hardening if it does not.

Tuesday  4:50  Oak 1 & 2  FS27

Visualization of secondary flow formation by NMR methods
Norman Wagner
Chemical Engineering, Stanford University, Stanford, CA 94305

Viscoelastic fluids are known to exhibit a variety of flow transition at low Re numbers. During entry flow viscoelastic fluids are known to form secondary flows in corners of abrupt tubular contractions. We have applied NMR methods to perform spatial mapping of areas where vortices are formed by measuring volume-averaged dispersion coefficients of a flowing liquid. We also measured velocity fields in the same spatial locations. In both types of experiments the observation time was varied. We found no time dependence in the velocity fields while dispersion coefficients were strongly depended on the observation time. Based upon these results some information about the dynamics of vortex formation could also be deduced.

Tuesday  5:15  Oak 1 & 2  FS28

Ergodicity-breaking and conformational hysteresis in polymer dynamics near a surface stagnation point
Victor A. Beck and Eric S. Shaqfeh
Chemical Engineering, Stanford University, Stanford, CA 94305

We study the dynamics of long chain polymeric molecules tethered to a plane wall and subjected to a stagnation point flow. Using a combination of theory and numerical techniques, including Brownian dynamics (BD), we demonstrate that a chain configuration hysteresis exists even for freely draining (FD) chains. We also perform BD simulations including hydrodynamic interactions (HI) between the polymer and the wall. We find qualitative agreement between the FD and HI simulations, with both exhibiting simultaneous coiled and stretched states for a wide range of fixed flow strengths. The range of state coexistence is understood by considering an equivalent projected equilibrium problem of a two state reaction. Using this formalism, we construct a Kramer's rate theory for the hopping transition from coil-to-stretch and vice versa. The activation energy for this rate is found to scale proportionately with chain size, and in the thermodynamic limit of infinite chains the states are “frozen.” We present results that demonstrate this “ergodicity breaking” and generalize these results to other non-linear flows and driving forces. The consequences for polymer dynamics and solution rheology in microscale flows will also be discussed.

Symposium SC
Suspensions, Colloids, and Multiphase Fluids
Organizers: Dan Klingenberg and Nina Shapley

Tuesday  1:30  Salon 1  SC20

Yielding and flow of colloidal glasses and gels
George Petekidis, Khoa Pham, Dimitris Vlassopoulos, Stefan Egelhaaf, Wilson C. Poon, and Peter N. Pusey
IESL-FORTH, Heraklion, Crete 71110, Greece; School of Physics and Astronomy, Edinburgh, United Kingdom

The yielding and flow of a colloidal glasses and gels in systems where the interparticle interactions are varied from hard sphere like to short range repulsions and attractions is discussed. A series of rheological tests such as dynamic strain and frequency sweeps as well as flow curves, creep and recovery measurements and stress relaxation experiments provide a comprehensive picture of the non-linear rheological behavior of such metastable states. The macroscopic measurements are complemented by dynamic light scattering measurements under oscillatory shear (LS echo) which provide insight on the microscopic particle rearrangements under flow. For hard sphere glasses creep and recovery, dynamic strain sweeps as well as LS echo have revealed significant yield strain of 10-15% which was attributed to "cage elasticity". Moreover, flow curves have identified the yield stress of the glass and find that it compares favourably with mode coupling predictions. Shear induced crystallization, which further complicates the rheological behavior of hard sphere glasses, will also be discussed. Moreover, the effects of short range resistive and attractive interactions in the macroscopic and microscopic response under shear will be presented through a selected rheological and LS echo tests. Attractive glasses formed at high volume fractions (6=0.6) colloid-polymer mixtures exhibit an interesting two-step yielding attributed to distinct bond and cage breaking mechanisms. On the other hand, lower volume fraction colloid-polymer gels exhibit a single low yield strain corresponding to bond breaking. This serves as a distinction between gels and attractive glasses.

Tuesday  1:55  Salon 1  SC21

Shear thickening in polymer stabilized colloidal dispersions
Norman Wagner, Lakshmi Krishnamurthy, and Jan Mewis
Chemical Engineering, Univ. of Delaware, Newark, DE; K. U. Leuven, Leuven, Belgium

The shear thickening transition in polymer stabilized colloidal dispersions is analyzed in terms of a micromechanical model that incorporates both the stabilizing forces of the polymer brush and the associated modification of the hydrodynamic interactions due to the brush. Comparison is made to simulations and experiments on model, well characterized dispersions. The model is shown to provide a quantitative prediction for
the onset of shear thickening. Comparison with experiment indicates the sensitivity of the shear thickening transition to both the interaction potential arising from the brush as well as the hydrodynamic permeability of the brush.

Tuesday 2:20 Salon 1

Non-monotonic variations in viscosity for dense ergodic suspensions with depletion attractions
Vijay Gopalan-Krishnan and Charles F. Zukoski
Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801

Colloidal hard sphere suspensions are known to form a glass above a volume fraction of ~0.58. The addition of a small amount of non-adsorbing polymer of sufficiently small molecular weight results in a drastic increase in the rate of decay of correlations in density fluctuations thereby inducing fluidity and reducing the viscosity of the suspension. This phenomenon of “glass melting” is the result of a disruption of cages that localize particles and prevent long-time diffusion. Our experiments on hard sphere systems at volume fractions of ~0.40-0.55 show that the phenomena of increasing fluidity with addition of polymer is not restricted to jammed systems. At constant volume fraction, the viscosity goes through a minimum with increasing polymer concentration before it finally diverges at the gel transition. This minimum in viscosity is found to track the non-monotonic shift of the first peak in the structure factor, S(q), suggesting a close correlation of cage dynamics with the zero shear viscosity. Preliminary predictions of the viscosity from the Binary Collisions in a Mean Field (BCM) model modified by the recently developed "Naïve" mode coupling theory (NMCT) with activated dynamics are found to qualitatively predict identical trends in the viscosity at similar volume fractions. These findings suggest that the dynamics of localization in cages which is dominant in glassy colloidal suspensions originates at lower volume fractions where the dense suspensions are ergodic and display a distinct zero shear plateau in viscosity.

Tuesday 2:45 Salon 1

Retraction behavior of PPG drops in PEG with added Pluronic surfactants
Jeffrey Martin and Sachin Velankar
Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261

We are studying the effect of surfactant on interface-driven motion in fluid/fluid systems using model systems composed of polyethylene glycol (PEG), polypropylene glycol (PPG), and Pluronic (PEG-PPG-PEG) triblock copolymer surfactants. Here we report unexpected observations of the retraction and/or breakup behavior of elongated drops of PPG in a PEG matrix.

Experiments were performed in a Spinning Drop Tensiometer in which a drop of PPG suspended in a matrix of PEG was spun at high speed and drawn into an elongated cylinder. A subsequent decrease in rotational speed is expected to allow the drop to either retract into a sphere, or break by capillary instabilities; indeed this was observed for surfactant-free systems. Addition of small amounts of Pluronic produced two unusual observations.

Firstly, at room temperature, the drops did not retract completely, but instead retained elongated, non-spherical shapes at the end of the retraction. This suggests that addition of Pluronic surfactant gives the interfaces a weak yield stress that can resist the capillary pressure driving retraction. Similar effects are seen for a variety of Pluronic and Pluronic-R (PPG-PEG-PPG) triblocks. Preheating the system to temperatures above 50°C seems to erase this apparent yield stress altogether. Secondly, under some circumstances, the interfacial tension temporarily reduced to extremely small values when heating to above 50°C. This suggests that an excess of block copolymer can be trapped at the interface at room temperature, and it can desorb rapidly upon raising the temperature.

That both of the effects above are associated with heating to above 50°C, suggests that some crystallizable component in the Pluronic is responsible. Yet, remarkably, the effects are evident even in liquid Pluronics that are not crystalline in their bulk state.

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Tuesday 3:35 Salon 1

Experiments and modeling to characterize the manufacture of a physically blown foam
Lisa A. Mondy1, Rekha R. Rao1, Thomas A. Baer1, Douglas B. Adol1, Ed Russick1, Andrew M. Kraynik1, Anne M. Grillet1, and Stephen A. AltoBelli2

1Sandia National Laboratories, Albuquerque, NM 87185-0834; 2New Mexico Resonance, Albuquerque, NM 87106

Polymeric foam systems are widely used in industrial applications due to their low weight and abilities to thermally insulate and isolate vibration. However, processing of these foams is still not well understood at a fundamental level. We combine experimental observations with finite element model development to help understand the manufacture of a physically blown, thermosetting foam. A simplified computational model is developed based on the growth of volume source points scattered in a polymer matrix. These source points produce volume, depending on the local temperature and a description of the gas diffusion. Microscopy data are used to set the initial size of droplets of blowing agent. The spatial distribution of blowing agent is determined with Nuclear Magnetic Resonance imaging, which can detect both the protons in the epoxy matrix and the 19F in the volatile blowing agent. Differential Scanning Calorimetry is used to determine the kinetics for modeling the epoxy reaction. Finally, temperature instrumented visualization experiments are used to provide phenomenological estimates of the temperature dependence of the expansion rate as well as model validation.

*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
Investigated. Comparison with experimental data shows a fair agreement. The individual stress can be identified as in the formulations of Milner and that of Minale and Marrucci and thus stress induced demixing can be determined of the average size of the dispersed phase. In this paper, the study of the emulsion viscoelastic behaviour is extended to the non-linear regime. To this end, the dynamic response of an immiscible polymer blend subjected to large amplitude oscillations (LAOS) is investigated. The blend is composed by poly-dimethylsiloxane (PDMS) and poly-isobuten (PIB). Experiments are carried out by a strain controlled ARES Rheometer equipped with cone and plate fixtures. A dedicated data acquisition system is used to directly sample both the deformation and the stress periodic signals. The raw time-sequence data are subsequently transformed into the corresponding Fourier spectra. When the non linear stress response is analysed in the Fourier domain, higher-order odd harmonics are found to occur, whose magnitude is much larger than that of the pure components. This is a clear indication that the non-linear behaviour observed in the blend is due to the interfacial contribution. The LAOS experimental measurements are compared with the predictions of the Maffettone and Minale model coupled with the Batchelor formulation for the interfacial stress tensor. One first result is the determination of the blend average drop size. The extension of this procedure to the estimation of the drop size distribution is also presented and discussed.

Polymer blends and solutions under shear can phase separate showing regions of high polymer concentration of a few micron size aligned along the flow direction. Stress induced demixing has been studied in the mainframe of the two-fluid theory. Minale and Marrucci [XIIIth Int. Cong. Rheol., Cambridge (UK), 2000] showed that even in rectilinear shear flows an initially homogeneous polymer solution, with purely viscous solvent, becomes unstable if the stress applied exceeds a critical stress. It then evolves towards a new phase-separated steady state where two layers with different concentrations and shear rates can be identified. To deal with this situation, theory must make sensible assumptions for the interface boundary conditions. Different formulations of the two-fluid theory are available in the literature and with all of them it is not possible to identify the individual fluid stress so to write the required boundary conditions in terms of stresses. The only exceptions are the formulation of Milner [Phys Rev E 48, 3674-3691 (1993)] and that of Minale and Marrucci that are, however, limited to dilute conditions. To overcome this limitations the two-fluid theory is here reformulated starting from a variational principle. It is shown that to study problems with a concentration profile both the individual fluid must be compressible even if the whole solution is incompressible. The compressibility of the "two fluids" is then taken into account in the variational formulation and the momentum balance for the "solvent fluid" and for the "polymer fluid" are derived. The individual stress can be identified as in the formulations of Milner and that of Minale and Marrucci and thus stress induced demixing can be investigated. Comparison with experimental data shows a fair agreement.

The phenomena of single drop deformation in an uniform immiscible matrix under simple shear flow is widely studied in the literature. On the other hand, direct observations on drop deformation in concentrated polymer blends, which is the situation encountered in most applications, are rather scarce. The system investigated in this work was a blend of Silicon Oil in Poly-Butene at different dispersed phase concentrations (2.5%, 5%, 10% wt). Two different flow cells were used to observe the sample under shear flow both along the vorticity direction or the direction of the velocity gradient. In the experiments, several drops of the dispersed phase were individually followed during motion by computer-assisted optical microscopy and the shape was characterised by image analysis. Drop shape, as measured by the three main axes, the orientation angle and the deformation parameter, did not reach any steady state configuration, but rather oscillated around an average value. Such average value, which was dependent on the capillary number of the drop, was found to increase as function of the dispersed phase concentration. All these effects can be taken into account by interpreting the data by a mean field hypothesis, i.e., by assuming that the viscosity of the fluid surrounding each drop is not the viscosity of the matrix, but the viscosity of the blend. By using this correction, all the data are found to collapse to the case of an isolated drop, as represented both by experimental measurement and theoretical predictions.
Tuesday 1:30 Salon 2  
**Terminal and segmental dynamics in miscible polymer blends**  
Timothy P. Lodge, Jeffrey C. Haley, Ilan Zeroni, and Sahban Ozair  
*Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN 55455*

In this paper we present new results for the composition and temperature dependence of chain dynamics in miscible PEO/PMMA blends, and compare the results with measurements of segmental dynamics reported in the literature. Measurements include tracer diffusion, measured by forced Rayleigh scattering, and "tracer rheology", in which as small amount of high molecular weight component is dissolved in a low molecular weight blend. These results are discussed both in terms of the connection between terminal and segmental dynamics in general, and also with respect to the ability of various models to explain the experimental phenomena. Particular attention will be given to the zero shear viscosity, which has been previously shown to exhibit a strong minimum with composition at fixed temperature.

Tuesday 1:55 Salon 2  
**The shear rheology and single molecule fluorescence microscopy of entangled DNA in solution**  
Rodrigo Teixeira¹, Eric S. Shaqfeh¹, and Steve Chu²  
¹Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025; ²Lawrence Berkeley Laboratories, Berkeley, CA

We present rheological measurements of lambda phage DNA solutions and single molecule fluorescence microscopy measurements of individual DNA molecules in the same solutions for increasing DNA concentrations. The measurements are presented for concentrations up to 35 c*, or approximately 17 entanglements per chain. The measurements demonstrate clearly the now standard characteristics of entangled solutions including a clear nonlinear shear stress plateau, a broad range of decreasing loss modulus, a clear cross over of storage and loss modulus, as well as very large overshoots in the shear viscosity as a function of shear strain. These measurements are compared qualitatively with the characteristics of entangled polystyrene solutions as presented for example by Bent et al. Science, 301, (2003). The single molecule microscopy measurements demonstrated a bimodal relaxation behavior and when accomplished for increasing concentration show a short time relaxation which is nearly independent of concentration and a long time relaxation time which scales with concentration as the reptation time. Moreover the ratio of the short and long times is approximately 3 x the entanglement number. The short relaxation time is found to be nearly 10 times the estimated Rouse time. Distributions of extension in nonlinear shear flow are presented and when the shear rate is scaled with the short time relaxation time these distributions are demonstrated to be quite broad at values of the resulting Deborah number greater than unity. Analysis of the length fluctuations at these large values of De (again based on the measured short time relaxation time) indicate that tumbling, much as occurs in dilute solutions, is found even in these highly entangled solutions.

Tuesday 2:20 Salon 2  
**Effect of edge instability on the non-linear rheology of a highly entangled polymer solution in a torque-controlled rheometer**  
Yong Woo Inn, Kurt F. Wissbrun, and Morton M. Denn  
*Benjamin Levich Institute for Physico-Chemical Hydrodynamics, City College of New York, New York, NY 10031*

Torque-controlled rheometers (commonly called "stress-controlled rheometers") should, in principle, provide the same steady rheological data as displacement-controlled ("strain-controlled") rheometers. Tapadia and Wang [1,2] have recently reported a discontinuity in the flow curve of a highly entangled solution of 1,4-polybutadiene in oligomeric butadiene in a torque-controlled rheometer, but they did not observe a discontinuity in a displacement-controlled rheometer; they argue that the torque-controlled result is more reliable because of the uniformity of the stress field. They attribute the discontinuity to an entanglement-disentanglement transition. We have measured the linear viscoelastic response and the flow curve of a 7.5% solution of the same polymer and solvent using a torque-controlled rheometer with a cone-and-plate fixture. We found that the reported discontinuity is a consequence of an edge instability in the plateau region, leading to loss of material from the fixture, and that the flow curve is continuous if care is taken to minimize the edge instability. Material loss because of edge instability is difficult to visualize with a small cone angle, and small edge effects can profoundly influence the apparent flow curve.

Exploring consequences of constitutive flow discontinuity in simple shear of entangled polymer mixtures
Prashant Tapadia and Shi-Qing Wang

Our recent observations [1] of constitutive flow behavior of entangled polymer solutions, which largely deviated from the conventional wisdom [2], have prompted us to examine the aftermath. The model entangled polymers under study are binary mixtures of 1,4-polybutadiene. Flow behavior of these samples was examined under various experimental conditions where shear flow was imposed by applying either a constant torque or a constant velocity on one of the two surfaces in a cone-plate shear cell (commonly known as controlled-stress or controlled-rate measurements respectively). Particle tracking and flow birefringence observations have been carried out to reveal the detailed characteristics of the flow responses from these entangled liquids. As expected, we found the local shear rate to vary smoothly across the gap in such a simple shear device as cone-plate or parallel plates when the sample is sheared in controlled-rate mode in the stress plateau regime. In addition, unlike the common belief that a uniform shear rate would be established upon a start-up of a sudden buildup of one plate in a planar Couette geometry and that the stress overshoot would be the material's response to this imposed uniform simple shear, we found the velocity gradient varies along the gap direction, changing with time during the transient stress response. These results show explicit breakdown of the fundamental premise of the experimental polymer rheology that a simple shear with uniform shear rate can be prescribed by such devices as planar Couette shear cells.

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Stress relaxation dynamics in entangled linear polymer liquids following step strain flow
David C. Venerus and Ritesh R. Nair

The flow behavior of entangled linear polymers with narrow molecular weight distribution has attracted the attention of experimental and theoretical rheologists for many years. One of the most successful theoretical models to date for such systems is the tube model of de Gennes developed into a constitutive model by Doi and Edwards. The tube model prediction for the damping function, the ratio of the non-linear to linear shear modulus for times greater than the longest Rouse relaxation time, has been found to be in good agreement with experimental data on a large number of linear, mono-disperse polymer liquids. There are, however, a significant number of cases where tube model predictions are not consistent with experimental stress relaxation data. A common observation is that the measured damping function is substantially smaller than the tube model prediction at intermediate strains (type C behavior). Even more troubling is the fact that these differences are observed for the gap direction, changing with time during the transient stress response. These results show explicit breakdown of the fundamental premise of the experimental polymer rheology that a simple shear with uniform shear rate can be prescribed by such devices as planar Couette shear cells.

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Responses of monodisperse entangled polymers to large step-strains
Prashant Tapadia1 and Shi-Qing Wang2

We have recently revealed that entangled polymer solutions undergo a discontinuous bulk flow transition under controlled shear stress due to chain entanglement-disentanglement transition.[1] The implication of such results is far reaching, the least of which is that the experimental system, when sheared in the so called stress-plateau region, would avoid any constitutive instability by developing a shear rate gradient across the sample thickness in planar Couette flow under the condition of imposing a constant velocity on either surface of a cone-plate apparatus. A separate set of experimental studies involving large step-strain shear of entangled polymers may also gain insight from our study of the continuous shear flow behavior of entangled polymers. Here we study the widely-known problem [2] of so called "strain softening" (or type C behavior) in entangled polymers during stress relaxation upon large step-strain, where the relaxation modulus G(t) makes an unusually large drop when the applied "instant" strain exceeds, say, 100 % for melts. The current theoretical knowledge cannot account for the type C behavior. Is this always due to some experimental artifacts [3] such as slip [4] or something inherent and constitutive? New experimental observations have led us to reach a completely different conclusion regarding the origin of the nonlinear behavior of entangled polymers in step strain experiments.

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References:
For polymeric systems many empirical or semi-empirical rules exist. One of the most prominent is the Cox-Merz rule, which correlates the shear viscosity from a given shear rate to the complex viscosity measured in a frequency sweep. A generalized Cox-Merz rule correlates the first normal stress difference \( (N1) \) with the elastic modulus \( G' \). In transient tests Gleissles mirror rules relate the transient behavior of the shear viscosity and first normal stress coefficient with steady state results. The Lodge-Meissner rule gives a relation between \( N1 \) and the shear stress in a step strain experiment. For simple polymeric fluids all this rules are expected to hold and they provide a rather straightforward check on the validity of the rheological data. However, still literature is published in which this relations are not considered and the published results are doubtful. A recent example are the data listed in the certificate to Standard Reference Material SRM 2490 supplied from NIST in which for example the zero shear viscosity measured by a frequency sweep and a rotational test differ significantly. The aim of this paper is a complete check of the above rules for SRM 2490. All data have been measured using a Physica MCR501 rheometer from Anton Paar. In frequency sweeps deviations up to 20% to the certified values have been found at 0°C, whereas in rotational testing only small deviation to the certified values exist. To further validate the measured results extensive testing has been performed at various temperatures between 0°C and 50°C. All with the MCR 501 measured results form different tests like flow curve, step rate, step strain and frequency sweep are perfectly consistent and the Cox-Merz rule, the generalized Cox-Merz rule, Gleissles mirror rules, and the Lodge-Meissner rule are fulfilled, respectively. The measured data and the inconsistency of the certified values with the Cox-Merz rule itself indicate that the published oscillatory data in the Certificate to the SRM 2490 are wrong.

Validation of empirical rules for a standard polymer solution

Joerg Laeuger and Patrick Heyer
Anton Paar Geramany, Ostfeldern D-73760, Germany

For polymeric systems many empirical or semi-empirical rules exist. One of the most prominent is the Cox-Merz rule, which correlates the shear viscosity from a given shear rate to the complex viscosity measured in a frequency sweep. A generalized Cox-Merz rule correlates the first normal stress difference \( (N1) \) with the elastic modulus \( G' \). In transient tests Gleissles mirror rules relate the transient behavior of the shear viscosity and first normal stress coefficient with steady state results. The Lodge-Meissner rule gives a relation between \( N1 \) and the shear stress in a step strain experiment. For simple polymeric fluids all this rules are expected to hold and they provide a rather straightforward check on the validity of the rheological data. However, still literature is published in which this relations are not considered and the published results are doubtful. A recent example are the data listed in the certificate to Standard Reference Material SRM 2490 supplied from NIST in which for example the zero shear viscosity measured by a frequency sweep and a rotational test differ significantly. The aim of this paper is a complete check of the above rules for SRM 2490. All data have been measured using a Physica MCR501 rheometer from Anton Paar. In frequency sweeps deviations up to 20% to the certified values have been found at 0°C, whereas in rotational testing only small deviation to the certified values exist. To further validate the measured results extensive testing has been performed at various temperatures between 0°C and 50°C. All with the MCR 501 measured results form different tests like flow curve, step rate, step strain and frequency sweep are perfectly consistent and the Cox-Merz rule, the generalized Cox-Merz rule, Gleissles mirror rules, and the Lodge-Meissner rule are fulfilled, respectively. The measured data and the inconsistency of the certified values with the Cox-Merz rule itself indicate that the published oscillatory data in the Certificate to the SRM 2490 are wrong.

Shear flow behavior in entangled polydisperse polymer solutions

Amy Philips and Shi-Qing Wang
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Recent studies from our lab have revealed a discontinuous constitutive flow transition in shear flow of monodisperse entangled polybutadiene (PBD) solutions. There are many questions that remain to be investigated. Is the transitional behavior unique to the PBD solutions? Does the discontinuity occur only in monodisperse samples? Is it a flow property only of solutions? To begin to answer these questions, we examined several other entangled polymer solutions based on polystyrene, polyisobutylene and polyisoprene. These systems all share a common characteristic of being somewhat polydisperse in their molecular weight distribution. Also included in this family is a slightly polydisperse PBD solution. Due to polydispersity, the rheological flow behavior in both controlled-rate and controlled-stress modes appears to be continuous, and there seems to exist an approximate one-to-one correspondence between shear stress and rate in steady state, which was not the case for the PBD solutions. In addition to the various standard rheological methods, we apply the techniques of particle-tracking and flow birefringence measurements developed in our concurrent PBD work to determine whether these polydisperse polymer solutions show characteristics in line with or in contradiction to the expectations based on the conventional wisdom.

Symposium SS
Viscoplasticity and Viscoelasticity of Solids and Semi-Solids

Organizers: Ian Frigaard and Gregory B. McKenna

Nanoscale confinement modifies physical aging in polymeric glasses

Rodney D. Priestley\textsuperscript{1}, Perla Rittigstein\textsuperscript{1}, Linda J. Broadbelt\textsuperscript{1}, and John M. Torkelson\textsuperscript{2}
\textsuperscript{1}Chemical and Biological Engineering, Northwestern University, Evanston, IL; \textsuperscript{2}Chemical and Biological Eng. and Material Sci. and Eng., Northwestern University, Evanston, IL

Many properties of glassy polymers, ranging from modulus to permeability, evolve over time due to physical aging or structural relaxation in the glassy state. Using fluorescence and enthalpy relaxation, we have characterized the effect of nanoscale confinement on the rate of physical aging of glassy polymers. Systems under study range from ultrathin films supported on a substrate to nanocomposites; polymers include polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(2-vinyl) pyridine, and substrates/nanofillers include silica and alumina. The effect of nanoscale confinement on physical aging is complex in part because of how confinement can modify glass transition temperature (Tg) at the nanoscale. For example, a 20-nm-thick PMMA film supported on silica exhibits physical aging at 7 K above bulk PMMA Tg; this is because the Tg of the ultrathin film is increased by 14 K relative to bulk. However, the most common effect of nanoscale confinement is to reduce or suppress the rate of physical aging. For example, the rate of physical aging in a 35-nm-thick PMMA film at 305 K is about one-fourth that of bulk PMMA. Fluorescence measurements on multilayer films have revealed that there is a reduction in physical aging rate relative to bulk polymer at the free surface of a film. For example, a 25-nm-thick free-surface layer of PMMA on a bulk PMMA film exhibits an aging rate that is about one-half that of bulk PMMA. In addition, when there are attractive substrate- or nanofiller-polymer interactions, e.g., via hydrogen bond formation, the layer closest to the substrate exhibits an even greater reduction in physical aging than that of the free surface. The possible
mechanisms by which aging is reduced or suppressed at the nanoscale by surfaces and interfaces and a comparison of the length scale over which the Tg is affected by confinement to that over which physical aging is affected will also be presented.

Tuesday 1:55 Seymour SS7

Nanobubble inflation to measure the viscoelastic response of ultrathin polymer films: Membrane and bending limits

Paul A. O'Connell and Gregory B. McKenna

Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121

In prior work we have presented the viscoelastic response of ultrathin poly(vinyl acetate) (PVAc) films of 27.5 nm thickness determined by the inflation of micron diameter bubbles imaged in an atomic force microscope. [1] In that work, the membrane stretching approximation was used and a viscoelastic solution was provided through the glass transition regime. In the present work, we show that the prior results are valid because the deflections of the circular membranes were sufficiently large that the membrane approximation was reasonable. However, in further work to exploit the nanobubble inflation method, we have been working in an effectively stiffer regime and the membrane materials exhibit smaller deflections and the biaxial creep compliances can be dramatically in error unless the bending of the membrane is accounted for. We show the solution to the bending membrane problem [2-4] and our adaptation for the viscoelastic case. We then analyze our results for inflation of ultrathin polystyrene membranes from the glassy state to the rubbery state. The former case requires that bending be accounted for and, in the latter case, the membrane approximation remains reasonable. Our results indicate two things. First, unlike the PVAc material where the glass transition temperature seemed independent of film thickness, the Tg of polystyrene decreases dramatically (by up to 40 K) for the thinnest films tested (25 nm). At the same time, both the polystyrene and the PVAc exhibit dramatic stiffening in the rubbery plateau regime—a result that currently is unexplained.


Tuesday 2:20 Seymour SS8

Viscoelastic responses of hybrid poly(styrene-butadiene-styrene) triblock copolymers

Andre Lee and Dan Drazkowski

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Hybrid organic/inorganic tri-block copolymers of polystyrene-butadiene-polystyrene (SBS) containing grafted polyhedral oligomeric silsesquioxane (POSS) molecules were synthesized by the hydrosilation method. The POSS molecules were designed to contain a single silane functional group, which was used to graft onto the dangling 1,2 butadienes in the polybutadiene soft block. The well-defined grafting mechanism enables us to investigate the effect of POSS additions on various properties (morphology, thermal transitions and mechanical responses) without any change to the main SBS backbone. In general, with small amounts of POSS grafting, the overall morphology of triblock copolymers is not affected, however, depending on the chemical moiety of POSS used, the periodicity of microstructure may be altered. The order-disorder transition temperature of different weight fractions of POSS grafted hybrid SBS copolymers was studied using in-situ small angle X-ray scattering (SAXS) technique and compared with value observed by rheological method. The overall orientation of microstructure is studied using SAXS by in-situ unaxial stretching of hybrid SBS at different temperatures below Tg of polystyrene phase. Although the POSS moiety was grafted to the soft polybutadiene phase, however, these hybrid copolymers exhibit higher tensile strength without affecting the rupture characteristic at temperatures investigated.

Tuesday 2:45 Seymour SS9

Solid and semi-solid characteristics of block copolymers with cubic phases

Prashant Mandare and H H. Winter

Chemical Engineering, University of Massachusetts Amherst, Amherst, MA 01003

We have carried out a detailed investigation of the rheological behavior of block copolymers near their transition where they form cubic microphases. The material system used in the study (abbreviated as SEBS) consists of 20 wt% of a symmetric tri-block copolymer, poly(styrene-b-ethylene-co-butylene-b-styrene) containing 29 wt% polystyrene and and being of size Mn = 94000 and Mw/Mn = 1.1, swollen in 80 wt% hydrocarbon oil that selectively swells the midblock. Recent studies have shown that the structure of the nano-phase separated block copolymer can be broken at very low stress and, instead of a yield stress, the SEBS shows a zero shear viscosity at very low shear rates just like a homopolymer. The purpose of this study is to investigate, in depth, rheology of SEBS and ascertain whether the material behaves as solid, semi-solid or liquid under given conditions. Results from five different types of experiments were compared, viz., dynamic oscillatory shear, isothermal strain sweeps at different frequencies, creep in a stress controlled rheometer, transient shear experiments in a strain controlled rheometer and long time stress relaxation studies in a newly built device, the Relaxometer. In transient shear experiments, in a range of shear rates, the viscosity reaches a steady value when a "critical strain" of about 0.06-0.07 is reached. However, the plot of steady shear viscosity versus shear rate does not show a zero shear viscosity and instead shows yielding. The results from creep experiments are in good agreement with those from transient shear experiments. Comparisons of oscillatory and steady shear experiments showed that the Cox-Mertz rule is not obeyed except for high frequencies/shear rates.

The Society of Rheology 77th Annual Meeting, October 2005
The viscoelastic response of polyurethane open cell foams filled with concentrated silica suspensions under high rate loading conditions is studied. The stress response of these composites at high strain rates is of particular interest for possible applications in energy absorption and load dissipation. Open cell polyurethane foam with relative density of 0.03 and average cell size of 360 μm was cut into cylinders of diameter of 2.8 cm and height of 2 cm. The foam samples were impregnated with a shear thickening fluid composed of monodisperse spherical silica particles with median diameter of 300 nm (standard deviation of 30 nm) dispersed in ethylene glycol. The behavior of this nonlinear fluid-solid composite was studied over a range of filling fractions under quasi-static deformation rates (strain rates between $10^{-2}$ - $1 \text{s}^{-1}$), under dynamic impact loading (with energy densities of $e = 10^7$ - $10^5 \text{J/m}^3$) and under high strain-rate deformations (strain rates up to $800 \text{s}^{-1}$). The results show that, if the foam is filled with a shear thickening suspension, the composite stiffens even at strain rates of $10^5 \text{s}^{-1}$ as the impregnated fluid shear-thickens due to the high local strain rate that develop at cellular length scales. High impact load experiments show two different mechanisms for energy absorption: at lower impact energies viscous dissipation is dominant; whereas, after a critical impact energy is reached, the fluid undergoes a transition from liquid-like to solid-like. High-speed digital video-imaging shows that cracks form and propagate through the sample and the impact energy is absorbed by viscoplastic deformation. These observations are interpreted in the context of a nonlinear poroelasticity constitutive model.

**High deformation rate behavior of polymeric foams filled with concentrated silica suspensions**

Giorgia Bettin and Gareth H. McKinley

Dept. Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

The viscoelastic response of polyurethane open cell foams filled with concentrated silica suspensions under high rate loading conditions is studied. The stress response of these composites at high strain rates is of particular interest for possible applications in energy absorption and load dissipation. Open cell polyurethane foam with relative density of 0.03 and average cell size of 360 μm was cut into cylinders of diameter of 2.8 cm and height of 2 cm. The foam samples were impregnated with a shear thickening fluid composed of monodisperse spherical silica particles with median diameter of 300 nm (standard deviation of 30 nm) dispersed in ethylene glycol. The behavior of this nonlinear fluid-solid composite was studied over a range of filling fractions under quasi-static deformation rates (strain rates between $10^{-2}$ - $1 \text{s}^{-1}$), under dynamic impact loading (with energy densities of $e = 10^7$ - $10^5 \text{J/m}^3$) and under high strain-rate deformations (strain rates up to $800 \text{s}^{-1}$). The results show that, if the foam is filled with a shear thickening suspension, the composite stiffens even at strain rates of $10^5 \text{s}^{-1}$ as the impregnated fluid shear-thickens due to the high local strain rate that develop at cellular length scales. High impact load experiments show two different mechanisms for energy absorption: at lower impact energies viscous dissipation is dominant; whereas, after a critical impact energy is reached, the fluid undergoes a transition from liquid-like to solid-like. High-speed digital video-imaging shows that cracks form and propagate through the sample and the impact energy is absorbed by viscoplastic deformation. These observations are interpreted in the context of a nonlinear poroelasticity constitutive model.

**Strong through to weak sheared gels**

Nara Altmann¹, Jason Stokes², David E. Dunstan¹, and Justin J. Cooper-White³

¹Chemical and Biomolecular Engineering, The University of Melbourne, Melbourne, Victoria 3010, Australia; ²Colworth House, Unilever Corporate Research, Sharnbrook, Bedford MK44 1LQ, United Kingdom; ³Division of Chemical Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

The gelation of an agar biopolymer solution under quiescent conditions enables the formation of a strong network structure capable of sustaining mechanical deformation up to a critical strain or stress above which it fractures. Gelation of the same solution under shear conditions results in a weak gel capable of sustaining mechanical deformation at small strain or stresses but which flows if subjected to higher deformations. The purpose of this study was to investigate the nonisothermal gelation behaviour of agar biopolymer gels prepared under both oscillatory and steady shear conditions. We present a dynamic phase diagram which summarises the effects of strain amplitude and frequency on the rheological properties of biopolymer gels formed at a constant cooling rate. We show that certain combinations of strain amplitude and frequency produce a new class of physical gel, a so-called 'soft' gel. Such gels present both yielding and cohesive characteristics. We propose that the imposition of shear changes the pathway through which structures are developed through the promotion of short range interactions beyond those possible through temperature change alone. Understanding the strength of such interactions and the time scales over which they occur will ultimately allow tuning of the structure development during cooling.

**Rheology of concentrated surfactants**

Mickael Y. Castro¹, Philippe Mongondry¹, Christopher W. Macosko¹, and Teanoosh Moaddel²

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Surfactants are of great importance in the both chemical industry and in consumer sectors. They appear in areas including food, detergent, lubricants, emulsifiers, surface treatments, pharmaceutical products, emulsions, and many other commercial fields. Most studies on the flow behavior of surfactant solutions, however, have focused on the dilute regime. Seldom reported are studies on the flow behavior of surfactant solutions for the highly-concentrated regime where typically these surfactants are processed and delivered. This work deals with a highly concentrated anionic system consisting of sodium salt of lauric acid, oleic acid and stearic acid with 10 to 30%w of water. Samples are prepared using a laboratory scale twin screw mixer that allows rapid and efficient mixing of such concentrated systems. Small angle x-ray, and thermogravimetric measurements were performed, and the rheological behavior was studied on both rotational (ARES, TAinsit) and capillary rheometers (Goettfert). First, we present the phase diagram for the ternary system: water and two anionic surfactants (sodium salt of lauric and oleic acid) at different temperatures, and provide x-ray results of the quaternary system. Then, we present both linear viscoelastic and steady shear flow results in the high (70 to 90%) surfactant regime at different temperatures.
Tuesday 4:50 Seymour

**Yield stress effects in Taylor-Couette flows**

Ian Frigaard¹, Florence Lepelletier¹, Dominic M. Martinez², and Costanza Piccolo¹

¹Mechanical Engineering & Mathematics, UBC, Vancouver, B.C., Canada; ²Chemical & Biological Engineering, UBC, Vancouver, B.C., Canada

A combined numerical and experimental study of the flow of a generalised Newtonian fluid between two rotating cylinders is presented. Focus is on the onset of Taylor-vortex flow in the annular region for fluids that exhibit a yield stress. Practical applications are various, spanning from thinning processes of foodstuffs, to flowing of papermaking suspensions, and oil drilling processes. The present work follows previous studies of linear stability of a Bingham fluid by Landry (2003), Peng & Zhu (2004), Landry et al (2005). For a fixed radius ratio, the parameters that characterise the flow transition are the rotational Reynolds numbers and the nondimensional yield stress.

In the experimental work, velocity profiles of both Newtonian and non-Newtonian fluids are measured employing an ultrasound doppler velocimetry technique. Results found for various Carbopol solutions moved by a rotating inner cylinder show that increasing Carbopol concentration, hence the yield stress, delays transition in the flow, resulting in a more stable flow. Also hysteresis effects are observed depending on the direction of acceleration of the inner cylinder.

In the numerical work, the governing equations for an axisymmetric flow are solved via a finite-volume method using a regularized Bingham & Herschel-Bulkley model. Comparisons with experimental measurements show similar stabilizing effects due to increasing yield stress. For yield stress above a certain value, regions of unyielded fluid are found at the outer cylinder, extending inwards for increasing values of yield stress. The effects of these regions on the onset of instability are studied.

Tuesday 5:15 Seymour

**Continuous casting of a thermoplastic paste**

Dean A. Barker and Ian Wilson

Chemical Engineering, University of Cambridge, Cambridge CB2 3RA, United Kingdom

A continuous casting process for a highly-filled paste requires continuous extrusion through a die cooled below the solidification temperature of the continuous phase, so that the extrudate emerges from the die as a solid. Numerical simulation of this process requires an understanding of the thermophysical and rheological behaviour of the paste over the temperature range. The former are necessary to solve the heat transfer problem and were quantified using novel power-compensated DSC techniques. The rheology of the material, including wall slip, was characterized across ten decades of apparent shear rate using controlled strain and controlled stress instruments in both steady state and oscillatory modes, with test geometries including concentric cylinder, smooth and roughened parallel disks, rotating vanes, and capillary rheometry using the multi-pass technique. The data have been modelled as a Carreau type fluid with pronounced wall slip and shear banding characteristics, with distinct changes as the melt enters the mushy zone. Initial results from numerical simulations are presented and compared with data from laboratory and industrial scale trials.

Symposium MS

**Dealy Symposium: Molecular Structure and Rheology**

Organizers: Marie-Claude Heuzey, A. Jeffrey Giacomin and Paula Wood-Adams

Tuesday 1:30 Salon 3

**Unsolved mysteries of polymer rheology**

Ronald G. Larson

Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136

Several unsolved issues in the theory of the rheology of polymer solutions and melts are reviewed. For low-concentration, nominally "dilute" solutions, these include the failure of light scattering data to show much polymer stretch even under prolonged strong flows, the failure of Brownian dynamics simulations of extensional stress to predict the experimentally observed plateau Trouton ratios, and the peculiar "quasi-dilute" behavior of polyethylene oxide and other water-soluble polymers at very low concentrations. For melts, unsolved mysteries include the uncertainty in whether an entanglement should be thought of primarily as the interaction of a chain with a single, or multiple, other chains, the lack of a rigorous definition of a "tube" or primitive path, and uncertainties in the choice of appropriate constants to be used in the tube model, including that controlling the fluctuation potential, the dilution exponent, and the diffusivity of branch points. While no solutions will be offered to these mysteries, key problems in rheology needing attention will be highlighted.
Tuesday Afternoon

Tuesday 1:55 Salon 3  MS2

Complex fluid interfaces
Gerald G. Fuller
Chemical Engineering, Stanford University, Stanford, CA 94305-5025

Complex, fluid interfaces are formed when molecular amphiphiles or particles collect to form structured surfaces that endow them with highly nonlinear and non-Newtonian responses to flow. This paper presents measurement techniques for the determination of surface viscoelasticity and presents data for two different systems: two-dimensional polymer melts and two-dimensional suspensions. Two-dimensional polymer melts result with amphiphilic polymer chains are spread onto a fluid/fluid interface. These systems are characterized by frequency dependent, dynamic moduli and lead to dramatic changes in interfacial flows in complex geometries. Data are presented on surface rheology for monolayers of poly(tertbutyl methacrylate) over a wide range of molecular weights. When the pressure-area isotherms of this system are plotted on a "per monomer" basis, the data for all molecular weights collapse onto a single master curve. The data indicate a transition from a fluid interface to a solid interlace as the system is compressed. Monte Carlo simulations suggest that the chains pile up on top of each other during compression. Two-dimensional suspensions can be formed by attaching arrays of colloidal particles onto fluid-fluid interfaces. These additives can effectively stabilize emulsions and produce very viscoelastic monolayers that resist coalescence and Ostwald ripening. Data are presented on droplets coated with particle monolayers that are subjected to volume reduction by draining their contents. During this process, the subsequent decrease in surface area of the drops ultimately causes the particles on the interface to jam and a liquid-to-solid transition ensues. Measurement of the internal pressure of the droplets during the drainage process signals the onset of buckling and wrinkling of the droplet surface.

Tuesday 2:20 Salon 3  MS3

Interpreting the elongational behaviour of monodisperse entangled melts and solutions
Giovanni Ianniruberto and Giuseppe Marrucci
Chemical Engineering Department, University Federico II, Naples I-80125, Italy

Recent accurate viscosity data in uniaxial elongational flow on monodisperse entangled melts [1] and solutions [2] seem not to be compatible with the tube model for entangled polymers unless a variable tube diameter is invoked [3]. Those data also reveal that melts and solutions do not behave alike. The model suggested in [3] is fully compatible with melt data only. We here suggest a possible reason for the discrepancy with solution data, starting from a more careful analysis of pressure effects of chains confined in tubes, already reported in [4].


Tuesday 2:45 Salon 3  MS4

Extensional rheology and tack of a multibranched adhesive
Shen-Kuan T. Ng1, Christopher G. Robertson2, Sandra Warren2, and Gareth H. McKinley1
1Dept. Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139; 2Center for Research and Technology, Bridgestone Americas, Akron, OH 44317

We investigate the transient extensional rheology of model polybутадиен-based pressure-sensitive adhesives. Pronounced strain hardening in extension is noted for an adhesive containing an entangled branched polymer with more than one branching junction per chain (multibranched polymer) dissolved in a melt of shorter linear chains. The analogous adhesive formulation which contains polymer species with only one branch point per molecule in a melt of linear chains exhibits similar shear rheology but does not show such upturns in the transient extensional viscosity. We illustrate the strong influence of the extensional rheology of the multibranched adhesive on the time-dependent stress measured in standard tack testing by using the differential Pom-Pom model of McLeish and Larson. The viability of using the axial-extension capability of a commercial shear rheometer for transient extensional measurements is also demonstrated in this study. The exponential axial displacement applied by the instrument is converted to the true Hencky rate experienced by material elements at the midpoint of the elongating sample by using a lubrication approximation (J. Non-Newtonian Fluid Mech., 64, 229 (1996)) and the axial stress is obtained from the normal force transducer. The results from this approach compare well to transient extensional data acquired on the same sample using a filament stretching rheometer.

Tuesday 3:35 Salon 3  MS5

What can be learnt from rheology with respect to branching of polymers?
Helmut Münstedt
Institute of Polymer Materials, University Erlangen - Nuremberg, Erlangen, Germany

Rheological properties like viscosity, elasticity, and elongational behavior very sensitively react on long-chain branches. It is demonstrated using polyethylenes and polypropylene that long-chain branching can already be detected by rheological means for samples which do not show any indication of branching by conventional methods like light scattering. Making use of the findings on model polymers some insight has been obtained on the branching architecture of electron beam irradiated polypropylene. From measurements of the zero shear viscosity as a function of the absolute mass average molar mass some conclusions could be drawn with respect to correlations between irradiation parameters and
molecular structure. Elongational experiments and particularly the determination of strain hardening are very helpful to generate polymers for special applications as film blowing and blow molding, for example. On polyethylenes polymerized with various metallocene catalysts it is shown in which way rheological experiments can be used to elucidate their efficiency in creating different branching architectures. Furthermore, it is demonstrated that rheological measurements are a valuable tool to control the branching structure developed during the polymerization process.

Tuesday  4:00  Salon 3  MS6

Nonlinear rheology of branched polymers
Lynden Archer, Jung H. Lee, and Lewis Fetters
School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853

Stress relaxation dynamics of entangled long-chain branched (LCB) polymers are investigated using model symmetric stars, asymmetric stars, and multiarm (pom-pom) polymer liquids subject to small-amplitude oscillatory shear and nonlinear step and steady shear deformations. This talk focuses on the effect of molecular architecture on nonlinear relaxation dynamics in bulk liquids and near solid substrates. It is shown that even small degrees of arm length asymmetry leads to large differences in the nonlinear relaxation dynamics of branched molecules both in the bulk and at surfaces. In the absence of strong contributions from chain stretch, we also find that the apparent steady-state shear viscosity and orientation angle can be quite accurately determined from the linear viscoelastic spectrum, i.e. without introducing processes such as convective constraint release. In step shear flows, we report a new type of damping characteristic for star-like polymers. Consequences of these observations on tube-based constitutive models for branched polymers are discussed.

Tuesday  4:25  Salon 3  MS7

The role of the chain length between branch points on branched polymer rheology
Ralph H. Colby
Materials Science and Engineering, Penn State University, University Park, PA 16802

We explore the role of the chain length between branch points on the molecular structure and linear viscoelastic response of polydisperse branched polymers, prepared by two classes of random branching utilizing condensation chemistry. Randomly branched polyesters were prepared by condensation polymerization of a mixture of diols and multifunctional acids, where the chain length between branch points was controlled either by adding difunctional acid or by using poly(tetramethylene glycol) as the diol. Hyperbranched polymers were prepared by slow addition of poly(ethylene glycol) (PEG) to an excess of 1,3,5-benzenetricarbonyl trichloride. Our molecular characterization results indicate that the kinetics of this reaction produce polymers with molar mass distributions in the hyperbranched class. In this case, the chain length between branch points was controlled by the molecular weight of the PEG precursor. Size exclusion chromatography with detectors for concentration, viscosity and light scattering, was employed to determine the molar mass distributions of the polydisperse branched polymers produced. The randomly branched polymers exhibit the expected crossover from critical percolation for short chains between branch points to mean-field percolation for long chains between branch points. The hyperbranched polymers with long chains between branch points have molar mass distributions consistent with Flory's hyperbranched model. Despite having very high molecular weight species in the molar mass distributions, both hyperbranched and randomly branched polymers have no entanglement effects in their linear viscoelastic response if the chain length between branch points is smaller than the critical molecular weight Mc for entanglement effects in the viscosity of linear chains. For both classes of polydisperse branched polymer, when the chain length between branch points exceeds Mc, entanglement effects start to become important and grow in importance as the chain length between branch points is increased.

Tuesday  4:50  Salon 3  MS8

Melt blown fibers from block copolymers
Alhad S. Phatak, Frank S. Bates, and Christopher W. Macosko
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55414

Fibers made from a variety of polymers are being increasingly used to make non woven products in a wide array of applications. Melt spinning, melt blowing and electrospinning are the most successful "single step" processes used for this purpose. While melt spinning is limited to a minimum fiber size of ~15 μm, the other two methods lead to smaller fibers that have poor mechanical properties. Moreover, electrospinning suffers from being an inherently slow process, as well as having solvent-handling issues. We report a study that seeks to take advantage of the melt strength of microphase separated block copolymers and possible micro-structural orientation to obtain sub-micron melt blown fibers with good mechanical properties. Block copolymers offer a number of handles such as molecular weight, composition, morphology, and block sequencing, to control melt strength and fiber mechanical properties. As a first step, we performed melt spinning experiments, using a capillary rheometer and a take-up wheel, to obtain fibers having diameters of ~10 μm from lamellae-forming block copolymers composed of poly(ethylene) and poly(cyclohexylethylene). These fiber sizes are comparable to the smallest melt spun fibers reported in the literature. Small and wide angle x-ray scattering measurements from these fibers revealed a highly stretched lamellar microstructure, as well as oriented PE crystals. Breaking strengths of up to 200 MPa were measured from uniaxial tensile tests. Based on the above results, these block copolymers should be amenable to melt blowing as well. Experiments on melt blowing are currently in progress.
The influence of rheological knowledge in polyolefin product development

Steve Chum
Plastics R & D; Dow Plastics, The Dow Chemical Company, Freeport, TX 77541

Polyolefin products (e.g., PE, PP and polyolefin elastomers & Plastomers) had experienced high growth in the last decade, attributed to the development of the metallocene and post-metallocene based product technologies such as the INSpiRE® performance PP and VERSIFY® propylene based elastomers and plastomers from the Dow Chemical Company. The key attribute of the metallocene and post-metallocene catalyst technologies is its capability in making well defined polymer molecular structures, enabling the polyolefins product designers to design a product to match the performance requirements for their customers. Rheological knowledge for polyolefins has become the most critical piece of science to aid the product designer in developing many new products. Professor John Dealy has been a key scientist in leading the industrial researcher in this product design direction. This paper reviews some of the joint effort that Professor Dealy has accomplished with the polyolefins industry. *Trademarks of The Dow Chemical Company
Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Salon 1 & 2 PL3

Some amusing examples of polymer rheology: Knotted DNA and microfluidic logic
Stephen Quake
Bioengineering Department, Stanford University, Stanford, CA 94305

I will discuss two examples of polymer rheology. Using optical tweezers, it is possible to tie single molecules of DNA into knots. Unlike knots in your fishing string, molecular knots in polymers like DNA have unusual transport properties, and represent an interesting example of "self-reptation". In the second part of the talk, I will discuss how non-Newtonian flow in polymeric solutions have been used to create microfluidic logic devices, a possible alternative to the silicon integrated circuit.

Symposium BS
Rheology of Biomaterials and Biological Systems

Organizers: Denis Wirtz and Kate Stebe

Wednesday 9:45 Oak 1 & 2 BS1

Rheopexy of synovial fluid and reversible protein aggregation
Katherine M. N. Oates, Wendy E. Krause, Ronald L. Jones, and Ralph H. Colby
Materials Science and Engineering, Penn State University, University Park, PA 16802

Bovine synovial fluid and albumin solutions of similar concentration are rheopectic (stress increases with time in steady shear). This unusual flow characteristic is caused by reversible protein aggregation, and the total stress is enhanced by entanglement of this tenuous protein network with the long-chain polysaccharide sodium hyaluronate under physiological conditions. Scattering measurements on albumin solutions demonstrate protein aggregation and all measurements are consistent with a weak dipolar attraction energy (of order 3 kT) most likely augmented by hydrophobic interactions and/or disulfide bond formation between proteins. Protein aggregation appears to play an important role in the mechanical properties of blood and synovial fluid. We also suggest a connection between the observed rheopexy and the remarkable lubrication properties of synovial fluid.

Wednesday 10:10 Oak 1 & 2 BS2

Microrheology of evolving extra-cellular matrices
Thierry Savin and Patrick S. Doyle
Chemical Engineering, MIT, Cambridge, MA 02139

The mechanical and structural properties of the extra-cellular matrix (ECM) are known to deeply affect the individual behavior and fate of a cell during processes such as migration, division and differentiation. It is thus essential to characterize these properties at the length scale of a single cell, as well as to study their evolution in time.

We applied a multiple particle tracking technique (MPT) to perform microrheological and structural measurements in evolving ECM-like systems. We first studied a model artificial ECM scaffold formed by the self-assembly of custom designed oligopeptides that are currently used for 3D cell culture. For this system, we resolved the gelation kinetics of the matrix. We showed that kinetics is dependent on the pH and salt concentration, reflecting the screening of the molecular charge of individual peptides. The spatial heterogeneity of the microenvironment at different times of gelation were also interrogated for this system. Overall, this study gives a better knowledge in the cultivated cell environment, as well as opens new routes for future self-assembling peptides designs. Second, MPT was applied on a natural ECM extract, that was degraded by the addition of matrix metalloproteases, thus mimicking a possible natural route used by migrating cells.
Wednesday Morning

**BS3**

**The microrheology of semiflexible self-assembled β-hairpin hydrogels**

Cecile Veerman¹, Karthikan Rajagopal², Joel P. Schneider, Chandra S. Palla, and Eric M. Furst¹

¹Department of Chemical Engineering, University of Delaware, Newark, DE 19716; ²Chemistry and Biochemistry, University of Delaware, Newark, DE

Hydrogels are an important class of materials that have extensive uses in tissue engineering and drug delivery applications. Recently, a short, 20 amino acid β-hairpin peptide (MAX1) has been designed for the preparation of novel hydrogels that reversibly fold and gel by a process of hierarchical self-assembly. Little is known of the gelation kinetics and microstructure of these complex materials. In this study, the assembly process and microstructure of MAX1 hydrogels were investigated with the use of multiple particle tracking, laser tweezer microrheology and diffusing wave spectroscopy. We demonstrate that MAX1 networks exhibit the rheological characteristics of a highly cross-linked semiflexible network over a wide range of frequencies ($10^{-2} < \omega < 10^6$ Hz). Furthermore, by analyzing the self-part of the van Hove correlation function and a non-Gaussian parameter, we obtain insight into the microheterogeneity of the gel. A greater understanding of microheterogeneity is of particular interest, because we expect that it will impact the use of these gels as tissue engineering scaffolds by influencing the mechanical cues experienced by embedded cells.

**BS4**

**Shearing actin gels**

Jiayu Liu, Gijsje Koenderink, Itai Cohen, and David Weitz

Physics/DEAS, Harvard University, Cambridge, MA 02138

Filamentous actin (F-actin) is an important part of the cytoskeleton. It is also an excellent model for semiflexible polymers. Interesting nonlinear mechanical properties (shear stiffening and shear thinning) of actin gels have been observed (Gardel et al. Science 2004). Currently we are trying to investigate the origin of these nonlinear mechanical behaviors by visualizing rheology. Specifically, we combine shear cell and confocal microscope to visualize actin filament rearrangement under shear deformation. In this talk, I will present some very first experiment results.

**BS5**

**Live-cell microrheology**

Yiider Tseng¹, Thomas P. Kole², Jerry S. Lee², Porntula Panorchan², and Denis Wirtz²

¹Department of Chemical Engineering, University of Florida, Gainesville, FL 32611; ²Chemical and Biomolecular Engineering, The Johns Hopkins University, Baltimore, MD 21218

Cell migration proceeds through the highly coordinated translation of biochemical signals into specific biomechanical events. The biochemical and structural properties of the proteins involved in cell motility, as well as their subcellular localization, have been studied extensively. However, how these proteins work in concert to generate the mechanical properties required to produce global motility is not well understood. Using the method of particle-tracking microrheology applied to single living cells, we show that cytoskeleton reorganization produced by motility events results in regional stiffening of the cytoplasm of motile cells. We demonstrate that small GTPases Rho, Rac, and Cdc42 and their downstream effectors regulate cell mechanics and in turn control cell motility. We will also discuss recent advances in microrheology to compare the micromechanics of migrating fibroblasts in two-dimensional vs. three-dimensional matrices and study the intracellular mechanical response of endothelial cells subjected to shear flows.

**Symposium SC**

**Suspensions, Colloids, and Multiphase Fluids**

Organizers: Dan Klingenberg and Nina Shapley

**SC29**

**Jamming in carbon nanotube suspensions**

Erik K. Hobbie

National Institute of Standards and Technology, Gaithersburg, MD

We measure the anisotropy of sheared carbon nanotube suspensions over a broad range of concentration, aspect ratio, and strain rate using a variety of methods. In the semi-dilute regime, our measurements highlight the importance of hydrodynamic excluded-volume interactions with scaling in terms of a dimensionless shear rate, or Peclet number. In more concentrated suspensions, we find that the tubes form an elastic network in equilibrium with behavior reminiscent of 'jamming' below a critical shear stress. Above this threshold yield stress, we observe a variety of flow-induced structure as a function of confinement, concentration, and strain rate.
Colloidal particles coated and stabilized by DNA-wrapped carbon nanotubes

Erik K. Hobbie and B. J. Bauer

National Institute of Standards and Technology, Gaithersburg, MD; NIST, Gaithersburg, MD

Single-walled carbon nanotubes (SWNTs) are made hydrophillic through coating and wrapping with short segments of single-stranded DNA (ssDNA) containing alternating guanine (G) and thymine (T) units. Small-angle neutron scattering (SANS) measurements on dilute to semi-dilute aqueous suspensions of these colloidal SWNTs raise interesting questions about the degree of nanotube dispersion, with power-law exponents suggestive of weak attractive interactions. The SWNT-ssDNA complexes also act as nanoparticle surfactant, stabilizing the interface between water and toluene, for example. We exploit this to make hydrophillic cross-linked polymer particles coated and stabilized by the ssDNA wrapped SWNTs. Near-infrared fluorescence microscopy demonstrates the band-gap fluorescence of these SWNT-coated particles, suggesting potential routes to novel platforms and applications. Light scattering and optical microscopy from index-matched suspensions of the SWNT-coated colloids are compared with similar measurements on colloids made with conventional surfactants.

Effect of fiber aspect ratio and surface treatment on the rheology of dispersions of carbon nanofibers

Sushant Agarwal and Rakesh K. Gupta

Chemical Engineering, West Virginia University, Morgantown, WV 26506

Polymer nanocomposites containing carbon nanofibers are becoming more common due to their superior performance in terms of their mechanical, thermal and electrical properties. Carbon nanofibers have aspect ratios of the order of ~1000. Properties of such nanocomposites depend both on how well the fibers are dispersed in a polymer matrix and their aspect ratio. Here we have employed Pyrograf III carbon nanofibers melt mixed with polycarbonate in an internal mixer to study the effect of surface treatment and the nanofiber aspect ratio on the rheological behavior of such dispersions. Carbon nanofibers of different aspect ratios were obtained by treating the as received fibers with 0.1N solution of Ceric Sulfate for 24, 48 and 72 hrs which results in the oxidation of the fiber surface and breakage of the fibers. For each batch of fibers, nanocomposites containing 2, 5, 10 and 15 wt% nanofibers in polycarbonate were prepared. Carbon nanofibers were also dispersed in a silicone oil. Steady shear sand dynamic properties were measured using a CarriMed CSL100 rheometer and a Rheometric Scientific RMS800 spectrometer. Treated nanofibers were also characterized using SEM and TEM which showed considerable amount of damage to the fibers with increasing time of treatment. Dynamic measurements on polycarbonate nanocomposites at 210°C showed that for 5 and 10 wt% samples, G' and G'' were higher for the 24 hrs treated fibers than the pristine fibers. Steady shear measurements on nanofiber and silicone oil dispersions showed that these dispersions were shear thinning with a plateau at high shear rates but at low shear rates, a yield stress was observed. It was also found that carbon fibers treated only for 24 hrs showed higher viscosity than pristine fibers, which suggests that oxidation of the fiber surface results in better dispersion of the fibers. Results from this study are useful in determining the effect of surface treatment and the fiber aspect ratio on the percolation limit of polymer-nanofiber composites.

Rheological characteristic of model hemi-telechelic polystyrene-POSS copolymers

André Lee and Bryan E. Coughlin

Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824; Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003

Polyhedral oligomeric silsesquioxanes (POSS) are inorganic nano-sized particles and are potential candidates to control microstructure. These building blocks are of particular interest due to their molecularly precise structure as well as their solubility in common organic solvents. Although recently there are numbers of studies investigated effect of POSS additions on the rheological characteristics of hybrid polymer, relatively few studies detailing the synthesis and characterization of controlled architectures using this concept have been completed. Expanding the scope of novel hybrid materials is of interest not only from the standpoint of the overall synthetic challenge but also critical in order to validate the self-assembly properties. The tethering of POSS to an anionically synthesized polymer will extend the range of materials as well as the morphologies that can be achieved. The molecular weight range of the living anionic synthesized hydroxyl-terminated polystyrene samples was chosen so that the radius of gyration of the polymer was comparable to that of the POSS particle. Polystyrene chains with a number-average molecular weight, Mn, of 900 and 16 000 g/mol have radii of gyration of 8.5 and 34 Å, respectively, vs a radius of approximately 7.5 Å for the POSS particle. Tethering of the isocyanate-modified POSS particle (POSS-NCO) to the polystyrene chains was achieved through the formation of a urethane linkage. The morphology of different molecular weight of POSS tethered PS was investigated using small angle x-ray scattering and in addition, we also investigated the effect tethered POSS on the rheology of model polystyrene.

Shear alignment of nanoparticle arrays templated by block-copolymer mesophases

Danilo Pozzo and Lynn M. Walker

Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

Block copolymers form highly organized structures when they are dissolved in solvents that are selective between the different polymer blocks. We have recently presented a simple and general method to template nanoparticle and globular protein arrays using thermoreversible block copolymer cubic crystals (Pluronic(r)) has been recently presented.[1,2] Although the crystalline domains of unaligned block copolymer
Wednesday Morning

templates exist over micron lengthscales, their lattice orientation is different. Shear orientation of block copolymer cubic crystals into macroscopic single crystals has been previously demonstrated.[3] In this work, we show that this shear orientation is also possible for block copolymer nanocomposites containing nanosized additives (silica nanoparticles or the protein serum albumin) intercalated in the interstitial cavities of the micelle crystal. The shear-aligned nanocomposite is a single crystal macro-domain where the templated particles have the same lattice orientation. Using neutron scattering (SANS) under shear, we show that alignment is possible in mesophases of FCC micelle crystals and in close-packed arrays of cylindrical micelles. Contrast variation allows us to probe the alignment of the nanoparticle array and the polymer template independently. We characterize the effect of shear rate, relative size of nanoparticle and polymer template, relative concentrations, and temperature on the final state of alignment of the nanocomposite. The formation of aligned single-crystal arrays of nanoparticles using shear represents a simple but significant improvement in our ability to manipulate materials at the nanometer scale.


Symposium SM
Entangled Solutions and Melts
Organizers: Lynden Archer and Jay Schieber

Wednesday 9:45 Salon 2 SM15

Elongational viscosity of monodisperse and bidisperse polystyrene melts

Jens K. Nielsen, Henrik K. Rasmussen*, and Ole Hassager

1Department of Chemical Engineering, Technical University of Denmark, Kgs. Lyngby DK2800, Denmark; 2Department of Manufacturing Engineering and Management, Technical University of Denmark, Kgs. Lyngby DK2800, Denmark

The startup and steady uniaxial elongational viscosity have been measured for two monodisperse polystyrene melts with molecular weights of 52 kg/mole (PS52K) and 103 kg/mole (PS103K), and for three bidisperse polystyrene melts. The bidisperse melts consist of PS103K or PS52K and a monodisperse polystyrene melt with a molecular weight of 390 kg/mole (PS390K). The measurements have all been preformed on a Filament Stretching Rheometer (FSR) equipped with an oven: A cylindrical test sample is placed between two parallel, circular plates and stretched. A load cell measures the transmitted force, and a laser monitors the central diameter of the stretched filament. Our rheometer is located in a thermostated environment. Notice, a camera to ensure a centered sample during measurement monitors the location of the central necking in the filament. The distance between the end plates is adjusted online (closed loop proportional regulator) using the laser in such a way that the stretch rate at the neck is kept constant. The rheometer has been described in more detail in (A. Bach, H.K. Rasmussen and O. Hassager, Journal of Rheology, 47 (2003) 429). PS390K show a decrease in the steady viscosity as a power-law function of the elongational rate (A. Bach, K. Almdal, H.K. Rasmussen and O. Hassager, Macromolecules 36 (2003) 5174). PS52K and PS103K show that the steady viscosity has a maximum that is respectively 100% and 50% above 3 times the zero-shear-rate viscosity. The bidisperse melts show a significant different behavior. The steady elongational viscosity of PS390K blended with PS52K exhibit a maximum in the steady viscosity. It is up to 700% above 3 times the zero-shear-rate viscosity. The maximum for the blend of PS390K and PS103K is not as large though significant higher than the maximum observed in the PS103K melt. The maximum in the steady uniaxial elongational viscosity seems to relates to the amounts of anisotropy in the extended melt.

Wednesday 10:10 Salon 2 SM16

Optical rheology of polydimethylsiloxane melt in planar extensional flow

Ramesh Subramanian

School of Engineering, Laurentian University, Sudbury, Ontario P3E 2C6, Canada

Polymer macromolecules exhibit isotropic behavior when they are randomly distributed. However, flow deformation causes orientation of the macromolecules leading to anisotropy in the transport properties like birefringence (differences in refractive indices in orthogonal directions). In the case of flexible polymer solutions and melts, the net optical anisotropy caused by flow can be obtained by measuring differences in refractive indices in the direction of the principal stresses. When an optically anisotropic macromolecular fluid flows through a transparent channel, the difference in birefringence in the any two directions is related to the difference in the corresponding principal stresses via the stress-optical law. According to this law, there is a linear relation between the components of the refractive index or polarizability tensor (AN) and the stress tensor (Δσ) given by AN = C Δσ, where C is a material constant known as the stress-optical coefficient.

The rheo-optical behavior of a viscoelastic polydimethylsiloxane (PDMS) fluid in planar extensional flow was examined at room temperature for various flow rates along the centerline of a two-dimensional converging wedge flow cell using laser Doppler anemometry (LDA) and flow birefringence. The first normal stress difference (FNSD) was calculated using a two-term Goddard-Miller model with a single Maxwell-type relaxation time constant of 0.0174 s and a zero-shear viscosity of 300 Pa.s. A linear stress-optical coefficient of 1.41 x 10-10 Pa-1 was obtained for PDMS in planar extensional flow at room temperature. This compares well with values for PDMS in the range of 0.909 - 1.84 x 10-10 Pa-1 as reported by various researchers.
Wednesday 10:35 Salon 2

Characterization of sparsely long chain branched polycarbonate: Observations vs. predictions from tube models and Monte-Carlo simulations

Evelyne van Ruymbeke, Alice Kaivez, Chen-Yang Liu, Adrien Leygues, Roland Keunings, and Christian Bailly

Université catholique de Louvain, Louvain-la-Neuve, Belgium

We have characterized sparsely long chain branched polycarbonate and fractions thereof by a combination of solution and rheological techniques and we have compared the observations with the results of Monte-Carlo simulations and tube-based modeling.

On-line coupling of size exclusion chromatography with intrinsic viscosity (SEC-IV) yields values for the experimental branching index $g_1$ vs. molecular weight, which follow closely the predictions based on Monte-Carlo simulations of the polymer structure. This validates the assumption of random branching for these samples. The Monte-Carlo simulations also provide an explicit description of the molecular architectures present and can therefore in principle be used to test tube models suitable for sparsely branched polymers.

Experimental dynamic moduli of unfractonated and fractionated samples have been compared with predictions of a tube-based model recently published by the authors [1]. When the model is calibrated for polydisperse linear polycarbonate, discrepancies between the predicted and measured dynamic moduli are clearly observed at levels well below the detection limit of branching by the SEC-IV coupling method. The comparison between observed and predicted moduli can be considered as a very sensitive method for the detection of long chain branching.


Wednesday 11:00 Salon 2

Structure-property models to predict polyolefin rheology

Charles P. Lusignan and Thomas H. Mourey

Foundation Science Center, Eastman Kodak Company, Rochester, NY 14650-2109

Structure-property relationships are developed for commercial low-density polyethylene resins that relate viscosity, melt strength, and relaxation time with the molar mass distribution and degree of long-chain branching.

Oscillatory shear data are fitted by two models to extract rheological quantities to be correlated with molecular structure. The first is Havriliak-Negami (HN) model, the complex analogue of the Carreau-Yasuda (CY) viscosity function, which parameterizes the rheology in terms of viscosity, relaxation time, and two shape exponents. We discuss some issues with this model and propose a new equation to address them. The new model introduces a second relaxation time, near the longest relaxation time, as well as another shape exponent. This extra complexity insures that viscosity and phase angle are even and odd functions of frequency, so that $G'$ and $G''$ have the proper slopes as functions of frequency in the terminal zone.

Correlations are developed between the fitted model parameters and the weight-average molar mass, Z-average molar mass between long-chain branch sites, and the number of trifunctional branch sites calculated from SEC data using the Zimm-Stockmayer model. Different structure-property models are evaluated to understand these relationships. Melt strength and relaxation time are expressible as power laws of the zero shear viscosity with exponents that depend on molecular structure. Reasonable predictions for viscosity are made by a simplified version of the Janzen-Colby (JC) model and also by the classic Fox-Berry-Grassie (FBG) methodology. Both approaches require an average number of branches and average length between branch sites to capture the essential physics. For this data set the modified JC model reduces the data somewhat better than the FBG relationship, but the generality of this result needs to be confirmed for other systems.

Wednesday 11:25 Salon 2

Evidence of convective constraint release during hole growth in freely-standing polystyrene films at low temperatures

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Hole growth measurements were performed using optical microscopy on freely-standing polystyrene (PS) films at temperatures that were slightly larger than the bulk value of the glass transition temperature $T_g$. For the measured range of temperatures, we have observed a transition from linear growth of the hole radius $R$ during the early stages to exponential growth of $R$ at later times. We have characterized this transition as a function of molecular weight, $120 \times 10^3 < M_w < 240 \times 10^3$, film thickness, $61 \text{ nm} < h < 125 \text{ nm}$, and temperature, $101^\circ C < T < 117^\circ C$. The viscosity at the edge of the hole inferred from the long time exponential growth regime exhibits shear thinning due to the large shear strain rates present at the edge of the hole. We show that the viscosity at the edge of the hole inferred from the characteristic growth times obtained in this and previous studies exhibit shear thinning with reduced shear strain rates beta that span twelve orders of magnitude. The $R(t)$ data for all times can be fit very well using an expression that describes exponential hole growth with a time-dependent viscosity that allows for an initial, transient response due to the decay of elastic entanglements. The time scale for the decay of the transient behavior is interpreted in terms of the decay of entanglements by the convective constraint release (CCR) mechanism of the tube theory of entangled polymer dynamics.
Gelled fibre suspensions as ‘feel & function modifiers’ for food applications

Bettina Wolf, Sarah Adams, and Scott Singleton

Suspensions of gelled particles and their use as structural agent in food applications have been of interest to us for some time. Our interest was focussed on identifying preparation routes for suspensions of anisotropic gelled particles in the micron size range with varying aspect ratio, gelled fibres, and their rheological behaviour in shear flow. More recently, we have begun to study the ‘feel & function’ of gelled fibre suspensions focussing on food applications.

The flow behaviour of fibre suspensions is influenced by the rheological characteristic of the suspension medium, the fibre phase volume, and the fibre aspect ratio. For gelled fibre suspensions, it is hypothesised that the material properties of the fibres represent an additional influencing factor. In flow, the visco-elasticity of the gel impacts on the behaviour of an individual fibre as well as on fibre-fibre interaction.

Here we present results on the shear flow behaviour of gelled agar fibre suspensions. Flow curves for fibre content above a few volume percent show a yield stress followed by shear thinning. For suspensions with fibres of an aspect ratio > 1000 and those with an aspect ratio of O(10-100) it was found that above a certain fibre phase volume the yield stress appears to be independent of the aspect ratio. Below this concentration, the flow curves for suspensions of short fibres and long fibres can be matched by adjusting the fibre phase volume. Other than the bulk rheology of these agar fibre suspensions, we studied their microstructure related behaviour in the mouth by applying a novel in-mouth imaging technique. Suspensions from fibres, and spheres were taken into the mouth, swilled around and expectorated. Then, residues are directly imaged using an endoscope allowing analysis of residue amounts and determination of clearance rates. Other biopolymer gels such as pectin and carrageenan were also studied to elucidate the influence of the gel properties on the flow curves and the in-mouth behaviour.

Microrheological characterization of heterogeneous fluids containing polymers, colloids, and surfactants

Seth Lindberg and Pat Spicer

Processing complex fluid products on the industrial scale requires knowledge linking microstructure and rheology to product stability against phase separation. Although homogeneous complex fluids offer many challenges to reproducible processing, fluids with shear-dependent heterogeneous microstructures are especially complicated. Particle tracking microrheology is particularly valuable for characterization of heterogeneous structured fluids, both for the localized rheological characterization it offers and for the unique insight it provides into the effect of controllable process parameters like shear stress. An overview will be given of the consumer product industry’s needs with respect to microrheology and microstructure characterization. This talk will share several case studies when heterogeneous microstructure plays a central role in the stability of a consumer product and microrheology offers the only means of understanding the observed behavior. For example, a change in bulk fluid polarity can cause dispersed particles to consolidate and form highly elastic regions within a Newtonian fluid matrix. Biopolymer systems can also form colloidal gels that offer good suspension stability but are highly shear-sensitive and heterogeneous. A third example of polymer-surfactant aggregates is a system crucial to product performance but poorly understood from a rheological perspective. A combination of bulk rheology, microrheology, and polarized light microscopy is used to characterize the microstructure in these fluids and the impact of microstructure on long-term stability. The effects of applied shear on fluid microstructure are studied in situ using a programmable shear stage on an optical microscope.

Hydraulic fracturing of oil and gas wells with foams: Importance of foam rheology and recent advances in its characterization

Alejandro A. Peña, Laura Schafer, Lijun Lin, and Richard Hutchins

Foams are often used in the hydraulic fracturing of subterranean formations to increase oil or gas production from depleted wells. Common gases used in these operations are nitrogen (N2), carbon dioxide (CO2) or combinations thereof. In such operations, foams withstand severe and changing pressures and temperatures. Such changes affect properties of the foam that are critical to the success of the fracturing operation, particularly foam rheology. This presentation discusses the importance of rheology on the ability of foamed hydraulic fracturing fluids to generate fractures in subterranean formations. Recent advances in the development of instrumentation able to measure the rheology of foams at elevated temperatures and pressures are also summarized. Examples are provided showing the effect of pressure, temperature, foam quality, choice of gas (CO2, N2 or mixtures), rheology of the continuous phase and bubble size distribution on the rheology of foams and emulsions of...
Nuclear microrheology

Jerry S. Lee\textsuperscript{1}, Pornutla Panorchan\textsuperscript{1}, Yiider Tseng\textsuperscript{2}, and Denis Wirtz\textsuperscript{1}
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The microstructure of the nucleus, one of the most studied but least understood cellular organelles, is the subject of much debate. Through the use of nanotracking, we detect and quantify the micro-organization as well as the viscoelastic properties of the intranuclear region in single live interphase somatic cells. We find that the intranuclear region is much stiffer than the cytoplasm; it is also more elastic than viscous, which reveals that the intranuclear region displays an unexpectedly strong solid-like behavior. Dynamic analysis of the spontaneous movements of nanospheres embedded in the nucleus reveals the presence of putative transient nuclear microdomains, which are mostly absent in the cytoplasm. The strong elastic character and micro-organization of the intranuclear region revealed by particle nanotacking analysis may help to some of the common rheological phenomena of water-based fluids will be given. Finally, some of the challenges currently faced by the industry will be discussed.

Symposium MR
Microrheometry and Microfluidics

Organizers: Pat Doyle and Anubhav Tripathi

Microrheology with optical tweezers – measuring the viscoelastic properties of polymer solutions in the frequency domain using colloidal particles in oscillating traps

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Pairs of colloidal particles confined in two optical traps have been used by a number of authors to investigate both the properties of the surrounding medium [1,2] and interactions between the particles [3]. We extend the approaches of previous workers to allow measurements of the viscoelastic properties of polymer solutions as a function of frequency by applying an oscillatory displacement to one trap and monitoring the resultant motion of the particles in both traps. Using colloidal particles as probes offers a number of advantages over conventional rheology, in particular the ability to measure viscoelastic properties to much higher frequencies. Here we present results that extend to 10kHz and allow investigations to be made of the Rouse relaxation behaviour of the solutions. One problem associated with the use of colloidal particles as rheological probes is that interactions between the probe particle and the medium may lead to results that are not representative of the bulk sample. The use of pairs of trapped particles overcomes this, which in principle allows information about both the local environment surrounding the particle, and the bulk properties to be gathered simultaneously. Interestingly, whilst previous authors have found differences between these local and bulk behaviours [1], we observed no difference, possible reasons for this will be discussed, and include the nature of the samples investigated (aqueous biopolymer solutions in our case, non-aqueous polymer solutions in [1]) or the nature of the experiment (forced oscillations of the probe particles, rather than measuring their thermal motions). We also show that it is possible to use pairs of particles to...
investigate interparticle forces at smaller particle separations than previously (~10nm) so long as the interaction between the traps is taken into account.


Wednesday 10:35 Salon 3 MR3

Probing the micro-structure of Carbopol using dynamic light scattering and multiple particle tracking
Laurent Rubatat¹, Felix Oppong², Arthur E. Bailey¹, John R. de Bruyn¹, and Barbara J. Frisken¹
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We study the micro-rheology of dispersions of Carbopol ETD 2050 in water as a function of the gel concentration. To do so, we use dynamic light scattering and optical microscopy to track submicron spherical particles loaded in the gel, with diameter ranging from 50 nm to 1 micron. The Mean Square Displacement (MSD) of the particles is calculated and analyzed to obtain the complex mechanical modulus of the gel on micrometer length scales. The MSD of the particles can be described by the diffusive exponent alpha, which is equal to one for low Carbopol concentrations, indicating normal diffusion. At moderate concentrations alpha is between zero and one, indicating subdiffusion as the structure of the fluid constrains the particle motion. At high concentrations (of order 1%), alpha is close to zero at long times. At this concentration the Carbopol is a stiff gel and the particles are almost completely confined. The results obtained by microscopy and dynamic light scattering are in good agreement. In contrast, we find substantial differences between our micro-scale measurements and the results of classical shear rheometry. We will discuss the difference between the bulk results and the microscale results in the context of the gel structure.

Wednesday 11:00 Salon 3 MR4

A simple paradigm for active and nonlinear microrheology
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In microrheology, elastic and viscous moduli are obtained from measurements of the fluctuating thermal motion of embedded colloidal probes, reflecting the near-equilibrium (linear response) properties of the surrounding medium. By actively pulling the probe through the material, further information can be obtained, analogous to large-amplitude measurements in (macro-) rheology.

How well do microrheologically-measured properties compare with the more familiar (macro)rheological ones? To address this question, we consider perhaps the simplest paradigmatic system for the study of microrheology: a colloidal probe pulled through a dilute suspension of neutrally buoyant bath colloids, wherein hydrodynamic interactions are neglected, but hard-sphere interactions enforced. This model system is simple enough to permit analytic solutions, but non-trivial enough to raise issues important for the interpretation of experiments in active and nonlinear microrheology.

From the (calculated) microstructural deformation, we determine the average retarding effect on the probe for various pulling-rates. Significantly, different results are obtained for probes driven at constant velocity and constant force --- furthermore, a probe pulled with an optical tweezer can behave as fixed-force, fixed-velocity, or as a mixture, depending on the strength of the trap and on the pulling speed.

More generally, we discuss how these results relate to previous work on the rheology of colloidal suspensions. The present theory gives shear-thinning but no shear thickening, and a physical picture of shear-thinning emerges. Remarkably, the effective micro- and macro- viscosities, when appropriately scaled, are in semi-quantitative agreement. However, for more complicated or unknown materials, where such scaling relations may not be known in advance, the comparison between micro and macro may not be so favorable.

Wednesday 11:25 Salon 3 MR5

Particle dynamics in semiflexible polymer-colloid solutions
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Semi-flexible polymers demonstrate distinctive rheological properties due to their large persistence length. They are attractive rheology modifiers for industrial applications, and they play an important role in the microrheology of eukaryotic cells. In this work, we report diffusing wave spectroscopy (DWS) studies of the dynamics of particles suspended in F-actin solutions over time scales $10^{-6} < t < 2$ s, while varying the contour length density, polymer particle interactions. Filaments of varying average length (0.05-10μ-m) are prepared by polymerizing actin in the presence of the binding protein gelsolin. As the molar ratio of gelsolin to actin increases, an abrupt transition of the particle diffusivity occurs near the semi-dilute overlap concentration. In addition, we investigate the effect of particle concentration on the structure of F-actin solutions. For the ratio of length to particle diameter, L/D~10, the diffusivities decrease with increasing particle volume fraction or increasing actin concentration. These are related to recent theories of polymer-induced local clustering and the presence of depletion layers between particles [1, 2].

Finite deformation model of the cellular recovery process
Andres L. Gonzalez and Charles D. Eggleton
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The recovery of cells after large deformations has been widely used to measure its material properties. Current practice is to assume a membrane model a priori and then obtain the apparent internal viscosity by fitting in vitro recovery data to a relaxation parameter obtained from small deformation theory. We focus our attention on large deformations and study the influence of varying the viscosity ratio (internal viscosity / external viscosity), the interface constitutive model and the initial geometry of the cell on the recovery process. An axisymmetric computational model based on the boundary element method (BEM) is used to simulate the recovery of cells from large deformations. We varied the viscosity ratio over six orders of magnitude (0.001 through 1000) and observed that the recovery process exhibits two self similar regimes in the limits as the viscosity ratio approaches zero and infinity. Comparison is made of cells having the following membrane models: (1) constant cortical tension [CCT], (2) two-dimensional Hooke's law [H], (3) Mooney-Rivlin law [MR], (3) Evans and Skalak [ES] and (4) prestressed elastic [PE]. All of these membrane models are elastic except for CCT. At small initial deformations, all elastic models are in the linearly elastic regime and similar behavior is observed. The recovery process becomes dissimilar at large initial deformations and is highly dependent on initial geometry. At large initial deformations local strains can exceed a critical value where the membrane is either strain hardening or strain softening, causing the dissimilar behavior. The observed recovery of cells with constant cortical tension is similar to that of the non-linear elastic capsules. The simulations are used to suggest methods for interpreting the recovery of cells observed in vitro.

Cell mechanical response, polymer physics and cellular strain
John Crocker, Gladys Massiera, Brenton Hoffman, and Kathleen Miranda
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While the importance of mechanical stimuli to regulating cell differentiation and tissue morphogenesis is increasingly appreciated, the identity and function of the basic mechano-sensors remain largely unknown. We use four different methods to probe the frequency-dependent mechanical response of mammalian cells using different geometries, length-scales, a wide frequency range and both passive and active driving. We find a complicated consensus response whose high-frequency portion closely resembles the probe-size dependent response of F-actin solutions, and whose low frequency power-law fluid response corresponds to recent in vitro models of pre-stressed semi-flexible polymer gels with protein cross-links (e.g. F-actin and Filamin A). Simple mathematical models of the response suggest conformational changes to the cross-linking proteins that we hypothesize may report network deformation or strain, rather than stress, enabling cellular sensing of ECM stiffness. Cell biological implications will be discussed.

The role of relaxation time in blood rheology
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Relaxation times underlie the way blood flows in the human circulatory system. Because of the pulsatility of the flow in vivo, the relaxation times near the pulse time play a greater role in the flow. Relaxation times, activated by the flow, can be obtained from measurement of the viscoelastic properties of blood in oscillatory flow at frequencies near the pulse rate. The relation between the relaxation times and the timing of natural events in the circulation shows whether viscous effects or elastic effects will dominate the flow. The relaxation times depend on the way the red blood cells are organized in the microstructure of the blood. Cells may form large aggregates, be highly dispersed or aligned in layers. These microstructures can change with the size of the vessel, rate of flow, vessel geometry (straight tube, tapered vessel, bifurcation, etc.). Qualitative properties of the cells, such as the deformability and aggregation tendency, play significant roles in establishing the microstructure.
Blood exhibits a very wide range of relaxation times, but when the viscoelasticity is measured at a single frequency, a single effective relaxation time can be specified for that flow condition. This is illustrated for blood in bulk, blood confined in small spaces and blood forced through a small opening by extensional flow.

Deformability of red blood cells flowing in microcapillaries in a gel matrix

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The deformability of red blood cells flowing in microvessels is essential to maintain optimal blood circulation and to allow gas transfer between blood and tissues. From a pathological viewpoint, reduced RBC deformability is involved in a number of blood diseases, such as Thalassemia, Iron Deficiency, Congenital Spherocytic and Non Spherocytic Anemias, Idiopathic Myelofibrosis. In spite of such physiopathological relevance, measurements of RBC deformability are usually of difficult clinical application, being still carried out by approximate methods and under conditions quite different from those occurring in vivo. In this work, we started investigating RBC deformability in microcapillaries embedded in a gel matrix. The microcapillaries may have size similar to that of RBC diameter (down to 5 micron). The gel matrix hosting the microcapillaries is placed in a rectangular flow cell, where a dilute suspension of RBCs, isolated by centrifugation, is fed through a syringe. The flow cell is mounted on a motorized x-y stage of an inverted microscope equipped with a CCD camera. Images of RBCs under flow are visualized, digitized by a frame grabber, and stored on hard disk for later analysis to measure type and extent of deformation. Experimental variables include flow rate and size of microcapillaries. RBCs both from healthy donors and from patients have been investigated and compared.

Blood soluble drag reducing polymers improve tissue perfusion via modification of red blood cell traffic in microvessels

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This work is pertinent to understanding the basic mechanisms underlying the hemodynamic effects of blood soluble long-chain drag reducing polymers (DRPs). An addition of nanomolar concentrations of DRPs to blood was shown to produce beneficial effects in various acute and chronic animal models such as an increase in cardiac output and a decrease in peripheral vascular resistance, with no direct effects on blood vessel tone. The addition of these polymers to blood (at ~1 µg/ml) increased the number of functional capillaries and velocity of red blood cells (RBCs) flow in capillaries in normal and diabetic rats. Chronically injected, DRPs diminished the development of atherosclerosis in animal models. The DRPs added to resuscitation fluids increased tissue perfusion and oxygenation and reduced mortality in animal models of lethal hemorrhagic shock and hypobaric hypoxia. Previous hypotheses regarding the DRP effects on blood circulation associated the observed intravascular effects with the Toms phenomenon: the reduction of turbulent drag in a pipe by minute DRP additives. However, there is little or no turbulence in the animal vascular system. Thus, the exact mechanisms by which DRPs improve blood circulation are yet to be identified. We proposed an explanation for the DRP intravascular effects based on experimental observations that these polymers reduce flow separations at vessel bifurcations at low Reynolds numbers (Re)

High-frequency relaxation of semiflexible biopolymer networks

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We present measurements of the linear viscoelasticity of entangled and crosslinked networks of semiflexible F-actin filaments. Semiflexible filaments such as actin provide an essential mechanical component of the cytoskeleton of living cells. At the same time, semiflexible polymer networks have unique viscoelastic properties and dynamics that are very distinct from those of conventional flexible polymer networks. Accordingly, the rheological properties of semiflexible polymers have been the focus of intense research in recent years. It has proven challenging, however, to quantitatively probe the multitude of distinct dynamic regimes experimentally, because of the extensive bandwidth required. We have measured the dynamic shear modulus of F-actin solutions and gels over a large range of frequencies from 1 Hz to nearly 100 kHz, using an optical microrheology technique where the thermal fluctuations of pairs of embedded probe spheres held at varying distances in two optical tweezers are measured with optical interferometry. We demonstrate quantitative agreement with theory in both amplitude and functional form for the modulus at high frequencies, confirming the principal role of transverse thermal bending fluctuations in determining the network response. Further, we show compelling evidence for a recently predicted intermediate-frequency relaxation mode that is unique to semiflexible polymers; this mode is due to rapid stress propagation along the filament backbone that is abolished upon crosslinking. Finally, we show that our laser-based trapping and tracking technique also enables us to perform active microrheology, not relying on thermal fluctuations, which is particularly useful for non-equilibrium complex fluids such as the cytoskeleton. We will show first data for mixtures of actin filaments and myosin motor proteins, which are a model for contractile actomyosin networks that are part of the cytoskeleton.
Cyclodextrin association networks
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The synthesize of α- and β-cyclodextrin-modified PAA and novel associative polymer networks based on mixtures of CD-modified and hydrophobically-modified (HM) PAAs are described. The inclusion interactions between CD and hydrophobe grafts in PAAs lead to stronger associations and solution viscosities than purely hydrophobic interactions at the same polymer concentration. The screening of the association between hydrophobically modified poly(acrylic acid)s by free α- or β-cyclodextrins occurs at approximately a stoichiometric ratio of cyclodextrin to hydrophobe. And the maximum of solution viscosity for the mixed CDMPAA and HMPAA also occurs at a stoichiometric ratio of cyclodextrin-to-hydrophobe. This indicates that the network involves binary associations driven by cyclodextrin inclusion. These novel associative polymer networks with unique binary interactions should be ideal model systems to test the theoretical predictions for the statics and dynamics of associative fluids.

The shear, transient and elongational rheology of PHA-based copolymers
James P. Eickhoff and Graham M. Harrison
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Bio-derived polymers, which may be obtained from biological microorganisms or other renewable sources, are increasingly being considered for a range of commodity applications that are typically dominated by conventional, petroleum-based polymers. In this work, we consider the rheological behavior and degradation of one class of bio-derived polymers, namely copolymers based upon 3-hydroxybutyrate (3HB). These materials can have mechanical properties similar to those of conventional polymers, and can degrade under a range of conditions. In particular, we investigate the transient elongational viscosity and the degradation kinetics of a series of PHA copolymer melts. Transient elongational viscosity measurements are made with a TA Instruments Extensional Viscosity Fixtures (EVF). We employ transient dynamic shear rheology, coupled with GPC measurements and a random chain scission model, to understand the degradation of the polymers under typical processing conditions. The impact of copolymer type and concentration is investigated.

A coarse-grained simulation of rheology of polymer nano-composites
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We use a coarse-grained simulation approach to address the dynamical properties of nanoparticles in polymeric fluids. In this approach, the solvent particles (polymer segments) are represented as DPD particles. In contrast, the solute particles are represented as spherical hard particles of appropriate size. For polymeric fluids, we have studied influence of polymer-particle friction and particle concentration upon polymer matrix relaxation dynamics, particle diffusion and rheology of the composite. Our results suggest nontrivial impact of the polymer relaxations upon the particle dynamics. We also specifically address the rheological effects arising from the interplay between particle jamming and transient network phenomena. Our results provide insights into the microscopic origins of polymer nanocomposite rheology and the influence of various physical parameters governing them.

Nanoparticles can reduce the viscosity of polymeric liquids
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Addition of nanoparticles to polymer melts have been shown by us to change the viscosity in curious ways. A key parameter dictating the viscosity - concentration behavior is the dimensionless group given by the ratio of the polymer radius of gyration (Rg) divided by the inter-particle half gap (h), denoted as the confinement parameter (C). When C < 1 the polymer chains are not confined and we find the viscosity increases, however, when C > 1 the viscosity falls below the pure polymer viscosity. This is expected to be a complicated phenomenon since the glass transition temperature falls in some cases, while the polymer Rg increases under all circumstances, and viscosity observations can not be explained with a simple, single consequence model. Discussion will reveal the details of these observations as well as why these suspensions remain stable.
Constitutive equations relating total stress to rate of strain are not generally available for concentrated suspensions, even for relatively simple systems of hard spheres suspended in a Newtonian medium. The rheology of such suspensions is complicated by flow induced microstructure. A suitable treatment of the microstructure would therefore be useful in constitutive models of suspension flow. The commonly used pair distribution function, while an analytically exact and useful description of microstructure, has not given rise to widely usable constitutive equations at present. Alternatively, tensors that approximate suspension microstructure have been used with some success. This is our approach. Using a directionally dependent mean free path length and a truncated Cartesian tensor expansion, we define a second order structure tensor. A semi-empirical differential equation is developed for the structure tensor, where representation theorems have been used as a guide. A separate equation relates the stress tensor to the structure tensor and rate of strain tensor. These equations can be used to model structure and stress in both steady and time-dependent viscometric flows. Results from Stokesian dynamics simulations are used to demonstrate the utility of this modeling approach. The simulations were for monomodal suspensions in an infinite shear field, with hydrodynamic and a short-ranged repulsive forces between the particles. Steady state results and model fit are emphasized.

General nonlinear hydrodynamic description of non-Newtonian fluids

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We review conventional constitutive equations for non-Newtonian fluids from a hydrodynamic point of view. Using general thermodynamic and symmetry arguments and applying valid physical principles we describe viscoelasticity by setting up nonlinear dynamic equations either for a relaxing (Eulerian) strain tensor or for a transient orientational order parameter tensor. This covers the usual non-Newtonian effects, like shear thinning, strain hardening, stress overshoot, normal stress differences and non exponential stress relaxation. In both cases an effective dynamic equation for the stress tensor can be derived in terms of a power series and compared with conventional non-Newtonian rheological models. It is more general in structure than those, comprises most, restricts some, and discards a few of them. In addition, we generalize this approach into a 2-fluid description for multi-component fluids, which is appropriate, when the relative velocity of the different components is relaxing slowly. Special emphasis is laid on nonlinearities involving velocities that are governed by symmetry and other general invariance principles. It is shown that the proper velocities, with which the dynamic quantities are transported and convected, cannot be chosen at will, since there are subtle relations among them. Within allowed combinations the convective velocities are generally material dependent and not fixed by general principles. The so-called stress division problem, i.e. how the total stress is distributed between the different components, is shown to depend partially on the choice of the convected velocities, but is otherwise also material dependent. A set of reasonably simplified equations is given for viscoelastic fluids, polymeric gels, and ferrofluids focusing on an effective concentration dynamics that may be used for comparison with experiments.

Extensional viscosity of a dilute suspension of rigid spheres in a second order fluid

Dino Ferri\textsuperscript{1}, Francesco Greco\textsuperscript{2}, and Pier Luca Maffettone\textsuperscript{3}

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Melt stretching of polymer melts is involved in several industrial processes like thermoforming, fiber spinning and blow molding. Thus, the elongational viscosity of polymers plays a crucial role to predict the properties of final products. The presence of a rubber inclusion locally modifies the imposed uniaxial elongation flow and partially suppresses strain hardening. High Impact Polystyrene (HIPS) samples with different dispersed polybutadiene particles were investigated by means of a Meissner type elongational rheometer. A theoretical description of the observed features is proposed by assuming dilute conditions. The inclusions are treated as rigid spheres. The suspending liquid is considered a second order fluid. The effect of the spheres on the flow field is determined with a perturbative approach. The dependence of the predicted extensional viscosity of the dilute suspension on the strain rate suggests a possible explanation of the observed features.

The effect of the form of the interparticle force used in Stokesian dynamics

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We investigated the common practice, in Stokesian Dynamics simulations, to use an interparticle force to model an effective particle surface-roughness. Two functional forms of the interparticle force were used in Accelerated Stokesian Dynamics simulations to probe the effect that the functional form has upon the suspension properties. Specifically, these properties include the relative viscosity and the first and second normal...
stresses. We based the functional form of the interparticle force on the standard form used in many published Stokesian Dynamics simulations. This form arises from the Debye-Hückel solution of the Gouy-Chapman equation for the electrostatic interaction between particles, at constant surface charge-density. We used perturbations of this functional form to explore a range of interparticle-force effects in the simulations. The use of these different interaction-force functional forms produced significant changes in the suspension properties (relative viscosity and normal stresses). This observation corresponds to published Stokesian Dynamics simulations. We propose that this issue warrants further investigation.

Wednesday 5:15 Salon 1 SC42

Nonlinear properties of hard sphere suspension in a Newtonian medium under large amplitude oscillatory shear flow

Jung Gun Nam¹, Kyu Hyun¹, Yoon Jae Yim¹, Kwang Soo Cho², Kyung H. Ahn¹, and Seung J. Lee¹

¹Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea; ²Kyungpook National University, Daegu, Republic of Korea

Nonlinear behavior such as the shear thickening observed in suspensions is now well known. And control of the structure and flow properties of such suspensions is often vital to the commercial success of the product or of its manufacture. Therefore rheological properties are needed to understand the phenomena encountered and changes occurring during processing. Specifically the shear thinning/thickening of the steady state viscosity and underlying structural changes have been extensively studied. Recently we investigated that LAOS (large amplitude oscillatory shear) is very sensitive to the interactions or the shear induced formation of microstructure compared to steady shear. And using Fourier transformation (FT) rheology, comparing the stress signal in time domain with FT parameter in frequency domain, we could determine the nonlinearity of the materials. The nonlinearity represents the ratio of the first harmonic contribution to third harmonic contribution in frequency domain. Similarly these methods were applied to suspension systems. Under LAOS flow we could find the complex viscosity increasing behavior as the strain amplitude increased readily. This strain hardening behavior became severe at higher volume fraction of the suspension. The onset point of the strain hardening was moved to a lower strain amplitude as increasing volume fraction. The nonlinearity obtained from FT rheology increased to the onset point of the strain hardening, and then decreased. Consequently, we observed nonlinear properties of the suspension and tried to relate the result with structure of the suspension.

Symposium SM
Entangled Solutions and Melts
Organizers: Lynden Archer and Jay Schieber

Wednesday 1:30 Salon 2 SM20

The effects of supercritical CO₂ and pressure on the rheological properties of high density polyethylene

Hee Eon Park and John M. Dealy

Chemical Engineering, McGill University, Montreal, Quebec H3A 2B2, Canada

Supercritical carbon dioxide (SC-CO₂) is used as a physical blowing agent in the manufacture of plastic foam and as a plasticizer to reduce melt viscosity during processing. Pressure is also an important variable for processing, and the combined effects of dissolved SC-CO₂ and pressure on rheological properties must thus be known to achieve optimum processing conditions. However, until recently there was no method to measure these effects accurately. A high-pressure sliding plate rheometer in which the shear deformation, temperature, pressure, and CO₂ concentration are uniform, was used in the present study. Since the shear stress transducer senses the stress in the center of the sample, edge effects are not a problem. The effects of CO₂ and pressure on the viscosity, stress growth function, and creep compliance of a high-density polyethylene (HDPE) were determined. To separate the effects of pressure and CO₂, samples were first pressurized without CO₂, and then pressurized and saturated with CO₂. It was possible to use shift factors for pressure and CO₂ concentration to obtain a master curve.

Wednesday 1:55 Salon 2 SM21

Shear alignment of multiblock copolymers

Timothy P. Lodge, Frank S. Bates, and Lifeng Wu

Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN 55455

The ability of flow fields to induce macroscopic alignment of diblock and triblock copolymer lamellae has been amply documented. Of particular interest are the factors that determine whether the lamellae normals align with the gradient direction ("parallel") or vorticity axis ("perpendicular"). Lamellae formed from copolymers with greater than three blocks have been shown to have significantly superior mechanical properties than diblocks and triblocks, and it is therefore important to establish whether these materials can be macroscopically aligned. In this work we describe systematic measurements on a series of styrene-isoprene copolymers varying from diblocks (SI) to undecablocks (SISISISIS). The linear viscoelastic properties of both aligned and unaligned materials are characterized in detail, as are the alignment pathways under various non-linear conditions. The state of alignment is characterized by SAXS and TEM. The results are quite remarkable, and point to the central role of chain conformations, particularly in terms of the looping or bringing of the middle blocks.
Polymer-based nanocomposites are often accomplished by dispersing a nano-dimensioned filler within a polymeric matrix. However, an attractive alternative is to copolymerize polymers with a nano-dimensioned hybrid monomer, such as the polyhedral oligosilsesquioxane (POSS) moiety. The rheological behavior reported to date for materials from these two approaches appears to be quite different, and the present talk will elaborate on how styryl-POSS comonomers incorporated into atactic polystyrene broadly influences free volume, entanglement density, and flow activation energy. General features observed include significant lowering of free volume expansion coefficient, increase in entanglement molecular weight (and packing length), and lowering of flow activation energy - all monotonically with POSS content. Significant sensitivity to the POSS vertex "R" group has been observed, where "R" included isobutyl (iB), cyclohexyl (Cy), or cyclopentyl (Cp). While iB-based copolymers showed somewhat simple trends as described above, CyPOSS copolymers featured the appearance of a low-frequency plateau in storage modulus, suggesting a weak physical network, and a particular CpPOSS copolymer composition revealed critical gel behavior.

Wednesday 2:20 Salon 2

**Rheology of entangled PS-POSS copolymers**

Jian Wu1, Patrick T. Mather2, and Timothy S. Haddad3

1Chemical Engineering Department, University of Connecticut, Storrs, CT 06269; 2Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106; 3AFRL/PRSM, ERC, Inc, Edwards AFB, CA

Polymer-based nanocomposites are often accomplished by dispersing a nano-dimensioned filler within a polymeric matrix. However, an attractive alternative is to copolymerize polymers with a nano-dimensioned hybrid monomer, such as the polyhedral oligosilsesquioxane (POSS) moiety. The rheological behavior reported to date for materials from these two approaches appears to be quite different, and the present talk will elaborate on how styryl-POSS comonomers incorporated into atactic polystyrene broadly influences free volume, entanglement density, and flow activation energy. General features observed include significant lowering of free volume expansion coefficient, increase in entanglement molecular weight (and packing length), and lowering of flow activation energy - all monotonically with POSS content. Significant sensitivity to the POSS vertex "R" group has been observed, where "R" included isobutyl (iB), cyclohexyl (Cy), or cyclopentyl (Cp). While iB-based copolymers showed somewhat simple trends as described above, CyPOSS copolymers featured the appearance of a low-frequency plateau in storage modulus, suggesting a weak physical network, and a particular CpPOSS copolymer composition revealed critical gel behavior.

Wednesday 2:45 Salon 2

**Extensional behavior of PBT/PE blend nanocomposites**

Joung Sook Hong1, Han Namgung2, Kyung H. Ahn3, Seung J. Lee2, and Chongyoup KIM1


Poly(1,4-butylene terephthalate)(PBT)/polyethylene(PE) nanocomposites were prepared by melt mixing of PBT, PE, and organically modified nanoclay. Since the viscosity ratio of the PBT and PE was much lower than unity at mixing condition, the PBT domains were dispersed in the PE matrix with an average particle diameter below 1/μm. Although an effective size reduction couldn't be obtained by the addition of organoclay, the rheological properties of blend were improved, especially storage modulus at lower frequency region. Also, the strain hardening behavior of blend nanocomposite was significantly enhanced. The TEM observations showed that with very small amount of organoclay, the clay is first located in the interface between immiscible two components and all the organoclay is selectively dispersed only in the PBT with a high degree of intercalation as the amount of clay increases. This selective localization of organoclay significantly changed the rheological properties of the dispersed PBT during mixing and stabilizes the morphology by preventing coalescence each PBT domains. This study suggests that the addition of small amount of organoclay in immiscible polymer blends induces the significant strain hardening behavior by the improvement of adhesion in the interface between two components.

Wednesday 3:35 Salon 2

**Flow-induced crystallization of polypropylene-clay nanocomposites: Clay disorientation kinetics and morphology**

Mark A. Treece and James P. Oberhauser

Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904

This work investigates the quiescent and flow-induced crystallization kinetics and morphology of an intercalated/partially exfoliated polypropylene (PP) clay nanocomposite. A maleic anhydride functionalized PP (10 wt%) is melt-blended with an organically modified montmorillonite clay (3 wt% Cloisite 15A from Southern Clay Products) and a PP resin (MFI 12 g/10 min at 230 degrees C) in a twin screw extruder.

Quiescent kinetics are probed with isothermal differential scanning calorimetry (DSC) in conjunction and resulting morphology examined ex situ with polarizing optical microscopy (OM) and transmission electron microscopy (TEM). In the flow-induced crystallization studies, the nanocomposite is subjected to a finite shear pulse in a mini-extruder whose design is inspired by with in the research groups of Janeschitz-Kriegl and Kornfield. During and subsequent to the shear pulse, we monitor birefringence and turbidity as a function of shearing time and wall shear stress. Ex situ, both OM and TEM are utilized to examine morphology.

Results indicate that flow strongly orient clay domains, which then act as nucleation sites for crystallization; consequently, polymer crystallization kinetics are accelerated relative to the neat resin. Conversely, quiescent crystallization kinetics of the disordered clay nanocomposite are retarded, highlighting the critical role played by clay orientation. In order to further investigate the role of clay orientation on crystallization, we report on clay disorientation kinetics using DSC, mechanical rheology, and microscopy. We observe that the clay disorientation kinetics inferred from DSC data correlate with those deduced from rheological experiments. Thus, we offer strong evidence that crystallization kinetics and morphology are strongly dependent upon clay orientation, and the relaxation of flow-aligned clay particles to the original pre-shear state is slow but recoverable with sufficient annealing time.
Exfoliation of organically modified montmorillonite clay silicates and its effects on the rheology of polyethylene were studied. Variable proportions of maleic anhydride graft modified polyethylene (MA-g-PE) resins and clay were blended with the virgin polyethylene using twin screw melt compounding. X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) were used to characterize the dispersed clay compounds. Disappearance of diffraction peaks at low diffraction angles; reduction and shift at higher diffraction angles indicated a strong influence of MA-g-PE on the intercalation and eventual exfoliation of clay. TEM images graphically illustrated the extent of delamination of silicate galleries. Dynamic Oscillatory Rheological measurements were used to study the elastic and viscous behaviour in the compounds. Preponing of viscous to elastic transition and diminishing dissipation were observed with respect to increasing clay content that were in addition, complemented by increasing proportion of graft modified polyethylene in the blends. Organically modified clay was also observed to act as a processing aid in postponing the onset of flow instabilities in polyethylene to higher shear rate values.

Rheological properties of polyimide and oligoimide nanocomposites based on novel silicate hydroxide particles

Gilles M. Divoux, Joshua U. Otaigbe, Vladimir E. Yudin, Valentin M. Svetlichnyi, Viktor V. Gusarov, and Eleonora N. Korytkova

School of Polymers and High-Performance Materials Department, The University of Southern Mississippi, Hattiesburg, MS 39406; Russian Academy of Sciences, Institute of Macromolecular Compounds, Saint-Petersburg 199004, Russia; Russian Academy of Sciences, Institute of Silicate Chemistry, Saint-Petersburg 199004, Russia

Nanocomposites have attracted substantial attention because of their superior thermal and mechanical properties compared to those of their micro- and macro-composite counterparts containing an equivalent volume fraction of inorganic filler. Nanocomposites are commonly based on polymer matrices reinforced by nanofillers such as montmorillonite platelets. Nanotubes with chrysotile structure of Mg₃SiO₅(OH)₄ type were synthesized and used as a filler for polyimide nanocomposites also. We have demonstrated that polyimides based on 1,3-Bis(3',4',4'-diphenyloxophenoxy)benzene and Bis[4-(4-aminophenoxy)phenyl)sulfone type with relatively low molecular weights (Mn = < 10,0000 g/mol) can be melt blended in a micro compounder with organo-modified MMT or NT particles to yield nanocomposites with enhanced benefits. Application of a strong shear field in the micro compounder at relatively low temperatures close to the Tg of the respective oligoimide resulted in a nanocomposite with a significant increase in viscosity (nearly 3 orders of magnitude increase) that can not be interpreted by existing theories in the literature. The significant viscosity increase exhibited by the Oligoimide/MMT or Oligoimide/NT nanocomposites after application of the strong shear flow fields may be attributed to the partial exfoliation of the organo-MMT particles or better dispersion of NT particles and formation of the percolating (network) structure at low volume fraction (4-8%) of the particles in oligoimide melt. It is hoped that the results of the present study may stimulate a better understanding of the influence of the morphological evolution on the rheology and processability of the polyimide/nanoparticles composites. Because of their facile synthesis and desirable properties for a number of applications in protective coatings and films for microelectronic applications and flammability reduction, these low molecular weight polyimide nanocomposites are expected to be excellent model systems for future studies.
Surfactant solutions self-assembled into wormlike micelles exhibit linear viscoelasticity characteristic of model, entangled polymer solutions, but can exhibit unusual nonlinear responses such as shear banding and shear induced phase separation (SIPS). In this work we explore the mechanisms underlying this unusual nonlinear behavior. Model micellar solutions of identical surfactant concentration but varying salt concentration are explored by a combination of rheology, rheo-optics, particle tracking velocimetry, Rheo-SANS, and novel flow-SANS in the $1-2$ plane with gap resolution to investigate the structure of the shear-banded and SIPS state. In particular, two solutions of nearly identical linear viscoelasticity are compared, where one exhibits SIPS while the other remains a single phase, shear thinning fluid. The behavior can be connected to micellar branching in proximity to an underlying thermodynamic phase transition. Flow-SANS in the $1-2$ plane demonstrates morphological changes in the self-assembled microstructure in the shear-banding sample. Differences in the samples' behavior under shear flow is connected to the differences in molecular interactions due to the varying salt concentration.

### Symposium SS

**Viscoplasticity and Viscoelasticity of Solids and Semi-Solids**

Organizers: Ian Frigaard and Gregory B. McKenna

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**Wednesday 5:15 Salon 2**

**Shear-induced banding and phase separation in solutions of wormlike micelles**

Norman Wagner, Matthew Liberatore, Florian Nettlesheim, and Eric Kaler  
*Chemical Engineering, Univ. of Delaware, Newark, DE*

Surfactant solutions self-assembled into wormlike micelles exhibit linear viscoelasticity characteristic of model, entangled polymer solutions, but can exhibit unusual nonlinear responses such as shear banding and shear induced phase separation (SIPS). In this work we explore the mechanisms underlying this unusual nonlinear behavior. Model micellar solutions of identical surfactant concentration but varying salt concentration are explored by a combination of rheology, rheo-optics, particle tracking velocimetry, Rheo-SANS, and novel flow-SANS in the $1-2$ plane with gap resolution to investigate the structure of the shear-banded and SIPS state. In particular, two solutions of nearly identical linear viscoelasticity are compared, where one exhibits SIPS while the other remains a single phase, shear thinning fluid. The behavior can be connected to micellar branching in proximity to an underlying thermodynamic phase transition. Flow-SANS in the $1-2$ plane demonstrates morphological changes in the self-assembled microstructure in the shear-banding sample. Differences in the samples' behavior under shear flow is connected to the differences in molecular interactions due to the varying salt concentration.

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**Wednesday 1:30 Seymour**

**Computations and analysis of Rayleigh-Bénard stability of Bingham fluids**

Ian Frigaard$^1$, Didier Vola$^2$, and Jianying Zhang$^3$  
$^1$Mechanical Engineering & Mathematics, UBC, Vancouver, B.C., Canada; $^2$IRSN/DPAM/SEM/IC/LMPC, St. Paul-lez-Durance, France; $^3$Mathematics, UBC, Vancouver, B.C., Canada

We present results on Rayleigh-Bénard stability of a Bingham fluid. These flows are of relevance to many different applications: magma flows, switching devices for ER/MR fluids, cooking of chocolate, etc., as well as of fundamental interest. Our principal results are as follows. (i) For any positive yield stress the flow is linearly stable for all Rayleigh numbers, $Ra$. (ii) The flow is globally stable below a critical Rayleigh number, $Ra_E$, which is also the energy limit of the analogous Newtonian problem. (iii) For Rayleigh numbers that exceed $Ra_E$, we have conditional nonlinear stability, dependent on the size of the initial perturbations. (iv) The Prandtl number affects only the conditional stability bounds above $Ra_E$, and also the decay rates of the perturbation. (v) For all stable parameters we demonstrate that the velocity perturbation decays to zero in a finite time, (the timescale of which we are able to estimate), whereas the temperature perturbation decays exponentially. A series of computational results are presented that largely confirm the stability analysis. The computations are made using a numerical method based on the decomposition-coordination method of Fortin and Glowinski, with a suitable "cocktail" of numerical ingredients (low-order finite elements, velocity-pressure stabilisation, fully decoupled Uzawa-like algorithm). This solves the coupled thermo-fluid problem without need for regularization, which is necessary if one wishes to correctly model stopping of the flow. For sub-critical Rayleigh numbers, we observe that the fluid come to rest in a finite time by growth of the unyielded zones. The norm of the temperature decays exponentially, but we can observe two distinct decay timescales, depending on whether the fluid has stopped or not. For super-critical Rayleigh numbers we study the cellular flow patterns and attempt to use the computations to define a sharper conditional bound on the Bingham number.

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**Wednesday 1:55 Seymour**

**Parameter estimation of thixotropic Herschel-Bulkley fluids**

Andreas N. Alexandrou$^1$ and Georgios Georgiou$^2$  
$^1$Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia CY1678, Cyprus; $^2$Mathematics and Statistics, University of Cyprus, Nicosia CY1678, Cyprus

Semisolid slurries are a mixture of rounded, rosette-like solid particles and liquid at a temperature between the liquidus and solidus limits. The average solid volume fraction is a function of the bulk temperature of the suspension and varies from zero to unity depending on the local temperature. During processing the viscosity changes significantly due to the evolution of the internal structure. In general, semisolid materials behave as viscoplastic fluids characterized by a finite yield stress and by material properties that are time- and shear-rate dependend. Therefore, semisolid slurries are modeled as Herschel-Bulkley fluids with time-dependent parameters. An essential element for the integration of the semisolid metal (SSM) process in the production of complex commercial components is the availability of accurate mathematical and computational tools that could describe both the material characteristics and the dynamics of semisolid slurries during die filling. Computational simulation and modeling is also a powerful and an effective tool that can be used to understand complex physical phenomena, such as those observed with semisolid slurries, and to support theoretical models describing them. We show how important physics can be revealed using experiments combined with numerical simulations. We also investigate in detail the flow in a rotational viscometer which relates to a popular experiment commonly used to determine rheological constants of semisolid slurries. The goal is to use mathematical and computational tools to test postulates for physical and theoretical models used to describe complex semisolid slurry behavior. The ultimate objective of this work is to contribute to the development of a methodology, which relates simulations to actual experimental results in order to determine the material constants of Herschel-Bulkley fluids that exhibit complex thixotropic behavior.
Penetration into compressible rigid-viscoplastic media
Oana Cazacu¹, Ioan R. Ionescu², and Thomas Perrot³
¹Department of Mechanical and Aerospace Engineering, University of Florida, Shalimar, FL FL 32579; ²Laboratoire de Matheamtiques, University of Savoy, Le Bourger-du-Lac, Savoy 73376, France

We develop computational techniques for the tunnelling stage of the penetration into semi-infinite compressible(geological)targets of a hard (rigid) penetrator. An eulerian description and a fluid-type constitutive law are used in modelling large deformations. In order to capture the combined effects of high-strain rate and high-pressure con- finement on yielding, a compressible rigid viscoplastic fluid constitutive equation is introduced. To account for the experimentally observed characteristics of the response at high-pressures we have adopted the hypothesis of a locking medium (i.e. the density cannot exceed a critical limit). To compute the steady-state penetration, a mixed finite-element and finite-volume strategy is developed. Specifically, the variational inequality for the velocity field is discretized using the finite element method and a

Capillary rheology of extrudable cement-based materials
Roberta Alfani¹, Gian Luca Guerrini¹, and Nino Grizzuti²
²CTG Italcementi Group, Bergamo 24121, Italy; ³Chemical Engineering, University of Naples, Napoli 80125, Italy

In the last few years the development of new, very dry formulations of cement pastes has opened the way to the development of extrusion processes for this class of materials. Understanding the rheological behaviour of extrudable cement pastes obviously represents a crucial step in the development of these innovative materials and of the related processing technologies. In this paper, a newly developed capillary rheometer, dedicated to the viscous characterization of cement pastes is presented. A custom-made capillary station is fitted to a universal testing machine (Instron 5500). The Instron upper arm is connected to a piston that pushes the material into a lower, interchangeable capillary die. Two different die setups are employed. In the more standard configuration, a pressure transducer is placed before the die inlet, so that measurements with different die lengths allow for the determination of the entrance pressure loss. In a second configuration, the pressure transducer is placed directly on the wall of a rectangular slit die. In this way the pressure drop in the capillary flow region can be directly measured. Experimental measurements on a model cement paste formulation show that entrance flow effects are particularly relevant, dominating the overall pressure loss at the lowest shear rates investigated. As a consequence, the Bagley correction may become too sensitive to the entrance pressure drop, thus determining unreliable viscosity results. It is shown that these problems can be overcome by the direct pressure measurement inside the capillary. The viscosity vs. shear rate behaviour of the model cement paste is presented. It is shown that, at least in the shear rate range investigated, the material responds as a simple shear thinning fluid. The presence of a yield stress in the material and the possibility of its determination from the experimental results is also discussed.

Free boundary problems in flows of visco-plastic fluids
Vladimir M. Entov
Laboratory of Dynamics of Complex Fluids, Institute for Problems in Mechanics, RAS, Moscow 119526, Russia

The talk discusses some free-boundary plane problems that arise in mathematical theory of plane flows of viscoplastic fluids in porous media, Hele-Shaw cells and in antiplane shear. Mathematical analogy between these flows and antiplane deformation of elasto-plastic bodies is presented. Many of these problems allow exact analytical solutions that provide some insight into more complex behavior in general geometry. In particular, they allow to follow the limiting transition to rigid-plastic (‘Bingham-like’) behaviour and non-uniqueness of solutions in infinite domains. Tentative applications of the approaches suggested by analytic solutions to more complex flows studied by numerical modelling are discussed as well as some open problems of the theory.

Transient squeeze flow of viscoplastic materials
George Karapetasas and John Tsamopoulos
Chemical Engineering, University of Patras, Patras 26504, Greece

The transient, axisymmetric squeezing of viscoplastic materials under creeping flow conditions is examined. Both cases of the disks moving with constant velocity or under constant force are studied. This time-dependent simulation of squeeze flow is performed for such materials in order to determine very accurately the evolution of the force or the velocity, respectively, the highly deforming shape and position of all the interfaces, the effect of possible slip on the disk surface and the effect of gravity. All these are impossible under the quasi-steady state condition used up to now [Smyrnaios & Tsamopoulos JNNFM, (2001); Matsoukas & Mitsoulis, JNNFM (2003)]. The exponential constitutive model is employed. The governing equations are solved numerically by coupling the mixed finite element method with a quasi-elliptic mesh generation
scheme to follow the large deformations of the free surface of the fluid. As the Bingham number increases, large departures from the corresponding Newtonian solution are found. When the disks are moving with constant velocity, unyielded material arises only around the two stagnation points of flow at the center of the disks verifying our previous quasi-steady work. The size of the unyielded region increases with the Bingham number, but decreases as time passes and the two disks approach each other. Their size also decreases as the slip velocity or the slip length along the disk wall increase. The force that must be applied on the disks in order to maintain their constant velocity increases with the Bingham number and time providing a first method to calculate the yield stress. When a constant force is applied on the disks, they slow down until they finally stop, because all the material between them becomes unyielded. The final location of the disk and the time when it stops provide another method to deduce the yield stress of the fluid. Acknowledgement:

Wednesday 4:25 Seymour
Paste extrusion of PTFE: Experiments and simulations
Evan Mitsoulis1, Isaias Ochoa2, and Savvas G. Hatzikiriakos2
1Mining Engineering and Metallurgy, NTUA, Zografou 157 80, Greece; 2Chemical Engineering, UBC, Vancouver, British Columbia V6T 1Z4, Canada

In the process of paste extrusion, a paste is first formed by mixing the PTFE resin with a lubricant whose concentration varies from 16 to 25% wt, depending on the resin and the geometrical characteristics of the extrusion die. The system behaves then like a semi-solid material when it is extruded at 35ºC at various piston velocities in tapered capillary dies. During extrusion, the pressure in the system follows 3 distinct zones: (i) first rises to a maximum and then falls rapidly to a value just below the steady-state, (ii) a steady-state follows, and (iii) towards the end of extrusion, a slight pressure increase occurs. To solve numerically such problems of semi-solid processing, it is important to include in the constitutive modelling both the compressibility of the paste and its apparent yield stress, which has to be overcome to achieve flow and deformation. Several regularized models that overcome the discontinuity of the yield-stress models have been proposed and analyzed over the years. The exponential model is shown to give as good predictions as the ideal Bingham model for many cases of viscoplastic flow. Numerical simulations with the Bingham (or Herschel-Bulkley) model or Papanastasiou model have been pursued for PTFE paste extrusion flows with the purpose to see whether it is possible to predict the 3 distinct pressure zones. Compressibility is included together with yield stress in time-dependent simulations. The simulations are pursued for a wide range of apparent shear rates corresponding to the experimental ones, and conclusions are drawn regarding the paste behaviour in extrusion.

Wednesday 4:50 Seymour
Flow of viscoplastic liquids through axisymmetric expansions-contractions
Paulo R. Souza Mendes, Priscilla R. Vargas, Jane Celnik, and Monica F. Naccache
Department of Mechanical Engineering, Pontificia Universidade Catolica -RJ, Rio de Janeiro, Rio de Janeiro 22453-900, Brazil

The internal flow of viscoplastic liquids through an abrupt axisymmetric expansion followed by an abrupt contraction is studied. This situation is representative of numerous flows found in industrial processes, such as extrusion, mold filling and liquid displacement in porous media. The yield stress strongly affects the flow pattern as well as the pressure drop along the channel. In this work, numerical solutions were obtained by solving the conservation equations of mass and momentum via the finite volume method. In order to model the viscoplastic behavior of the liquid, the Generalized Newtonian Liquid constitutive equation was employed, in conjunction with a recently proposed viscosity function (Souza Mendes and Dutra, 2005). The numerical results were obtained for steady, inertialess flow. Flow visualization experiments were also conducted. The liquids employed were Carbopol aqueous solutions at different concentrations containing micron-size spheres to promote light reflection. The test section was built in transparent plexiglas. A metering pump was employed to move the liquid in open loop. A laser sheet was employed to illuminate a plane containing the channel axis. A CCD camera recorded the particle paths for a wide range of length-to-diameter combinations of these parameters. A dramatic change of flow pattern at a critical value of the length-to-diameter ratio of the large-diameter region, including an apparent discontinuity of the velocity field. For low values of the length-to-diameter ratio the viscoplastic liquid seems to "fracture" near the core region of the flow, and an unyielded region appears in the large-diameter portion of the channel, away from the symmetry line. For large values of the length-to-diameter ratio the flow has the same pattern as the one observed for Newtonian fluids.

Wednesday 5:15 Seymour
Rheology of mozzarella cheese
Edward B. Muliawan and Savvas G. Hatzikiriakos
Department of Chemical and Biological Engineering, The University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada

Cheese is a complex semi-solid material that has attracted the interest of many rheologists and scientists. Research on cheese has been ongoing due to the increasing demand of cheese related products and a healthier lifestyle. This leads to two major research areas; production of cheese and improvement of low fat cheese. The common aspect of these two research areas is the study of rheological behaviour of cheese. Empirical measurements on the rheological properties have been widely done. However, these tests generate parameters that are not acceptable rheologically since they depend on the geometries of the equipment and/or the sample. In the past decades, fundamental measurements have gained more importance. However, most of these have been restricted to dynamic oscillatory measurements and uniaxial and biaxial extensions which use small amount of cheese. Unfortunately, cheese is a highly heterogeneous sample, thus the samples used in these tests may not be a
good representative of the batch. In this paper, the rheological properties of mozzarella cheese are determined by using a capillary rheometer, which requires a relatively larger sample size. Interesting phenomena which occur during extrusion, such as slip and end pressure effects and also extrudate appearance, will be presented. The results obtained from capillary rheometer are compared to results obtained from dynamic oscillatory and extensional rheometers.

Symposium MR
Microrheometry and Microfluidics

Organizers: Pat Doyle and Anubhav Tripathi

Wednesday 1:30 Salon 3 MR6
Flow of DNA solutions in planar micro-contractions
Shelly Gulati1, Dorian Liepmann2, and Susan J. Muller3
1Joint Graduate Group in Bioengineering, University of California, Berkeley, Berkeley, CA 94720-1774; 2Department of Bioengineering, University of California, Berkeley, CA 94720-1762; 3Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462

The characterization of flows containing macromolecules such as DNA is critical for the optimal design of microfluidic systems for biochemical analyses. The effects on lambda-DNA transport in microscale flows are significant because the flow behavior may be influenced by molecular interactions, both viscous and elastic forces dominate inertial forces at this length scale, and the macromolecular length scale approaches the device length scale. Previous studies have shown that DNA can undergo dramatic stretching in microfluidic flow with conformational changes occurring in both elongational and shear flows (Shrewsbury et al., 2001). In the present work, planar micro-contraction geometries (gradual and 2:1 abrupt) are used as test structures because they are a canonical microfluidic components and a viscoelastic benchmark. In this microfluidic structure the DNA solution is subjected to regions of elongation along the channel centerline and shear at the walls. Digital Particle Image Velocimetry (DPIV), pressure measurements, and flow visualization are used to characterize the flows of water (0c*) and dilute (0.4c*) and semi-dilute (4c*) DNA solutions. The molecular contour length L approaches the device length scale D for these flows; L/D ~ 0.12 and ~ 0.22 for the 2:1 abrupt and gradual contraction, respectively. Recirculation regions observed just upstream of the contraction for 4c* DNA flows in both geometries are characteristic of strong elastic flow behavior; these regions are symmetric, stable, and grow with increasing Reynolds (Re) and Deborah (De) numbers. Velocity fields constructed using DPIV indicate that the presence of the DNA affects the flow field only at sufficiently high concentrations and De. The range of test conditions spans 0.5 < De < 180 and 0.0001 < Re < 0.9. Conformational studies of DNA flows in these geometries relate molecular conformation to the velocity fields across a similar parameter range.

Wednesday 1:55 Salon 3 MR7
Electrophoresis of large DNA molecules in microcontractions
Patrick S. Doyle and Greg Randall
Chemical Engineering, MIT, Cambridge, MA 02139

The ability to controllably position and stretch large DNA molecules in a microfluidic format is important for gene mapping technologies such as Direct Linear Analysis (DLA). Current technologies developed for DLA use controlled hydrodynamic flows created in a microfluidic device. The downside to this approach is that the imposition of the no-slip condition at the channel walls generates vorticity which can lead to DNA chain tumbling and incomplete stretching. We have recently shown that electric field gradients can be readily generated in a microfluidic device and the resulting field is purely elongational. We present here single molecule studies of DNA molecules driven by an electric field through a microfabricated contraction. Analogous to the hydrodynamic deformation of DNA, we can define an electrophoretic Deborah number (De) for our problem. We will discuss the effectiveness of the device to fully stretch DNA as a function of De and compare to stretching achieved in hydrodynamic flows. A detailed analysis of molecular stretching and the role of a non-homogeneous electric field will be discussed.

Wednesday 2:20 Salon 3 MR8
Controlling dynamics and conformations of DNA in flow through post arrays
Nerayo P. Teclemariam1, Susan J. Muller1, Victor A. Beck2, and Eric S. Shaqfeh3
1Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462; 2Chemical Engineering, Stanford University, Stanford, CA 94305

Separation in sieving media is a fundamental technique and of importance in a number of fields, especially life sciences. In electrophoresis, collisions of field-driven biomolecules with obstacles results in a length-dependent mobility and separation. Recent work of single molecule DNA flows in microfluidic separation devices have provided insight into their rich dynamics; however, systematic studies in well-defined ordered media are still lacking. We employ the use of single molecule fluorescence microscopy to examine the dynamics of pressure-driven DNA flows in high-aspect ratio arrays of microfabricated ordered obstacles. The ability to control the location and degree of stretching of single molecules in microfabricated ordered media is shown by appropriate selection of array geometry and field strength. Controlled collisions can be used to design improved separation systems.
Polymer chain dynamics in viscous flow through ordered arrays of posts

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DNA chain dynamics in the flow through periodic arrays of posts convected under the action of a viscous driving force are simulated using Brownian dynamics. We develop an understanding of the mechanisms that lead to hooking, and thus velocity reduction and ultimately separation, in the arrays. Dispersion in the cross-stream direction is found to be of paramount importance, and is isolated as the sole mechanism by which a post-chain collision in the array can occur. We show that ordered arrays can produce separation at flow strengths comparable to those observed in random arrays. By including the disturbance fields produced by posts in the arrays we also study the effect of spatial variations in the field. We discuss these results as they apply to the design and simulation of an ordered array of posts optimized for chain stretching and separation.

A computational study of drop formation in microfluidic devices

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Capillarity has a prominent role in flow in microfluidic devices because of the typically small linear dimensions, large curvature and large surface area in these geometries. Applications of micro-drops and micro-bubbles in small channels range from micro-pumps to ultrasound contrast agents [1]. In this study, we concentrate on the process of drop formation in microdevices, which has been used for generating uniform emulsions of Newtonian and non-Newtonian fluids, with an emphasis on the effects of fluid rheology. The bulk rheology and interfacial motion are described in a phase-field framework [2], and the numerical solution uses a finite-element algorithm with adaptive meshing to ensure proper resolution of the interfaces. We will present simulations of drop formation at the tip of a jet either within a quiescent medium or inside a flow-focusing device as demonstrated in recent experiments [1,3]. The rheology of the components may be Newtonian, viscoelastic or liquid-crystalline, with the Oldroyd-B and Leslie-Ericksen models being used for the latter. Results show that component rheology is a major determinant in the morphology of the jet, the details of the breakup process, and the size distribution of drops. The solutions compare favorably with experiments.


Effects of fluid elasticity on the dynamics of drop formation in microchannel flows

Joerska Husny and Justin J. Cooper-White

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The development of microfluidic systems which allow for the creation of micro and nano-drops inside microfluidic devices has received significant attention in recent years, due largely to foreseen applications of this technology in microreactor designs and in high accuracy drug and DNA delivery. Thorough understanding of the dynamics of monodisperse micro or nano-drops in microfluidic channels is thus essential to ensure that drops can be created based on any specific requirements, such as drop size, patterns and productivity. In this paper, we present a systematic comparative study of Newtonian and elastic fluids flowing in T-shaped (cross flow) drop formation microfluidic devices over a range of Capillary numbers (3x10⁻³ < Ca < 3x10⁻²), viscosity ratios (2 < η(continuous)/η((disperse) < 50) and polymer relaxation times (5x10⁻² < λ < 1x10⁻³). Dilute (c/c* ~ 0.5) aqueous solutions of Polyethylene Oxide (PEO) of various molecular weights (3x10⁶ to 2x10⁶ g/mol) were used as the drop phase fluid whilst silicone oils (5 mPa.s - 50 mPa.s) were used as the continuous phase fluid. The obvious presence of the filament during the drop detachment process of the elastic fluids over the Newtonian counterpart shows that fluid elasticity plays an important role in resisting drop pinch-off. The primary drop size was a discrete function of cross flow rate, elasticity and viscosity ratio. There were two distinct regions of necking observed for highly elastic fluids of viscosities approaching that of water, and the presence of each region are cross flowrate and molecular weight dependent. The presence of elasticity presents a significant problem when attempting to manufacture monodisperse drops from these fluids, with increased elasticity resulting in reductions in primary drop size, and increasing numbers of smaller secondary drops. We conclude by presenting a novel one dimensional model to predict the primary drop size as a function of Capillary number and device geometry.
Wednesday Afternoon

Wednesday  4:25  Salon 3  MR12

Wall effects on drop deformation under simple shear flow
Vincenzo Sibillo\textsuperscript{1}, Gilberto Pasquariello\textsuperscript{2}, Marino Simeone\textsuperscript{1}, and Stefano Guido\textsuperscript{1}

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The deformation of droplets in microchannels has recently received much attention in the literature, especially in view of the possible microfluidic applications. In such confined geometries, wall effects play a significant role on flow-induced drop deformation. In this work, the deformation of a drop undergoing shear flow in a translating parallel plate device is investigated. Wall effects become significant when the gap between the plates is less than two times the drop diameter. In such conditions, at a given value of the capillary number stationary drop deformation and orientation along flow direction increases by lowering the gap. Furthermore, complex start-up transients are observed, with the presence of overshoots and undershoots in drop deformation and a progressive slowing down of the kinetics towards stationary conditions with lower gap values. Drop breakup is also inhibited by the presence of the walls, which tend to stabilize drop shape. The above mentioned data are discussed and compared to results from the literature.

Wednesday  4:50  Salon 3  MR13

Formation of microspheres using a heat sensitive gel in a microfluidic device
Gordon Christopher and Shelley Anna

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Recent advances in microfluidic technology have moved past miniaturization of chemical assays to explore synthesis of microstructured materials. We present a microfluidic method of synthesizing microspheres using agarose, a heat sensitive gel commonly used as a platform for biomolecular separations and cell cultures. Our microdevice consists of a simple T-shaped junction molded into PDMS using standard soft lithography methods. The fluid channels lie above an aluminum four probe heater, which has been deposited onto a glass slide that forms one wall of the channel. Using the heater, a solution of agarose powder and water is melted into a sol as it flows toward the T-junction, where a second immiscible liquid shears the sol off into droplets. The sol droplets are passively cooled into a gel as they flow through the channels. This system allows for \textit{in-situ} creation of monodisperse droplets and control of their temperature.

Agarose exhibits a very pronounced hysteresis: the gel melts at 90 degrees Celsius, but the sol does not gel until 35 degrees. Furthermore, the final morphology and strength of the gel is highly dependent upon the cooling rate in comparison to the rates of phase separation, conformation changes, and crosslinking occurring within the sol. The fast quench rate of the sol in our device enables us to explore the relative importance of these processes on the final properties of the gel at very fast timescales, which to our knowledge has not been studied previously.

The ability to form gel beads of well-controlled size has potential for application toward the design of new protein and DNA assays, drug delivery vehicles, and other biotechnology applications. Work is ongoing to characterize the mechanical properties of the resulting particles and to quantify the particle size resulting from the applied liquid flow rates.

Wednesday  5:15  Salon 3  MR14

Surfactant effects on highly nonequilibrium surfaces: Surfactants and drop detachment
Fang Jin\textsuperscript{1}, Nivedita Gupta\textsuperscript{2}, and Kathleen J. Stebe\textsuperscript{1}

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When a viscous drop is injected into a viscous fluid, the drop evolves to form a distended shape that detaches via the rapid formation and pinching of a neck. We study how this process is altered by the presence of surfactant numerically. When surfactant adsorption-desorption is very slow, interfaces dilute significantly during drop expansion, and drops form necks which are only slightly perturbed in their dynamics from the surfactant-free case. When adsorption-desorption dynamics are comparable to the rate of expansion, drops break at the primary neck at low surfactant coverage, at a secondary neck at moderate coverages, or fail to neck at elevated coverages. When surfactant adsorption-desorption kinetics are rapid, the surface remains in equilibrium with the surrounding solution, and drops break like surfactant-free drops with a uniform surface tension. These arguments are used to construct a phase diagram of drop break-up modes as a function of surfactant sorption dynamics.
Thursday Morning

Symposium MR
Microrheometry and Microfluidics
Organizers: Pat Doyle and Anubhav Tripathi

Thursday 8:05 Oak 1 & 2  MR15
Inertio-elastic phenomena in complex flows through microfluidic devices
Lucy E. Rodd¹, Justin J. Cooper-White¹, David V. Boger³, and Gareth H. McKinley³
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We explore the effects of fluid inertia and elasticity on the flow of dilute polyethylene oxide (PEO) solutions through micro-fabricated abrupt planar contraction geometries. By varying the ratio of glycerol to water to tune the background solvent viscosity we are able to systematically vary the relative contributions of fluid inertia and fluid elasticity for dilute polymer solutions with a constant PEO concentration ($c = 0.87c^*$). The high strain rates achievable in micro-scale contraction geometries makes it possible to generate very high Deborah number flows (0 < De < 400), while maintaining moderate Reynolds numbers (0 < Re < 60). This enables us to access an expansive region of De-Re operating space, and is only achievable in micro-scale geometries. Micro-particle image velocimetry (microPIV) and epifluorescent streak photography are used to quantify the onset of elastic effects in the contraction region. We are also able to quantify the time-dependent kinematics of inertio-elastic flow instabilities as well as the growth and evolution of elastic corner vortices. We show that the elastic vortex growth observed upstream of the contraction in planar geometries relies on the synergistic interaction of both inertial and elastic effects; for a given Deborah number, the size of the vortex is substantially reduced as the Reynolds number tends to zero. This observation helps rationalize the heretofore puzzling lack of any substantial elastic vortex growth observed in macro-scale planar contraction flows of Boger fluids. Each of the observed flow structures are categorized into a number of flow regimes, which can be precisely located in De-Re space. We are able to quantify the shape of the boundaries between each of these regimes and their dependence on the elasticity number. Such results are relevant to "lab-on-a-chip" and inkjet printing applications, in which the flow geometry, length scale and fluid rheology are comparable to those used in the current experiments.

Thursday 8:30 Oak 1 & 2  MR16
Flow and confinement effects on the evolution of surfactant mesophases
Matthew Kerby¹, Arijit Bose², Anubhav Tripathi¹, and Jinkee Lee¹
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A microfluidic platform is used to examine evolution of surfactant aggregate microstructures in highly constrained domains. Surface effects dominate because of the high area/volume ratio in these channels, and because of the proximity of boundaries, steric constraints and boundary chemistry impact both the range of available morphologies as well as the dynamics of aggregate formation. The small liquid volumes and precise metering, the ability to control domain dimensions that can vary from several orders of magnitude greater than the aggregate size to the order of the aggregate size, and in-line optical imaging and spectroscopy permits rapid evaluation of kinetics, morphology and phase behavior. The micelle-to-vesicle transition in aqueous solutions of sodium octyl sulfate (SOS) and cetyl trimethyl ammonium bromide (CTAB) are explored using a probe fluorophore to track microstructure changes and turbidity to monitor size changes. Our results will focus on the differences in aggregation and flow behavior between bulk and confined systems.

Thursday 8:55 Oak 1 & 2  MR17
Morphological dynamics of salt-responsive block copolypeptide hydrogels
Jun Sato and Victor Breedveld
School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100

Stimuli-responsive hydrogels are of great interest for diverse applications in the fields of drug delivery, tissue engineering, cosmetics, and even gene therapy, due to their unique responses of structure and rheology to external stimuli, such as pH and solvent composition. Understanding the dynamic response of the hydrogels to these external stimuli is crucial for fine-tuning the gel properties.

We have studied block copolypeptide (BCP) hydrogels which possess a variety of tunable parameters: block architecture (di-block, tri-block), molecular weight, and amino acid composition of the individual blocks. We previously reported that BCP hydrogel rheology is sensitive to the addition of salt. In this study, we aim to investigate the response of the self-assembled local structure and local mechanical properties of the BCP gels to changes in ionic strength.
Particle tracking microrheology was performed in a microscopic dialysis cell, which enables non-invasive manipulation of the solvent composition in non-crosslinked hydrogel samples. We selected K160L40 (diblock copolypeptide of 160 mers of L-Lysine (K) and 40 mers of L-Leucine (L)); in the rheometer, hydrogels of this BCP become weaker upon the addition of NaCl. Microrheology provided a much more complete picture, revealing the occurrence of microscopic phase separation upon the addition of salt. In DI water, the motion of tracer particles in the hydrogel was homogeneous. After the addition of salt, microrheology revealed the co-existence of a population of freely moving particles and a population of immobilized particles. It was also observed that the changes in local microstructure are reversible when the ionic strength of the solution is lowered. Results will be presented on the structure and dynamics of these morphological changes.

**Thursday 9:20 Oak 1 & 2**  
**Quantitative prediction of experimentally observed radial migration of DNA in micro-capillary flows**  
**Jeffrey Sugarman**

Polymer motion influenced by confinement and interactions with boundaries has been a long-standing problem with few direct measurements and fewer fundamental models that predict the effects. Recent large-scale simulations permit the prediction of forces that drive molecules away from the wall. These forces arise from anisotropic hydrodynamic interactions between the polymer chain elements and the wall. Most experiments on confinement and wall effects have been accomplished in channels where the chain (DNA) is strongly confined; that is, the wall separations is smaller than the radius of gyration of the chain. For chains in larger channels the measurement of average chain velocity versus the fluid average velocity provides a way of indirectly measuring radial forces on the chain. Experiments using 20 micron capillaries and lambda-DNA show strong segregation to the center of the channel. The average DNA velocity becomes very nearly twice the average fluid dispersion of the peak demonstrate consistence of the data with a radially directed force. The molecular dynamics simulations, with velocity - indicating centering of the DNA along the centerline - for De >> 1. A theory developed by Lightfoot shows that the peak velocity and separation is smaller than the radius of gyration of the chain. For chains in larger channels the measurement of average chain velocity versus the fluid average velocity provides a way of indirectly measuring radial forces on the chain. Experiments using 20 micron capillaries and lambda-DNA show strong segregation to the center of the channel. The average DNA velocity becomes very nearly twice the average fluid velocity - indicating centering of the DNA along the centerline - for De >> 1. A theory developed by Lightfoot shows that the peak velocity and dispersion of the peak demonstrate consistence of the data with a radially directed force. The molecular dynamics simulations, with independently determined model parameters, shows quantitative agreement between the simulations and data.

**Thursday 10:35 Oak 1 & 2**  
**Drug reduction and micro-PIV measurements of the flow past ultrahydrophobic surfaces**  
**Jia Ou and Jonathan P. Rothstein**

In devices where the fluid flow is laminar, there are currently no methods for reducing drag. We will present a series of experiments which study in detail the flow kinematics of water past hydrophobic surfaces with well-defined micron-sized surface roughness. These ‘ultrahydrophobic’ surfaces are fabricated from silicon wafers using photolithography and are designed to incorporate precise patterns micron-sized ridges and posts aligned in the flow direction. These micro-features are made hydrophobic through a chemical reaction with an organosilane resulting in contact angles greater than 150 degrees. An experimental flow cell is used to measure the pressure drop and the velocity profile as a function of the flow rate for a series of rectangular cross-section microchannel geometries and ultrahydrophobic surface designs. Pressure drop reductions up to 40% are obtained using these ultrahydrophobic surfaces. A physical model will be presented which explains the drag reduction in terms of a shear-free air-water interface between microposts supported by surface tension. Confirmation of the model will be presented with optical measurements of the displacement of the air-water interface under flow. The velocity profile across the microchannel is determined through micro particle image velocimetry (μ-PIV) measurements. Slip velocities of nearly 50% of the average velocity are found at the center of the air-water interface supported by the hydrophobic microridges. The experimental pressure drop and velocity measurements are compared to numerical simulations and the predictions of analytical theory with good agreement.
Thursday  11:00  Oak 1 & 2  MR21
Microfluidic rheometry in complex fluids using flow-induced birefringence
Jai A. Pathak and Steven D. Hudson
Polymers Division, NIST, Gaithersburg, MD 20899-8544

The rheological characterization of complex fluids in micro-scale flows presents an important technical challenge. With a view to integrate synthesis of model polymers with their physical and rheological characterization on a lab-on-a-chip platform, we present quantitative measurements of flow-induced birefringence in complex fluids undergoing planar elongational flow (PEF), produced in microchannels that are micro-analogs of cross-slot flows. These channels are produced by soft-lithography using standard photoresists, and have small (0.5 aspect ratios) (height/width). PEF flow kinematics is verified by micro-particle imaging velocimetry (μ-PIV), and near the mid-plane the three-dimensional flow closely approximates PEF. We carefully apply the stress-optical rule and use birefringence data to measure the rheology of wormlike micellar surfactant solutions of CTAB and sodium salicylate undergoing PEF.

Thursday  11:25  Oak 1 & 2  MR22
Micro-flow in microcapillary films
Bart Hallmark, Christian Hornung, Malcolm R. Mackley, and Tri R. Tuladhar
Department of Chemical Engineering, University of Cambridge, Cambridge, Cambridegshire CB23RA, United Kingdom

This paper describes three different micro-scale flow phenomena through a novel polymer product. The product, termed a micro capillary film or MCF, consists of an extruded flexible film containing parallel, continuous, hollow microcapillaries running along its length. The MCF product and its manufacturing process have already been described (Hallmark et al. 2005a and Hallmark et al. 2005b).

The final physical properties of the MCF depend on the rheology of the polymer melt. MCF has been produced from a polyolefin exhibiting a degree of elasticity at low strain rates (Dow Affinity PL-880) and experiments have shown that the resultant MCF product is effective as a micro-scale peristalsis tube in a peristaltic pump.

One of the proposed application areas for MCFs is in the manufacture of thin-film heat exchangers. The effect of the heat-transfer fluid rheology flowing through the MCF on its behaviour as a heat-transfer device is examined, and initial experimental results and modelling is presented to compare and contrast Newtonian and shear-thinning theromofuids.

Furthermore, the capillary diameters within MCFs have been found to be suitable for capillary rheometry. Initial experimental results are described where low-viscosity fluids have been characterised by using MCFs as the working section within a novel twin-piston rheometer, the MultiPass Rheometer (Mackley et al., 1995).

REFERENCES

Thursday  11:50  Oak 1 & 2  MR23
Visco-thermal instabilities in microchannels and a novel micromixing concept based on thermally responsive polymer solutions
Boris Stoeber1, Dorian Liepmann2, and Susan J. Muller3
1Departments of Mechanical Engineering and Electrical and Com, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada; 2Department of Bioengineering, University of California, Berkeley, CA 94720-1762; 3Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462

Aqueous solutions of Pluronics, which are (polyethylene oxide)-(polypropylene oxide)-(polyethylene oxide), triblock copolymers, undergo gelation at elevated temperatures. This reversible phase change has promise for various microflow control applications. Rheological characterization of these materials reveals their thermo-thickening and shear-thinning behavior.

At ambient temperatures close to the phase transition viscous heating within the fluid can lead to flow unsteadiness. It can cause gel formation along the channel walls either in a periodic manner or until the entire channel is pinched off. When the solution temperature of pressure driven flow is slightly higher than the gel temperature, the Pluronic solution will behave as a highly viscous non-Newtonian liquid. Flow velocity fluctuations develop at increased temperatures. In this flow regime flow instabilities might result from the competing mechanisms of shear-thinning and thermo-thickening of the solution.

Rapid heating of a Pluronic solution from below the gel temperature to far above results in fast gelation of the material. This effect can be used to build a fast microfluidic valve with integrated electric heaters in a microchannel because heat transfer occurs rapidly across the small channel dimension. Local heating of the fluid results in gel formation and subsequent channel blockage within less than 33 ms as shown previously. A novel laminar mixing concept employs such active valves that are placed in specific locations in a microchannel system. Cyclic actuation of these valves results in periodic flow redirection in the channel system leading to substantial stretching and folding of the fluid layers. Mixing occurs rapidly and effectively through diffusion across the resulting thin layers.
Effects of anionic and cationic surfactants on the sol-gel transition of methylcellulose in water

Lin Li and Qiqiang Wang

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Methylcellulose (MC) is able to form a thermoreversable hydrogel in water, depending on temperature. When the solubility of MC or the hydrophobicity of a solvent (e.g. water) is modified by an additive such as a salt or a surfactant, the sol-gel transition of MC is expected to change. It has been found that there are notable effects of various salts on the sol-gel transition of aqueous MC solutions [1,2]. However, there is lack of understanding of the effects of anionic and cationic surfactants on the sol-gel transition of MC in aqueous solution. It is expected that when surfactant molecules are bound to polymer chains to form associated structures with polymer, the gelation behavior and rheological properties of MC aqueous solutions will be varied significantly. In this work, we have studied the effects of one anionic surfactant (SDS) and one cationic surfactant (CTAB) on the sol-gel transition of aqueous MC solutions by means of micro differential scanning calorimetry (micro DSC) and rheology. When the surfactant concentration is lower than its critical micellization concentration (CMC), the salt-out like effect is observed. On the other hand, when the surfactant concentration is higher than CMC, the salt-in like effect is shown. The rheological results prove that the G' and G'' crossover point is consistent with the onset of the endothermic peak but the significant formation of the gel network occurs beyond the crossover point or around the endothermic peak temperature. The mechanisms and microstructures included in the unique thermal and rheological properties will be proposed and discussed.


Reversible thermal gelling of crosslinked polymers in organic fluids

Gerald H. Ling1 and Montgomery T. Shaw2

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The rheological properties, particularly steady and dynamic viscosities of polymer systems show varying behavior with temperature. Typically, however, the viscosities of most non-aqueous polymer systems including melts, solutions, and suspensions decrease with increasing temperature. Although many polymer solutions gel on cooling, there are only rare cases where a non-aqueous system forms physical gels on heating. Often this process is irreversible, implying a metastable fluid state before the gelation temperature was reached. We have hypothesized that reversible gelation might be achieved by exploiting a first-order phase transition that permits or encourages organization of particle suspensions. Some indication was found several years ago that this behavior occurs for suspensions of micron-size crosslinked poly(ethylene) (XLPE) suspended in squalane. Reported here is a detailed investigation of this phenomenon using a variety of systems including the above-mentioned XLPE-squalane suspension and crosslinked polystyrene particles in a dibutyl phthalate suspension. The subject suspensions were characterized using a variety of methods including rheological, rheo-optical and thermal analysis tests. Preliminary results on a 10 wt% XLPE-squalane system indicate that the suspension undergoes thermal thinning up to the onset of gelation at which point, the steady shear viscosity spikes over a decade in magnitude from 0.02 Pa s to 0.37 Pa s at c.a. 110 °C. The abrupt gelling mechanism is hypothetically attributed to the formation of clusters causing a jamming of the swollen interpenetrating globules triggered by the melting of XLPE particles. Attempts to achieve the same behavior using liquid-liquid transitions were largely unsuccessful.

Effects of halogen benzoate counterions on drag reduction, rheological properties and micelle microstructures of cationic surfactant solutions

Wu Ge1, Ying Zhang1, Judith Schmidt2, Ellina Kesslerman2, Yeshayahu Talmon2, and Jacques L. Zakin1

1Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH; 2Chemical Engineering, Technion-Israel Institute of Technology, Haifa, Israel

The influence of halogen counterions on the drag reduction (DR), viscoelasticity and dynamic properties of micellar solutions of a cationic surfactant, cetyltrimethylammonium chloride (CTAC) was investigated. Zeta potential, static and dynamic light scattering and cryo-TEM imaging were used to characterize the microstructures of micelles. Their DR properties were also studied. The counterions used were para substituted F-, Cl-, Br- and I- benzoate which were compared with sodium salicylate (NaSal). The presence of organic counterions leads to micelle growth in CTAC solutions with an increase in viscoelasticity and a decrease in the micellar surface potential. Different halogen benzoate counterions have dramatic effects on the microscopic features of micelles in CTAC solutions. The measured zeta potential of CTAC/F- benzolate micelles decreased with increasing counterion to surfactant molar ratio (Cc/Cs) and equilibrated at a positive value at a Cc/Cs ~4. Cl-, Br- and I-
benzoate counterions in the 5mM CTAC solution resulted in charge reversal on the micelle surface at Cc/Cs of about 2, 3.3 and 5, respectively, with the zeta potential approaching to equilibrium values at Cc/Cs =8. At the same Cc/Cs, zeta potential of these micellar solutions decreased in the order of Hofmeister series, F- < Cl- < Br- < I-. The influence of counterions on micelle morphology and DR may be rationalized in terms of the degree of hydration and the polarizability of the halides.

Thursday 9:20 Salon 1 SC46

**Behavior of polymer modified asphalt in steady state shearing**

Zora Vlachovicova, Jiri Stastna, and Ludo Zanzotto
Bituminous materials chair, University of Calgary, Calgary, Alberta T2N1N4, Canada

Conventional asphalt is a complex organic material with large number of constituents and various molecular associations. Macroscopically it is a homogeneous material with linear viscoelastic behavior in small deformation (or stress) fields. In attempts to improve engineering properties of conventional asphalt they are frequently blended with small amounts of various polymers. Such blends can have very different rheological properties from those of the base (conventional) asphalt. Two types of polymer modified asphalt (PMA) are discussed, here. The first one is a blend of a soft asphalt with styrene-butadiene-styrene (SBS) copolymer and the second one is a blend of the same base with ethylene-vinyl acetate (EVA) copolymer. The above mentioned PMAs were prepared in several concentrations (from 2% to 8% by weight) of the respective polymer. All the tested materials were characterized in linear viscoelastic region by their relaxation spectra (small amplitude oscillations).

Steady state shearing of the studied PMAs revealed an interesting behavior of the shear viscosity function. The base asphalt has a constant viscosity over the wide domain of shear rates. For blends with 4%, 6% and 8% of the polymer the shear viscosity function exhibits a typical non-Newtonian behavior at most of the tested temperatures (40°C - 90°C) however, at some temperatures (depending on the type of polymer and its concentration) the shape of viscosity function was changed unexpectedly. In these cases, the low shear rate plateau is followed first by shear thinning, then another plateau appears and it is followed by the final shear thinning part. In some blends with SBS there appears to be also a small maximum ("overshoot") between the first two regions. When the temperature is lowered or increased the regular non-Newtonian behavior reappears. A possible simulation of this type of behavior by nonlinear generalization of the rubber like liquid model and comparison with other systems exhibiting similar behavior will be discussed.

**Symposium BS**

**Rheology of Biomaterials and Biological Systems**

Organizers: Denis Wirtz and Kate Stebe

Thursday 10:10 Salon 1 BS15

**Environmentally responsive hydrogels with tunable rigidity and constructed via peptide folding and consequent self-assembly**

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By using peptidic molecules in the materials self-assembly design process, one can take advantage of inherent biomolecular attributes, intramolecular folding events and secondary structure, in addition to more traditional self-assembling molecular attributes such as amphiphilicity, to define hierarchical material structure and consequent properties. Intramolecular folding events impart a molecular-level mechanism for environmental responsiveness at the material level (e.g. infinite change in viscosity of a solution to a gel with changes in pH, ionic strength, temperature). Design strategies based on small (less than 24 amino acids) beta-hairpin peptides will be discussed. The self-assembly process is predicated on the peptides first intramolecularly folding into the beta-hairpin conformation from a random coil conformation. Importantly, the scaffold assembly can be reversible with pH or temperature by reversibly folding and unfolding the constituent peptides that, in turn, assembles or disassembles the scaffold. In addition, the rigidity of the gel scaffold can be tuned via the magnitude of the environmental stimuli, e.g. gels triggered with temperature form a more rigid network when assembled at higher temperatures due to faster folding and self-assembly kinetics. Local hydrogel structure, both fibrillar struts and crosslink points, can be altered by changing peptide length. Finally, the hydrogel networks are also mechanically responsive in that they can almost immediately re heal into a rigid material after shear thinning due to the self-assembled nature of the underlying network. The molecular design and self-assembly principles, including a model to explain the inherent tunability of the final gel networks that underlie the observed morphological and rheological material, will be presented. Laser scanning confocal microscopy, cryo transmission electron microscopy, oscillatory rheology, small-angle neutron scattering, spectroscopy, and cytotoxicity results will be presented.
Tunable hydrogels from PLA-PEO-PLA triblocks: Effect of crystallinity of the PLA block

Sarvesh K. Agrawal1, Naomi Sanabria-Delong2, Gregory N. Tew2, and Surita R. Bhatia1
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We present rheology and structural characterization (WAXD and SANS) of gels formed from poly(lactic acid)-poly(ethylene oxide)-poly(lactic acid) (PLA-PEO-PLA) triblocks. These materials are biocompatible and are of interest for several applications in tissue engineering and drug delivery, yet their detailed rheological properties have remained largely unexplored. In aqueous solutions, these polymers form associative micellar gels analogous to those formed by hydrophobically-modified telechelic polymers, with the PLA domains serving as the junction points. We show that polymers containing only L-lactide (PLLA) have PLA domains that are crystalline. These crystalline junction points lead to gels with elastic moduli of ~10 kPa, roughly an order of magnitude larger than had been previously observed with PLA-based associative gels. These elastic moduli are also in the range of several soft tissues, making these materials excellent candidates for cartilage and soft tissue repair. Copolymers containing a racemic mixture of D-lactide and L-lactide (PRLA) form amorphous PLA domains, leading to gels with elastic moduli that are several orders of magnitude lower than the corresponding PLLA copolymers. In addition, the viscoelastic moduli of the PRLA copolymers are frequency-dependent, with a crossover frequency that is within the range measurable by mechanical rheometry. We believe this corresponds to the characteristic time for exchange of PLA endblocks between micelles. By contrast, the PLLA gels have an elastic modulus that is nearly independent of frequency, indicating either a very slow or nonexistent PLA exchange time.

Gelation kinetics of alginate hydrogels: Effects of PEG crosslinker concentration, arm length and arm number

Helena Hadisaputra1, Andrea J. O'Connor2, and Justin J. Cooper-White1
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Synthetic hydrogels have been proposed by many researchers as viable scaffolding candidates for tissue engineering applications. In this study, an often-used biopolymer (alginate) is chemically cross-linked with polyethylene glycol (PEG). The gelation kinetics of this hydrogel system as a function of temperature, cross-linker concentration and cross-linker architecture have been investigated using small amplitude oscillatory shear. The effects of these variables on the gel point and final shear modulus of the gels are detailed. The average pore sizes of the hydrogels (inspected using CryoSEM and proton NMR) are shown to display a highly nonlinear relationship with cross-linker concentration. Counter intuitively, at least within a rubber elasticity framework, the largest pore sizes were observed in the alginate-PEG hydrogels which recorded the highest recorded shear modulus. This outcome suggests that molecular interactions within the 'walls' of the individual pores dominate over the resident macroporous structure of these particular hydrogels. We conclude by presenting possible reasoning behind this structure - function anomaly.

Phase transition of cellulosic biopolymer solutions

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Dipartimento di Ingegneria Chimica, Università di Napoli "Federico II", Napoli 80125, Italy

Aqueous solutions of some cellulosic biopolymers, such as HydroxyPropylCellulose (HPC), form reversible gels upon heating. The phase transition is due to temperature dependent changes in the quality of polymer-solvent interactions and takes place around the human body temperature. This interesting feature of HPC solutions, along with their well-known biocompatibility, makes the system attractive as an injectable drug delivery matrix. In this work, the thermogelation of aqueous HPC solutions is investigated by means of Dynamic Mechanical Spectroscopy in the linear viscoelastic range. Under both heating and cooling temperature ramps the viscoelastic moduli display a non monotonic trend. In particular, upon rising temperature, storage and loss moduli first show a sharp reduction, followed by the expected increase caused by network formation. This particular behavior is related to the occurrence of HPC precipitation before the gelation. Different experimental evidences are presented to support this double-step phase transition mechanism. Crucial parameter of this process is the temperature window where the thermogelation takes place. The possibility of modulating the phase transition temperatures upon changing chemical-physical parameters, such as HPC Molecular Weight and ionic strength of the aqueous solution, are presented and discussed.
The mechanical behavior of the flowing liquid was described by the Generalized Newtonian Liquid model in conjunction with a viscosity function. The influence on final property of thin-walled articles produced by thermoforming (such as wall thickness variations, physical instability during inflation-shrinkage and warpage exhibited in the final part) was studied. This process suggested a rheological model in this paper not only solves some structural plastics for usage in high temperature conditions. We determined a quantity relation between stress and technical parameters of plug-assisted stretching polymeric preform. Analysis of these equations shows, that mechanical pre-stretching with plug causes a non-homogeneity and a non-stationary deformation effect on polymer. We determined a quantity relation between stress and technical parameters of plug-assisted thermoforming process and also made comparison of theoretical and experimental results. These results let us predict stable sizes of final structural plastics for usage of them in high temperature conditions. We realized that deformation process in stage of plug-assisted has a direct influence on final property of thin walled articles produced by thermoforming (such as wall thickness variations, physical instability during inflation-shrinkage and warpage exhibited in the final part). This process with suggested rheological model in this paper not only solves some kinds of technical defects (wall thickness variations, shrinkage and rupture of sheet) during thermoforming process, but also creates conditions for production of plastics with high performance.

Symposium SS
Viscoelasticity and Viscoelasticity of Solids and Semi-Solids
Organizers: Ian Frigaard and Gregory B. McKenna

Thursday 8:05 Salon 2 SS24
Gas displacement of viscoplastic liquids in capillaries
Paulo R. Souza Mendes, José R. Siffert, Eduardo S. Dutra, and Monica F. Naccache
Department of Mechanical Engineering, Pontificia Universidade Catolica -RJ, Rio de Janeiro, Rio de Janeiro 22453-900, Brazil

The displacement by gas of viscoplastic liquids in a tube is studied. Potential applications are the displacement of heavy oils in reservoirs and a wide variety of industrial process flows involving viscoplastic liquids. The existence of yield stress alters the stress/kinematics relationship and changes dramatically the amount of liquid left attached to the capillary wall as compared to the Newtonian case, studied by Taylor in 1960. The mechanical behavior of the flowing liquid was described by the Generalized Newtonian Liquid model in conjunction with a viscosity function proposed by Souza Mendes and Dutra in 2004. This constitutive equation, together with the momentum and continuity equations, were solved numerically via a finite-volume method for the two-dimensional free surface flow near the gas-liquid interface. Visualization experiments with Carbopol aqueous solutions were also performed for wide range of the capillary and jump numbers. The numerical predictions and the experimental visualizations were found to be in good agreement. The results show the effect of viscoplastic character of the liquid on the free surface shape and the film thickness attached to the capillary wall. It is observed that there is a critical capillary number value below which the displacement is perfect, i.e. there is no liquid film left attached to the wall. The relationship between this critical value and yield stress is explained. Beyond this threshold value of the capillary number, the film thickness decreases as the jump number is increased.

Thursday 8:30 Salon 2 SS25
Measuring dough extension and memory
Sumana Chakrabarti1, Eric Lindskog2, Greg Swanson2, and Tam Sridhar3
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Bread dough is an important material for the food and agricultural industries world-wide. In the industry, the qualities of wheat, flour and dough mix formulations are assessed using empirical measures for dough extensibility and dough elasticity. Although significant progress has recently been made in measuring dough extension rheologically, the results have not fully related to industry's experiences of dough behaviors or to product & process performances. We undertook the task of determining true material properties of dough in extension and in the process identified a range of variables that affected test results and explained some of the perceptions about dough. The uniformity of rate of stretch had a bigger impact on dough extension than the rate of stretch. The factors affecting uniformity included the test method, sample loading procedure and specimen shapes. Much of the perceptions of dough behavior had originated from tests not performed at constant stretch rates. Our work encompassed testing with a commercially available material tester as well as a home-built dough extension rheometer (the LDER, Lindskog's Dough Extensional Rheometer, named after one of the authors). The latter was built following the principles of the filament stretching device per Tirtaatmajda and Sridhar (1). The 2-way stretch with a constant mid-point was not sufficient in providing consistent data, as sample preparation techniques needed to be controlled. We believe we now have a method for obtaining consistent and definitive data for stress-strain-rate behaviors of doughs in uni-axial extension. Dough mixes have been characterized through loading and unloading tests performed at various rates. The development of this apparatus, lessons learnt for dough as a material along with data for stress-strain-rate and recovery functions of doughs will be presented.

Mechanism of shear banding in entangled micellar solutions
Yuntao T. Hu
Unilever, Trumbull, CT 06611

The mechanism of shear banding in an entangled micellar solution is investigated using a combination of spatial and time-resolved particle tracking velocimetry, microscopic visualization, and small angle light scattering (SALS). We observe two stages of the shear banding process: 1) Shear rate tilting: During this stage, the local shear rate increases towards the inner side and decreasing towards the outer side; 2) Shear banding: When shear rate at the outer surface reaches a lower boundary $1/\tau$, where $\tau$ is the terminal stress relaxation time, a low shear band becomes discernible and expands towards the inner surface. The tilting is found to be generic for entangled polymer and micellar solutions with or without showing shear banding. The effective lifetime of the shear bands is the same as the chain re-entanglement time. We propose that the tilting and subsequent banding is caused by chain disentanglement coupled with the local shear rate. Visualization and SALS suggests the low shear band consists of homogeneous micellar entanglements whereas the high shear band consist of micellar chains of various degrees of disentanglement. The interface between the low and high shear band is not stationary and the shear rate appears to be continuous across the interface most of the time. A constitutive curve is constructed from the local shear rate and stress.

Constitutive modeling of the linear and nonlinear rheology of flour-water doughs and other complex entangled materials
Shen-Kuan T. Ng¹, Mahesh Padmanabhan², and Gareth H. McKinley¹
¹Dept. Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139; ²Basic Sciences, Kraft Foods, Glenview, IL 60025

We perform small amplitude oscillatory tests on model flour-water doughs that have been shear-mixed in an instrumented mixograph for varying length of time. We find that the linear viscoelastic properties exhibit a broad power-law dependence on the imposed oscillatory frequency that is very reminiscent of that exhibited by a critical gel. We use the critical gel model of Winter-Chambon (Winter and Chambon 1986; Chambon and Winter 1987) to construct a constitutive equation for the stress in the material by combining the relaxation modulus for the critical gel with a Lodge rubber-like liquid form for the kinematics. We compare the transient uniaxial extensional behavior recorded from filament stretching rheometry to the predictions of the resulting constitutive equation. The model captures the initial power-law response and subsequent strain-hardening; however additional physics is required to describe the phenomena at very large strains, including finite extensibility effects and filament rupture in extensional flows. A similar approach can be used to model the linear viscoelastic and transient extensional properties of other complex and highly-entangled materials such as ultra-high molecular weight polyethylene.

A new hybrid temperature control unit for polymer melts and semi-solids
Jint Nijman, Wolfgang Platzek, and Michael Feid
Thermo Electron (Karlsruhe) GmbH., Karlsruhe 76227, Germany

Thermo Electron recently announced the launch of its new HAAKE MARS rheometer. In this presentation we will present an entirely new, wide range, temperature control unit for measurements on polymer melts and semi-solids, which was especially designed for the HAAKE MARS rheometer. The unit consists of two "clam-shells" mounted on sliding rails which allows an easy movement of the "clam-shells" in two dimensions, sideways and backwards. When slid backwards completely, the unit can be closed with the temperature inside the unit kept at the desired temperature, while at the same time the sample fixtures are easily accessible. This hybrid temperature control unit ingeniously combines the advantages of radiant heat transfer (fast temperature changes) with those of convection heat transfer (uniform temperature distribution). The two heat transfer systems are controlled by a state of the art "model predictive" digital temperature control loop. With the optional nitrogen evaporator the temperature range reaches from -160 °C to + 600 °C. The maximum heating and cooling rates are 20 K/min. Due to the double walled, vacuum insulated tubing used for the nitrogen, the forming of ice on the outside of the unit is negligible. The entirely new solid clamping fixtures provide self-centering and automatic clamping force adaptation for the sample as well as a very simple semi-automatic gap adjustment for a wide range of sample thicknesses with just one fixture. In this presentation we will show the performance of the MARS rheometer in combination with the new temperature control unit and the new sample fixtures for polymer melts and semi-solids. We will show the results of the measurements on some typical and some less typical, rather interesting polymers.

The Society of Rheology 77th Annual Meeting, October 2005
Accessory for cone-plate rheometry of high vapor pressure solvent samples

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In general, complex fluids are multi-component systems, often in volatile solvents, e.g. water and toluene. For measuring samples with high vapor pressure solvents in a rheometer, the Couette geometry is often selected, because a layer of nonvolatile immiscible fluid can be placed on top of the sample to prevent evaporation. However, a much larger sample volume (several ml) is required as compared to cone plate and plate plate geometries (less than 1 ml), which is disadvantageous for precious samples.

For measuring dynamic rheological properties, oscillatory shear measurements are performed. During oscillatory experiments, the required time for sampling data is proportional to the inverse frequency. Therefore, measurements at low frequencies take a long time and, as a result, solvent evaporation is a major concern. At elevated temperatures, the evaporation of most solvents, even water, becomes very relevant.

We report on the design and implementation of a new rheometer accessory (evaporation blocker) for cone plate and plate plate geometries that minimizes sample evaporation. The underlying concept is to minimize evaporation by trapping the saturated vapor inside a sample chamber and minimizing sample evaporation. The underlying concept is to minimize evaporation by trapping the saturated vapor inside a sample chamber and

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by reducing the wall area on which condensation happens. The use of vapor locks has been explored before by rheometer manufacturers and academic researchers, but we found that the suppression of condensation was equally crucial through the elimination of "cold spots".

In a simple validation test, the viscosity of DI-water was monitored as a function of time at 40°C. The evaporation blocker dramatically decreased sample evaporation. Results of experiments on other complex fluids, in particular hydrogels and colloidal suspensions, will be discussed as well to demonstrate the effectiveness of the evaporation blocker. The accessory has enabled experiments on temperature-sensitive hydrogels that were previously impossible to perform and provide new insight into the molecular organization of these materials.

Thursday 8:30 Salon 3

**Creep and creep recovery measurements of polymer melts using a controlled stress rheometer with a magnetic levitation thrust bearing**

Aloyse J. Franck

*Application, TA Instruments, Alzenau, Bavaria 63755, Germany*

Creep recovery (recoil) experiments are very sensitive to the elastic deformation of polymer materials in the molten state. Creep measurements at low stress, followed by recovery, are performed to evaluate the effect of the structure upon the material's elasticity at long times. These results are then used to enhance the dynamic mechanical characterization at low frequency.

Recoil measurements provide a very sensitive means to determine the elasticity of a polymer melt. However, recoil measurements are difficult to perform and the results are dependent on the ability of the rheometer to eliminate parasitic torques during the measurement. The AR-G2 rheometer, due to its magnetic levitation thrust bearing, has a very low parasite stress level (approximately 1 mN.m). The recoverable deformation is therefore much less affected by residual torques and a more accurate and reliable total recovery can be obtained. In order to eliminate effects of the instrument inertia during the initial fast recoil phase of the recovery experiment, an active inertia control (AIC) feature has been implemented. The AIC stops the rotating cone at the end of the creep experiment instantly. As such, energy stored in the system during the creep phase does not disturb the recoil experiment.

Creep recovery experiments have been performed on a series of narrow distributed polystyrenes and commercial polyethylenes. The results of the recoil experiments are compared to data obtained from oscillation and normal stress growth experiments.

Thursday 8:55 Salon 3

**Transient phenomena in shear flow of polymer modified asphalts**

Chaminda Wekumbura, Ludo Zanzotto, and Jiří Štastná

*Bituminous Materials Chair, University of Calgary, Calgary, Alberta T2N 1N4, Canada*

Asphalt is one of the oldest construction materials. Typically it is used as a binder in the construction of pavements. Other applications include water proofing membranes and coatings. Rheological behaviour of asphalt resembles the one of low molecular weight polymers. With increasing traffic and loads on highways and air fields one can encounter nowadays binders which are blends of conventional asphalt and various polymers. These new materials exhibit highly viscoelastic behaviour and can not be classified in the same way as conventional asphalts. Moreover it is believed that in many distress modes asphalt can be exposed to large deformations or stresses. In this case the usual dynamic testing (small amplitude oscillations) is not able to characterize the behaviour of binders in pavements.

The stress growth in simple and exponential shear is discussed for the blends of a soft conventional asphalt with SBS and EVA copolymers. The interrupted shear flow of these blends is also studied. The destruction and reformation of internal structure is demonstrated for polymer modified asphalts. None of these effects were observed in conventional asphalts. Rubberlike liquid model, in Wagner's generalization, was used for the modelling of the observed effects. With a simple modification (each relaxation mode accompanied by its own damping function) a relatively small set of parameters is needed for the description of the observed phenomena.

Thursday 9:20 Salon 3

**A camera for viewing and image capture within a closed oven**

Bernard A. Costello, Nigel R. Doe, Peter W. Foster, and Raoul E. Smith

*TA Instruments Ltd., Crawley, West Sussex RH10 9NB, United Kingdom*

Rheologists are well aware that effects such as sample edge fracture, expulsion from the gap or buckling can produce erroneous experimental data. Although these effects can often be detected by simple visual inspection, this is not easily done within a closed heating chamber. Although some oven designs include viewing ports, these are usually of only marginal value. To provide a complete solution to the problem, TA Instruments have designed a camera that mounts within the wall of the Environmental Heating Chamber (ETC) of their AR-G2 rheometer, and can be used over the full temperature range of -150°C to 600°C. The camera is cooled by air passing through a jacket surrounding the lens mountings, and is both admitted and vented externally to the oven, so that there is no mixing of the cooling air and the ETC internal circulating gas. Primary illumination is through an LED array mounted on the camera; separate secondary illumination can also be used to improve the image definition. The camera is designed to provide a broad field of view and depth of focus, so that the sample centre and edges can be viewed simultaneously. It can easily be removed from the ETC for cleaning, and can be replaced by a plug.

The operation of the camera is entirely through the regular instrument software, which controls the focussing and illumination intensity. The output can be viewed as a streaming video within the instrument software status page or during the experiment, and an image can be captured with each data point. These can be viewed within the regular data analysis module, either individually or as pseudo playback. The same software
works with any USB camera so a webcam can easily be used with other heating systems. In this presentation we describe the ETC camera more fully, and show images of each of the effects mentioned above.

Thursday 10:10 Salon 3

**Transient rheology of a polypropylene melt reinforced with long and short glass fibers**  
*Donald G. Baird, Aaron Eberle, and Gregorio Velez*

Chemical Engineering, Virginia Tech, Blacksburg, VA 24061

In this paper we investigate the transient shear rheology of a polypropylene containing long fibers (initial lengths 6 to 11 mm and L/D > 150) and short fibers (initial lengths of 0.5 mm and L/D < 50). The objectives of this work are to determine the relation of stress growth and relaxation behavior to fiber orientation and interaction and matrix rheology and determine the feasibility of extending Doi’s theory for rod-like systems to these materials. A parallel plate rheometer was used as the gap size could be altered to assess the interaction of the fibers with the boundaries imposed by the test fixtures. Samples were prepared with different degrees of initial orientation including random, perpendicular, and parallel to the flow direction. The orientation of the fibers under start up and cessation of shear flow was assessed and compared to predictions of the theory. The interaction of the long fiber fibers with each other seems to require that an additional modification of the theory be used. It is also observed that the presence of the long fibers retards the relaxation processes leading to enhanced viscoelastic effects.

Thursday 10:35 Salon 3

**Determination of rheological parameters for the Doufas-McHugh FIC fiber spinning model**  
*Ae-Gyeong Cheong*

Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC 29634

The two-phase flow-induced crystallization (FIC) model of Doufas and McHugh is applied to one-dimensional fiber melt-spinning. The fiber spinning process is modeled from the point of maximum die-swell to the feed-roll. The amorphous phase is modeled as a viscoelastic fluid using a modified Giesekus constitutive equation with a temperature-dependent relaxation time and a constant shear modulus. Of particular interest is the determination of modeling parameters (e.g. viscosity, shear modulus, and relaxation times) based on curve fits to rheological data, and the sensitivity of the simulation to all input parameters. It will be shown that model predictions of axial velocity, diameter, and temperature along the spinline are in good quantitative agreement with on-line experimental data for PET and isotactic polypropylene generated at the Center for Advanced Engineering Fibers and Films. The effects of model parameters and processing conditions will also be discussed.

Thursday 11:00 Salon 3

**Evaluation of carbon black loading effects on rate constant and activation energy of SBR/BR vulcanization using rheology tests**  
*Massoud Ghasemzadeh Barvarz* and *Gholm Reza Bakhshandeh*

C.O.R&D, N.P.C.R&T/Tarbiat Modarres University, Tehran 14965/115, Iran

Effect of carbon black type and loading on kinetic parameters such as rate constant and activation energy of vulcanization were studied using special method by Rheometer and Rubber Process Analyzer (RPA) instruments for SBR/BR and SBR/NR blends. Then results were compared to each other. Overall rate of the vulcanization was SBR/BR < SBR/NR and its activation energy was SBR /BR > SBR /NR. Carbon black reduced activation energy and increased overall rate of the vulcanization in all blends. Effect of N330 in this reduction and increment was more than N660.

Thursday 11:25 Salon 3

**The effect of nanoclays on the processability of polyolefins**  
*Edward B. Muliawan, Nimish Rathod, and Savvas G. Hatzikiriakos*

Department of Chemical and Biological Engineering, The University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada

In the recent years, the use of nanoparticle has been a major area of research, especially in the area of polymer composites. The possibility of widening the usage of nanoparticles, specifically nanoclays as an aid in polymer processing is investigated. Different grades of nanoclays were tested using an Instron capillary rheometer. Standard capillary dies and a special annular die (Nokia Maillefer wire coating crosshead) were used to study the effect of nanoclays. The polymers tested were Ziegler Natta and metallocene polyethylenes and a polypropylene. It was found that the nanoclay additive had a significant effect on the extrudate appearance of the polymers. It eliminates surface melt fracture and postposes the critical shear rate for the onset of gross melt fracture to significantly higher values depending on resin type, temperature, and additive concentration (typically 0.05 to 0.5 wt %). Extensional rheological measurements were also carried out for the pure resins as well those loaded with the nanoclay additives to explain the possible mechanism for the effect of the additive on the processability of the resins. Finally, the synergistic effect of the combination of nanoclays and fluoroplastic was also investigated.
Reactive polymer fluid systems at high temperature gelation can be difficult systems to handle in conventional rheology measurements. In the presence of solvents and/or gases either contained in the formulation or formed in condensation reactions, such fluids are not readily conducive to routine gel point determinations using parallel plate or cone/plate geometries. The primary interest of our research involves such two or three phase fluid systems for gelation studies through the gel point, tan(δ)=1.0. Application can be extended to powder systems as well.

Gelation studies in conventional rheometry typically involve isothermal controlled stress or strain time sweeps measurements at a fixed frequency and amplitude. Additional measurements include thermal sweeps, under single dynamic conditions. In either case, fluid measurements which involve gas evolution can be difficult to run and quite tolling on instrumentation. Disposable plates are helpful in this venue, but the resins can easily coat tooling, ovens, mounts, etc, making such measurements not only questionably accurate but difficult to remove.

While these may be routine problems in R&D within the coatings industry, transitioning such methods to the manufacturing environment is not routine. In fact, devising automated QC rheology methods for these systems can be daunting. As a result, there are many types of subjective tests that are frequently devised and implemented, ranging from simple tube or spatula measurements or other manual mechanical evaluations as well as other test methods. The objective of our research has been to identify a rheology metric for both R&D and QC to measure the gel point of coatings in a simple format.
Investigation rheological properties of Fitofague's gelatin
Hedieh Alavi Talab
Faculty of Engineering, Azad University Branch of Science & Research, Tehran, Iran

In this study extraction of gelatin from skins and fins of Fitofague by two methods of acidic and alkaline were investigated and it compared with another sources. Results showed that rheological properties of Fitofague's alkaline gelatin is better than Fitofague's acidic gelatin.

Gelation point determination using fast Fourier transform rheometry
Jaepyoung Cho¹, Marie-Claude Heuzey¹, Andre Begin², and Pierre J. Carreau¹
¹CREPEC, Ecole Polytechnique de Montreal, Montreal, QC, Canada; ²Canada Food Research and Development Centre, St-Hyacinthe, QC, Canada

The physical heat-induced gelation of chitosan in an aqueous solution of glycerophosphate (GP) and acetic acid was investigated using rheometry. The chitosan used was a highly deacetylated (93%) high molecular weight (8.5E5 g/mol, PDI = 2.8) material. Before the gelation tests, the linear viscoelastic zone was determined in the sol state by strain sweeps at different frequencies between 0.3 and 5 Hz at 45°C. During the heat-induced gelation, the evolution of the rheological properties was monitored as a function of temperature. The measurements were carried out under various strains (0.01 - 0.3) and frequencies (0.3 - 5 Hz). The application of Fourier transform (FT) analysis during the temperature sweeps allowed us to follow changes in the first and third harmonics. The gel point, or gelation temperature ($T_{gel}$), was determined using three different criteria/methods: 1) the crossover point of $G'$ and $G''$, 2) the temperature at which tan of the loss angle is frequency-independent (Chambon & Winter (JOR, 1987, 31, 683)), and 3) the temperature at which we recorded a sudden increase in the intensities of the first and third harmonics. According to the first criterion, the gelation temperature was nearly independent of the strain in the range investigated, though the gelation kinetics were slightly higher at the highest strain. At the gelation point, $G'$ and $G''$ scaled with frequency, and the power-law exponent was 0.68 for this chitosan system, similar to the value predicted by the percolation theory (0.67). From FT rheology, we found that the intensities of the first and third harmonics increased noticeably past the gelation point. We compared the gelation temperatures according to each criteria/method. They were all very similar, but among them the highest one was obtained using the crossover point. FTR resulted in the lowest determined gelation temperature. It shows that FTR is very sensitive to changes in a material microstructure and can be used to detect the onset of pre-gels.

Hydrogels via beta-hairpin peptide self-assembly: Stiffening below a peptide fibril/ion complexation transition temperature
Bulent Ozbas¹, Karthikan Rajagopal², Joel P. Schneider², and Darrin J. Pochan¹
¹Materials Science and Engineering, University of Delaware, Newark, DE 19716; ²Chemistry and Biochemistry, University of Delaware, Newark, DE

We study de novo designed oligopeptides that intermolecularly self-assemble into rigid hydrogel networks after an intramolecular folding event. The peptides are locally amphiphilic with two linear strands of alternating valine and lysine amino acids flanking a central tetrapeptide turn sequence. The irreversible folding transition of the beta-hairpin molecule is around 25°C at pH 9. When the temperature is raised above the folding transition, the hydrophobic interactions dominate over the electrostatic repulsions between the lysine residues and the peptide arms are forced into a beta-sheet secondary structure by the turn sequence. This intramolecular folding event is followed by the intramolecular self-assembly of beta-hairpins into semiflexible fibrillar structures with permanent, physical-crosslink points. As the folding and assembly proceeds the low-viscosity, dilute peptide solution changes into a soft-solid hydrogel. The rheological behavior of these hydrogels can be modulated with the arm length of the peptides that inherently dictates the cross-sectional diameter of the fibrils. These networks exhibit a second type of transition on cooling when borate is used as a buffer salt. This transition stiffens the hydrogel and leads to a more than an order of magnitude increase in storage modulus. Oscillatory measurements show that this transition is reversible and that the rigidity of the hydrogels increase with decreasing temperature below the transition point. These transitions can be tuned with peptide design, borate concentration and ionic strength. SANS and DLS data reveal that during this transition static structure is preserved while the dynamics of the network is slowed down significantly. These transitions are also observed with DSC and NMR techniques. Although it has been shown that the borate ions form...
complexes with polyols and polysaccharides, rheological experiments with different peptide sequences suggest the formation of new type of complex between lysine residues and borate ions.

Wednesday 6:00 Salon A

PO4

Rheology and kinetics of thermal-induced gelation in waterborne polyurethane dispersion
Samy A. Madbouly and Joshua U. Otaigbe
Polymers and High Performance Materials, Southern Mississippi, Hattiesburg, MS 39406

Abstract: Isothermal and non-isothermal kinetics studies of thermal-induced gelation for waterborne polyurethane dispersions, PUDs has been investigated rheologically. The change in the viscoelastic material functions such as elastic storage modulus, $G'$, viscous loss modulus, $G''$ and complex viscosity, $\eta^*$ during the gelation process was accurately evaluated for the first time for this system. The isothermal kinetics reaction was described using a phenomenological equation based on the Malkin and Kulichikhin model that was originally developed for predicting isothermal curing kinetics of thermosetting polymers based on differential scanning calorimetry (DSC) data. The model was found to be conformed excellently well for the rheokinetics data presented here. The rate of the gelation reaction was found to be a first order regardless of the temperature. The temperature dependence of the gelation rate constant was well described by an Arrhenius plot with an average apparent activation energy equal to 120 kJ/mol, in reasonable agreement with the value obtained from the temperature dependence of gel time, $t_{gel}$ reported previously. The non-isothermal kinetics reaction rate were interpreted using the classical rate equation, the Arrhenius equation and the time-temperature relationships. The high value of activation energy is thought to be due to the strong interaction between the polymeric chain during the gelation process.

Acknowledgments: This work was supported by the National Science Foundation Materials Research Science Engineering Center (Contract grant No. DMR 0213883).

Wednesday 6:00 Salon A

PO5

Impact into a yield stress fluid
Herve Tabuteau, Darek Sikorski, and John R. de Bruyn
Physics and Astronomy, The University of Western Ontario, London, Ontario N6A 3K7, Canada

We have carried out experiments on the impact of a sphere on the free surface of a yield-stress fluid, and have studied the motion of the sphere as it travels below the surface. Sphere of various densities and diameters are dropped from different heights above the surface, reaching the surface with a non-zero velocity. The subsequent dynamics involves three distinct regimes: a rapid fall of the sphere just after the impact at almost constant velocity; a slower fall during which the velocity of the sphere decreases continuously leading to an apparent stoppage, and finally a constant-speed motion of the sphere. We show that just after the impact, the dynamics of the sphere is purely inertial. In the second regime, we obtain a scaling relationship involving the penetration of the sphere, its kinetic energy, and the elastic modulus of the fluid. Finally, we show that the last regime corresponds approximately to the equivalent of Stokes flow of the sphere in a Bingham fluid.

Wednesday 6:00 Salon A

PO6

Displacing yield-stress fluids in near-horizontal eccentric annuli: Numerical simulations and experimental results
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Eccentric annular displacement flows of yield stress fluids are of interest principally as a model for the primary cementing of oil wells, in which drilling mud is displaced by a cement slurry. Since the 1990's there has been a phenomenal increase in the number of near-horizontal oil and gas wells drilled worldwide. These wells frequently have high productivity but are more difficult to construct due to a number of mechanical and process issues. Here we address the issue of laminar displacement fluid mechanics. In horizontal wells significant density differences, that are beneficial in vertical displacements, tend to cause slumping and stratification. Therefore, the emphasis is control of the fluid rheologies and flow rate. Our numerical simulations are based on the model derived in [1,2]. We also extend the lubrication model in [3] to provide a simplified description of the interface motion. The model consists of a 1-dimensional advection-diffusion equation for the interface, in which all rheological effects manifest in a single nonlinear flux function. We us a nonlinearly stable compact scheme to solve this equation and illustrate the effects of density and rheology. Two-dimensional simulations, using the model in [1,2], are carried out for comparison. In parallel, we report ongoing work to simulate the same displacements experimentally using Carbopol & Xanthan solutions in a lab-scale pilot flow loop. We show our initial results and make qualitative comparisons with the numerical simulations.

The time independent rheological properties of low fat sesame paste/date syrup blends as a function of fat substitutes and temperature

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The rheological behavior of 20% reduced fat sesame paste/date syrup blends were determined using Brookfield rotational viscometer and the effect of fat replacers with guar gum, Xanthan and modified starch, and temperatures at 25, 35, 45 and 55°C were investigated. All sesame/date blends were found to exhibit non-Newtonian pseudoplastic behavior at all temperatures and fat substitutes levels. Apparent viscosity versus shear rate data was successfully fitted to the Power-law model. The flow behavior index, n varied in the range of 0.35-0.51. The consistency coefficient, K was in the range 108-240.04 mPa.sn. In addition, the fat substitutions led to the consistency increasing for all samples in comparison with the control. An Arrhenius equation was also used to describe the effect of temperature and Ea value appeared in the range of 16010.3-24330.1 J/mol.

The effect of fat substitutes on the time dependent rheological properties of low fat sesame paste/date syrup blends (Ardeh)

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Ardeh (semi solid paste) is a traditional food in the Iran, which is produced by crushing the dehulled sesame seeds and then mixing with proper fruit juice concentrate such as date syrup. In this paper, the time-dependent flow behavior of 20% reduced fat sesame paste/date syrup blends were assessed using Brookfield rotational viscometer as a function of fat replacers (guar gum, Xanthan, and modified starch). Two models were used to predict the flow behavior, namely; first-order stress decay with a zero equilibrium stress and Weltman models. It was found that time-dependent behavior of samples was good fitted with these models and all Ardeh samples exhibits a thixotropic behavior that increases with increasing shear rate. For Weltman model, the A and B constants varied in the range of 189.234-730.6 Pa and 0.09-1.571 Pa respectively. While for first-order stress decay model, the initial shear stress ($\tau_0$) was in the range of 196.966-794.025 Pa and the breakdown rate constant (K) varied in the range of 0.006-0.0146 s$^{-1}$.

Modification of Bostwick method to determine tomato concentrate consistency

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Tomato concentrated products were diluted to Brix 12 for measure their consistency by Bostwick consistometer. Evaluation the consistency of tomato concentrate with different °Brix showed that the error in consistency measurement of tomato concentrate by Bostwick method arised especially at high °Brixes. The studies indicated that the drying rate of insoluble solids and the lacking of reconstituting properties of them, caused error in the measurement of tomato concentrate consistency. In this research the effect of variety, concentration and the temperature of consistency measurement were evaluated to determine variation of error in Bostwick consistometer and to modify it. The results showed that variety had no effect on the accuracy of consistency measurement by Bostwick method, but concentration and temperature had a highly significant effect on the accuracy of this assay and thus the error of Bostwick consistometer increased, especially at high °Brixes. Results showed that heating of diluted tomato concentrate (up to 45 °C) and then cooling it could decrease the error of consistency measurement considerably. Consistency can also be estimated accurately using the regression between °Brix, temperature and Bostwick consistency (R²=0.94).

Rheological behaviour of soybean protein and cellulose xanthate blending solution

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The influence of protein contents and temperatures on rheologic curves, non-Newtonian flow index and structural viscosity index of soybean protein and cellulose xanthate blending solution were studied. The results showed that soybean protein cellulose xanthate blending solution is a typical pseudoplastic fluid. The viscosity of the blend decreases, structural viscosity index increases and spinnability deteriorates with protein contents and temperature. The phenomena that the viscosity of the blend decreases with temperature weakens over 30°C.
In industry, food products are developed using sensory to gauge formulation and process effects on texture, flavor and quality. Texture is equated with the consistency of products e.g., hard, soft, thick, thin, etc. are texture attributes for foods. Some of the important texture terms, like sticky, creamy, rubbery etc. are integrated terms in sensory analysis and cannot be measured independently of other attributes. Thus, sensory often is not effective in generating cause and effect relationships. A material science approach, based on the hypothesis that texture is the embodiment of the material properties of the product, has been applied to characterize foods and is proving to be useful. The goal of this talk is to present an overview of progress made in this area by some researchers, including that of the author. Testing foods for material properties posed challenges, both practical and technical. Preparing specimens with soft solids was not easy. Eliminating interfacial effects from bulk measurements required multiple tests and complex analyses. However, the process of testing foods for true material properties was found to be insightful for understanding how sensory perceptions occurred and for developing structure - function relationships. Mechanistic insights for texture have resulted from analyses of material properties, namely the rubbery feel of cheeses, lubricity of mayonnaises, staleness of breads, and stickiness of bread dough mixes. Case examples have been cited to show that while bulk consistency was affected strongly by changes in formulations, interfacial characteristics were affected more by structure, which resulted from both formula and processing. Data would be presented to show that (many) foods are self-lubricating, soft solids and that sensory is exceptionally sensitive to changes in lubrication characteristics.

Solid-liquid pastes featuring high volume fractions of particulates are frequently used in net shape forming operations, where the material is extruded and subsequently dried, or as products themselves, e.g. solder pastes. Their rheology is often dominated by particle-particle interaction phenomena such as yield stress behaviour and wall slip, so that the local solids fraction is a key parameter. The stresses imposed during extrusion processing can, however, promote differential flow between the solid and liquid phases giving rise to product and processing problems. Designing a paste formulation a priori so that it does not undergo liquid phase maldistribution is not currently available as reliable models for these multiphase systems are in their infancy.

This paper describes work on modelling paste flows using soil mechanics approaches to encapsulate the inherently multi-phase nature of these systems. The modified Cam-Clay model has been implemented in a Finite Element Method simulation of (a) ram extrusion and (b) squeeze flow using the ABAQUS code. The simulation requires regular and extensive re-meshing and code optimisation. Predictions of extrusion pressures and deformation behaviour are compared with experimental data obtained using model mixtures of glass spheres and Newtonian liquids, and a micro-crystalline cellulose/water system representing formulations employed in pharmaceutical extrusion-spheronisation processes.

Purpose: To compare the rheological and particle characterization properties of different retinol formulations following FDA Q3 requirements for topical products. Methods: Tests were performed on several formulations of encapsulated retinol containing different waxes, polymers and esters. Rheological data includes plots of shear stress versus strain rate, viscoelastic response (G' and G" versus frequency), and a determination of the yield stress, all performed on a Bohlin Gemini rheometer. Particle size analysis was performed on a Malvern Zetasizer Nano ZS system at both dilute phase and original sample concentrations to investigate the effect of sample dilution. Particle size studies were performed before and after exposure to shear forces in the rheometer to investigate shear induced agglomeration. The effect of pH on zeta potential was investigated to quantify how different surface chemistries might affect stability and reactivity. Results: Product A, B and C exhibited a trend towards larger particle size and polydispersity index. This was also reflected in the viscoelastic data. Rheological analysis indicated that product C had exceeded its effective shelf life at the time of this study. The poorer stability of sample C had been predicted through previous particle characterization studies. Variations in zeta potential in sample B compared to A and C indicate that a shift in the isoelectric point may arise from different surface functionality of the wax component in this formulation. Onset of shear-induced aggregation was confirmed through dynamic light scattering particle size analysis studies.
**Study on the transferability of the time temperature superposition principle to emulsions**

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The instability of emulsions is basically clarified by a phase separation. The separated phase can either creaming or sediment. Destabilization is mostly compounded by coalescence and gives a first indication through extension of droplets. In the cosmetics industry as well as many other branches of industry such as the food industry and paint and coatings industry, product stability is one of the most important quality criteria. Many stability tests have already been performed with the widest variety of methods from different fields of technology. In research and development it is especially important to obtain quick results on the stability of a formulation. Such results represent a tool that can help developers find an optimal formulation in a short time. In addition, they can shorten development times, leading to quicker introduction of a product in the market. Moreover, they can help reduce storage stability tests to a minimum, making less climatized rooms, space and work necessary to predict shelf-lives. The cycle test is an example of such a method developed in the field of rheology [1]. In this test the sample is subjected to continuously changing temperatures and its behavior observed. However, other methods can also conceivably used to predict stabilities. The aim of this work is to find a new model to predict the long-term stability. This model should be based on empirical data and it should determine the applicability of the time temperature superposition principle (TTS) to emulsions.

**Viscoelastic compound-drop models for neutrophil deformation and transport in capillaries**

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It is well known that neutrophils take much longer time to traverse the pulmonary capillary bed than erythrocytes. This results in their accumulation in the lungs and formation of a reservoir readily recruited when needed. In recent years, neutrophil transport in the lungs has been modeled using increasingly realistic representation of the capillary network. However, the cell deformation has mostly been accounted for empirically. Thus, the determination of the transit time is often ambiguous for lack of a direct knowledge of the cell shape during the transit. In this talk, we will describe a detailed numerical simulation of a neutrophil passing through capillaries. Motivated by the intuition that the difference in transit time is due to the white cells’ higher rigidity than red cells, we explore how the cell rheology affects its deformation and passage through capillaries. Using a novel phase-field representation, we first test the well-known Newtonian and viscoelastic drop models. Then we examine whether the apparent cell viscoelasticity can be captured by accounting for the existence of a more rigid nucleus. Comparison with measurements will determine which model features are appropriate. Finally we discuss geometric effects relevant to the pulmonary capillary network as well as various microfluidic devices developed for analysis and separation of blood cells.

**Stability and rheological properties of fluids with monodisperse microbubbles**

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Microbubbles are micron-scale hollow spheres (normally 1-100 μm) with a gaseous core coated with a thin shell. Pure saturated phospholipid coated microbubbles are widely used as an ultrasound contrast agent in biomedical applications. Bubbles also play a significant role in manufacturing of many food products such as cakes, ice creams and soft drinks. The advantages of introducing microbubbles in food include lowering cost, forming novel structures and texture, modifying digestibility and tuning the intensity of flavors. Compared to traditional aerated food, the potential applications of microbubbles are replacement of carbonated drinks, reduction of price per volume in products such as candy bars and enrichment of the nutrition value of the food.

In food applications, using lipid-coated microbubbles is very high cost. A food grade emulsifier is used to as an alternative to generate microbubbles. The relationship between bubble size, stability and emulsifier concentration is studied. A fluorescence microscopy technique is used to determine the microstructure of these microbubbles.

Monodisperse coated microbubbles can be generated using a flow focusing technique. Microscopy imaging of size distribution and air entrainment measurements are used to obtain a relationship between emulsifier concentration and bubble size. Since the microbubbles are very stable for a short time period, the rotational rheometer is used to measure the relationship of "real time" bubble size and rheological properties. Results for the flow behavior of the fluids with monodisperse microbubbles show that they are viscoelastic and behave as a gel.
Shape response vs. interfacial viscoelasticity of emulsion drops in shear flow
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We report results from a study of the role of interfacial viscoelastic properties in the bulk rheology of oil-in-water emulsions. A globular protein, beta-lactoglobulin, is used as the surface-active molecule. Our approach is three-fold: (i) Interfacial rheometry (shear and dilatation) is used to study the rheological response of adsorbed interfacial films. (shear deformation: biconical bob rheometer, Erni P et al., Rev Sci Instrum 74 (2003): 4916, dilational deformation: oscillating pendant drop tensiometer) (ii) Deformation experiments with single emulsion drops are performed in a computer-controlled shear cell (Birkhofer B et al., Ind Eng Chem Res 44 (2005): 6999) (iii) Rheometry and morphology analysis (rheo-SALS). In particular, we compare the relaxation time spectra of emulsions produced with protein emulsifiers with those containing only small-molecular surfactants. While in emulsions produced with small-molecular surfactants the relaxation spectra suggest a single relaxation process associated with the shape relaxation of the deformed drops, we find a markedly different relaxation behavior in emulsions with interfacial rheology. In the case of small interfacial shear moduli, drops can still be deformed in shear flow, and a second relaxation timescale, which might be associated with in-plane interfacial stresses, is found. If the interfacial moduli are large, deformations are limited to a much smaller degree, therefore shape relaxation is not found at large interfacial moduli. An attempt is made to describe the rheological data with existing emulsion models accounting for interfacial viscoelasticity (Paliere JF, Rheol Acta 29 (1990): 204; Jacobs U et al., J Rheol 43 (1999):1495; Van Hemelrijck E et al, J Rheol 48 (2004):143).

Modeling the electrorheological effect in suspensions
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A simple kinetic structural rheological model is used here to predict the complex rheological behavior of materials under flow that switch from liquid-like to solid-like upon application of an electric field. The model requires six parameters that have physical meaning and can be evaluated from independent electrorheological measurements. Agreement with predictions from models proposed in the current literature is obtained in particular cases. Several steady and unsteady flow situations are analyzed. The yield stress dependence on the electric field strength is also examined.

The extended Rutgers-Delaware rule for MR suspensions under magnetic fields
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The interrelation between apparent viscosity in steady shear flow and complex viscosity in oscillatory shear flow for MR suspensions was investigated. Series of experiments were conducted using a MR rheometer. An extended Rutgers-Delaware rule is proposed, in which an effective shear rate for oscillatory shear flow is defined as wDh. Here Dh is the strain amplitude (g0) dependent shift factor, which was found to be similar for different MR suspensions under different magnetic fields. At high strain amplitudes (g0 > 100%), Dh = g0, the Rutgers-Delaware rule is approximately obeyed. At low strain amplitudes (g0 < 100%), the curves of Dh fall between the line of the Cox-Merz rule and that of the Rutgers-Delaware rule. The curve of Dh at low strain amplitudes depends on the ingredients of the MR suspension. For samples with same ingredients, a unified curve of Dh can be identified in a range of magnetic field and/or for a range of volume fraction of magnetic particles.

Mesoscopic simulations of nematic polymer flows
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We investigate spatial structure in the coupled velocity and molecular fields of flowing nematic polymers in a parallel-plate Couette cell, with both steady and time-dependent simulations, employing a mesoscopic Doi-Marrucci-Greco model. We identify co-existence of in-plane and out-of-plane steady structures, determine their stability, and show unsteady structure transitions may be activated by device controls (plate speeds), molecular properties (strength of elasticity potentials), and most intriguing, by modifying anchoring conditions. This is joint work with Greg Forest at UNC Chapel Hill and Qi Wang at FSU.

Time dependent shear flows of particulate suspensions: Application of a new constitutive model
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A constitutive model for microstructure and total stress in particulate suspensions has been recently developed. A second order tensor representation of the microstructure is a key element of the model. An evolution equation for this structure tensor provides a means to predict
changes in microstructure with time. A separate equation relates the stress tensor to the structure tensor and rate of strain tensor. These equations can be used to model structure and stress in both steady and time-dependent viscometric flows (see paper SC37). Presented here are model predictions and simulation data for three transient flows: startup flow, step-change flow, and flow reversal. The Stokesian dynamics simulations were for monomodal suspensions in an infinite shear field, with hydrodynamic and a short-ranged repulsive forces between the particles. The transient nature of the microstructure is examined Good agreement between the simulation data and model predictions is demonstrated.

Wednesday 6:00 Salon A

**Analysis of the effect of flow-induced crystallization on the stability of fiber spinning process**

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The stability of fiber spinning process exhibiting spinline flow-induced crystallization (FIC) has been investigated using the method of linear stability analysis. Effects of various process conditions such as fluid viscoelasticity and the spinline cooling on the spinning stability have been found closely related to the development of the spinline crystallinity. It also has been found that the FIC makes the system less stable or more unstable than no FIC cases when the spinline crystallinity reaches its maximum possible value, whereas the FIC generally stabilizes the system if the crystallinity doesn't reach its maximum value on the spinline. It is believed that the destabilizing effect of the FIC on the process when the crystallinity is fully developed on the spinline is due to the reduction of the real spinning length available for deformation on the spinline. On the other hand, the increased spinline tension caused by the FIC when the maximum crystallinity is not reached on the spinline and thus no reduction in the spinning length, makes the sensitivity of spinline variables to external disturbances smaller and hence stabilizes the system. And also the accompanying linear stability analysis explains the fact that the spinline neck-like deformation stabilizes the spinning process, corroborating a recent experimental finding (Takarada et al. 2004).

Wednesday 6:00 Salon A

**Extensional rheology of poly(acrylamide) and hydroxypropyl cellulose studied using capillary break-up**

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Capillary break-up extensional rheology of hydroxypropyl cellulose and poly(acrylamide) samples is reported. The technique is based upon the formation of an unstable fluid filament which is allowed to undergo break-up governed by its own dynamics (www.campoly.com). The filament mid-point diameter is monitored with respect to time using a laser micrometer. Via the application of various models a longest relaxation time and apparent extensional viscosity can be acquired [McKinley & Tripathi, J. Rheol., (2000), 44(3), 653].

Solutions of hydroxypropyl cellulose in 70:30 water:propylene glycol are shown to exhibit Newtonian decay of the mid-filament diameter over the entire filament lifetime. The scaling behaviour of the zero shear viscosity and apparent extensional viscosity as a function of polymer volume fraction display unusual behaviour inconsistent with expected scaling laws. Specifically, the viscosity vs. volume fraction scaling plots for hydroxypropyl cellulose samples of different molar mass do not superimpose to give a master curve. Such behaviour is attributed to differences in the heterogeneity of substitution between samples of different molecular weight which is more pronounced for samples of high molar mass.

Dilute solutions of various high molar mass poly(acrylamide)s often exhibit pronounced extensional properties and are employed to control the atomisation of spray formulations, droplet bounce and rebound from surfaces and the break-up of viscous jets. The filament decay response for dilute concentrations of various poly(acrylamide) derivatives in 95:5 glycerol:water mixture is complex, dominated by a region of exponential decay. Scaling of the relaxation time demonstrates a concentration dependence consistent with the findings of others and is attributed to the increased interaction between stretched polymer chains [Stelter et al. J.Rheol., (2000), 46(2), 507, Bazilevskii et al. Polymer Science Ser. A., (1997), 39(3), 316].

Wednesday 6:00 Salon A

**Fluid webs: Tearing of viscoelastic films**

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We have performed a qualitative exploratory study on the collision of viscoelastic fluid jets of a wormlike micelle solution. The succession of patterns is similar to that of Newtonian flow, until the higher flow rates. First, we see a cascading ribbon. The central ring grows and becomes unstable, until finger formation around the outer ring becomes apparent. The effects of viscoelasticity and the large extensional viscosity of the fluid become much more noticeable as the outer ring becomes completely unstable and rather than droplets attached by thin tendrils, we see finger-like forms. At the highest flow rates, the outer ring seemingly detaches along with the fingers, and a portion of the central sheet tears away. The torn sheet fragments collapse, and the many fingers create the appearance of a web centered on the initial sheet formed at the colliding jet intersection. High speed video shows that the web-like form taken by the flow is the result of multiple rupture events within the central sheet. As the fluid recedes from the point of rupture, new fluid rings are formed and interact to form complex structures. The spray-like appearance of a Newtonian fluid at high flow rates is attributed to the Rayleigh instability which causes droplet formation and breakup. In contrast, the extensional viscosities of the non-Newtonian fluids are orders of magnitude greater than shear viscosity, and resist droplet breakup giving rise to the web-like structure.
Analytical solution of Couette-Poiseuille flow of nonlinear viscoelastic fluid through annular duct
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Laminar fully developed flow of Simplified Phan-Thien-Tanner (SPTT) fluid in an annulus was studied analytically. Inner cylinder was moving and outer one was stationary. The results of the velocity profile and product of friction factor and Reynolds number \(f_{Re}\) were obtained for a wide range of aspect ratio and dimensionless viscoelastic group. The dimensionless velocity profile and apparent viscosity have been reported. Results indicated the gap between two cylinders as well as viscoelastic behavior of the fluid have noticeable effect on flow.

Movement description of landslide Slano Blato
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The landslide Slano Blato is situated above the village Lokavec in the east of Slovenia. It has a long history and was first mentioned in a document in 1887. In the last decade, movement of the landslide was observed in November 2000, when it reached distances of 60-100 m/day. By means of geotechnical research work on the landslide in the year 2003, the depth of the landslide, geotechnical parameters and the mechanism of sliding were examined in detail. Several rheological tests were carried out. By increasing the shear stress during the rheological tests under destructive shear conditions the material deformed and in narrow shear stress range the viscosity drastically dropped. Due to high solid loadings and the nature of the samples, a homogenous shear flow field was not achieved. Critical shear stress, at which the transition from creep flow to shear flow occurred, was determined for samples with different contents of water. Geomechanical and rheological investigations of landslide materials showed that the material properties of the samples were strongly influenced by water content, as well as by the time in which the materials were exposed to wetting. From investigations of the examined landslide materials it was concluded that the critical water content for the formation of earth flow could be about 40%. In order to determine the parameters required for further numerical simulations of the earth flow, the rheological tests of the samples were performed under non-destructive shear conditions. A stability analysis of the landslide was carried out numerically by applying the Burger elasto-plastic model. The model took into account geomechanical and rheological characteristics of the landslide. By means of the Burger analyses it was possible to predict the displacement in a time dimension based on the results of rheological measurements. The aim of numerical modelling was to establish the most critical parts of the landslide and the mechanism of failure. For the calculation, the FLAC program was used.

Exploring the rheological properties required for adhesive locomotion in natural and robotic snails
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Snails and slugs depend on the rheological properties of their pedal mucus for locomotion. These gastropods use a unique method to crawl called adhesive locomotion. Unlike an inchworm, or humans for that matter, no part of the animal is lifted from the ground to create differential friction. Rather, the mollusk exerts differential shear stresses on the thin layer of mucus holding it to the substrate. The pedal mucus has an effective yield stress, which allows part of the foot to glide forward on 'liquid' while another part remains held to the substrate by the 'solid.' The current work explores the rheological properties required for adhesive locomotion, and is motivated by a robotic snail that uses the same technique. It is shown that any non-Newtonian fluid could be used for horizontal adhesive locomotion. A measure of efficiency is introduced to compare simulants. For inclined and inverted locomotion (e.g. wall climbing), a yield stress fluid is required. A number of possible mucus simulants are plotted in the design space for the RoboSnail2 project.

Rheo-particle image velocimetry of shear thickening micellar solutions
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The shear thickening behavior of an aqueous equimolar micellar solution 40 mM of cetylpyridinium chloride and sodium salicylate was studied by using rheometry and particle image velocimetry (PIV). The obtained flow curves exhibited a Newtonian behavior at low shear stresses, followed by non-Newtonian shear thinning and shear thickening, respectively, as the shear stress was further increased. Detailed velocity profiles obtained for the different regions of the flow curve showed excellent agreement with rheometrical data and helped to uncover characteristics of the flow behavior that are not distinguished from the pure rheometrical measurements. Velocity profiles showed the presence of slip and complex flow behavior in both, the apparently shear thinning and the shear thickening regions. Rapid temporal and spatial...
fluctuations of the flow kinematics were observed in the shear thickening regime. Such variations are related to creation and destruction of shear induced structures due to a stick-slip phenomenon at the walls of the used rheometers.

Wednesday 6:00 Salon A

**Velocity profiles of a lyotropic lamellar phase under shear flow**

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We use ultrasound apparatus to track particles suspended in a lyotropic lamellar phase of SDS, water, pentanol and dodecane. Under shear flow such phases can transform from a repeated stack of bilayers to multilamellar vesicles known as "onions". During this shear induced microstructural phase transition strange behaviour is observed in the stress sweep rheology flow curve. Velocity profiles are measured using an ultrasound particle tracking technique to identify regions of material flowing at different rates in the Couette flow cell. The velocity profiles are also used to identify the local rheology near the walls of the cell. Experiments are also performed in the one phase onion region (after the transition from lamellae to onions). Velocity profiles in the onion phase show homogeneous velocity profiles.

Wednesday 6:00 Salon A

**Displacements of generalized Newtonian fluids along a plane channel**

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We present preliminary results of a numerical study into the displacement of one generalized Newtonian fluid by another, along a plane channel. Our motivation comes from the oil and gas industry, and specifically from the primary cementing of oil wells. In this process, drilling mud is displaced first by a spacer fluid and then by a cement slurry, along a narrow eccentric annulus. Here we are concerned with the fully 2-dimensional displacements that occur along an azimuthal slice of the annulus.

For immiscible fluids we use the diffuse interface method and for miscible fluids a concentration-diffusion equation formulation. In both cases the focus of our study is on the potentially beneficial effects of a non-monotone variation in fluid rheologies, as might for example be caused by chemical reaction or fluid incompatibility.

Wednesday 6:00 Salon A

**Statistical and scaling properties of elastic turbulence**

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An experimental investigation of random flows of a dilute polymer solution in a regime of elastic turbulence is presented. We first focus on a detailed characterization of the flow structure as a function of Weissenberg number, Wi. A particular attention is paid to the fields of velocity fluctuations and the velocity gradients [1,2].

Next, the relation between the elastic stresses and the scaling properties of elastic turbulence is discussed. Analogy with fast dynamo on small scales in magnetohydrodynamics and with passive scalar turbulent advection is used to explain the experimentally observed flow structure [3], statistical properties [1,2], and scaling [1,4] of the global power injected into the system.


Wednesday 6:00 Salon A

**The rheology of aqueous cornstarch suspensions and the generation of roll waves**

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Aqueous suspensions of cornstarch show several remarkable features. For instance, it appears shear thickening: a spoon slides in easily when gently inserted, but hitting the material rapidly causes the surface to almost solidify and even fracture. Furthermore, a compressed handful initially appears solid but when allowed to relax flows away. The time for this change reflects a relaxation timescale, such as exists for viscoelastic fluids. We observe another curious feature: in flow down a constant incline, instabilities prompt the growth of roll waves that resemble propagating hydraulic jumps. Similar waves are seen on flowing films of water; however the waves in cornstarch arise at Reynolds numbers (Re) far below the critical value for Newtonain fluids. Also, the large-scale flow generates a high-frequency jitter seen at the crests of
the cornstarch roll waves. These observations are not reconciled with theoretical predictions based on simple rheological models (e.g., power law shear thickening, Oldroyd-B viscoelastic) that indicate stable flows at low Re.

To understand the observed waves, we measure properties of a 52 wt % cornstarch suspension with a cone and plate geometry in steady and oscillatory shear. At low shear rates the material is shear thinning: at 0.01 /s the viscosity is about 1 Pa s and then drops by a factor of 50 to its lowest value at ~1/s. At higher shear rates it shear thickens to a viscosity of 5 Pa s at a shear rate of ~15/s. Oscillatory data show that the material response is dominantly viscous except near 7 Hz where the suspension behaves elastically. Interestingly, this coincides with the frequency of jittering in our experiments. With these data we explore the critical Re for the formation of roll waves. Using the Oldroyd-8 constitutive relation we find that the critical Re can be made small if the fluid is both shear thickening and elastic.

Wednesday 6:00 Salon A
Interfacial instabilities in primary cementing displacement flows
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In primary cementing, a sequence of fluids are pumped through an eccentric annulus, displacing each other. These fluids include drilling muds, spacer fluids and a various cement slurries, all of which are rheologically characterised as inelastic shear-thinning fluids. These displacement flows, in the laminar regime, are still relatively poorly understood. The typical industry design of a primary cementing job is based on a one-dimensional hydraulics simulation, supplemented with a series of company-specific physical rules. This industry standard practice conflicts with the obvious fact that displacement flows in an eccentric annulus must be (at least) two-dimensional close to the displacement front. The ideal situation is that drilling mud is displaced all around the annulus and that the displacement front advances steadily up the well at the pumping velocity. Even better is that the wide and narrow sides of the front advance at the same speed. Conversely, if the fluid on the narrow side of the annulus does not move, or moves very slowly, a longitudinal mud channel can result. Although the possibility of a narrow side mud channel and the benefits of a steady state displacement have been recognised since the mid-1960s, there is still little quantitative understanding of when steady state displacements occur. We show how the three-dimensional flow can be modelled and analysed to give straightforward predictions of primary cementing displacements, i.e. when will fluid A displace fluid B? As well as explaining the answer to this fundamental question, we consider what happens when displacement is ineffective. In this case the displacement front advances ahead on the narrow side, eventually elongating into a near-parallel flow. In this flow there is the possibility of shear instabilities between the displacing fluid streams. We analyse this situation and also discuss some of the other instabilities that can occur in primary cementing.

Wednesday 6:00 Salon A
Development of a microfluidic rheometer for measuring the complex modulus of complex fluids
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The measurement of the rheology of complex fluids in microfluidic flows is an important technical challenge. We present our work on the development of a microfluidic rheometer based on a magnetically driven overdamped harmonic oscillator. We avoid the need for an explicit hydrodynamic model, which is typically required to infer the viscosity from the transfer function of an immersed oscillator, by relying on a hydrodynamic similarity. In the limit of low Reynolds number the fluid viscosity appears in the transfer function only through the viscous penetration depth \( \delta = (2\eta/\rho \omega)^{1/2} \), where \( \eta \) and \( \rho \) denote fluid viscosity and density, respectively, and \( \omega \) is the angular frequency. While wall effects doubtlessly influence the transfer function of an oscillator embedded in a microfluidic device, this approach implicitly accounts for those effects. Hydrodynamic similarity can be used to calibrate an oscillating body viscometer (of any shape) over a range of \( \eta \) by measurements with a standard Newtonian fluid of known viscosity and density over a corresponding range of \( \omega \), and hence \( \delta \). The viscoelasticity of an unknown fluid is then determined by comparing the measured (complex) value of \( \delta \) with the complex generalization of the calibration function. We will discuss the design and fabrication of this oscillating body microfluidic rheometer, and present results of oscillatory shear rheometry on diverse fluids.

Wednesday 6:00 Salon A
Microfluidic interfacial tensiometry
Jai A. Pathak, Steven D. Hudson, Joao Cabral, Wenhua Zhang, and Kathryn L. Beers
Polymers Division, NIST, Gaithersburg, MD 20899-8544

A microfluidic approach to rapidly measure interfacial tension of immiscible fluids is reported. This method rests upon quantitative real-time analysis of two-phase flow and drop-shape dynamics. Drops of prescribed dimension and spacing are produced, accelerated and deformed under extensional flow. These measurements, and comparison to previously reported standard measurements, demonstrate that we can measure a wide range of interfacial tension (e.g., from 2.5 mN/m to 60 mN/m).
Intrinsic viscosity provides insight into molecular structure and interactions in solution. A new microchip method is described for fast and accurate intrinsic viscosity measurements of polymer and biopolymer solutions. Polymer samples are diluted with a fluorescent dye in the microfluidic chip by imposing pressure gradients across the channel network. The concentration and flow dilutions of the polymer sample are calculated from the fluorescent signals recorded over a range of dilutions. The viscosities at various polymer dilutions are evaluated using mass and momentum balances in the pressure driven microchannel flow. The technique is applicable to many chemical, biological and medical applications where sample is available in very small quantities. The intrinsic viscosity experiments were performed for three classes of polymer solutions: (a) polyethylene glycol - polymers with linear hydrocarbon chains; (b) Bovine Serum Albumin - biopolymer chains with hydrophobic and hydrophilic amino acids, and (c) DNA fragments - biological macromolecules with double stranded polymeric chains. The measured values of intrinsic viscosity agree remarkably well with the available data obtained using different methods. The data is shown to obey power law in molecular weight described by Mark-Houwink-Sakurada equation. Experiments were performed to understand the effect of solvent quality and salt concentration on molecular conformations and the intrinsic viscosity of polymer. The new method offers a new way to study the conformational changes in proteins and DNA solutions in various buffer conditions such as pH, ionic strength and surfactants. The effects of shear rate in the micro channel and mixing time on the accuracy and limitation of the measurement method are discussed.

Reversible networks formed upon the treatment of aqueous solutions of the polysaccharide konjac glucomannan (KGM) with borate were probed using small deformation measurements. Whilst the tenacity of the networks in the polymer and cross-linker concentration ranges of interest proved problematic in conventional measuring geometries, their self-healing nature facilitated reproducible measurement using a four-bladed vane geometry. The latter was calibrated for use in oscillation by calculation of an effective reduced radius following measurement of a number of 'model' fluids. Relaxation spectra recorded for borate cross-linked KGM were complex, suggesting their origin in a number of relaxation mechanisms. One such mechanism could be resolved into a single element Maxwell model. An additional relaxation mechanism indicated by a second maximum in the loss modulus at higher frequencies was concordant with a 'sticky reptation' model. Further insight into relaxation mechanisms. One such mechanism could be resolved into a single element Maxwell model. An additional relaxation mechanism than the synthetic DRPs and better defined and reproducible during preparation than the natural DRPs. In addition, mechanical instability of the applied in previous in vivo studies. However, the search continues for new DRPs that would be more biocompatible and mechanically stable than the synthetic DRPs and better defined and reproducible during preparation than the natural DRPs. In addition, mechanical instability of the best drag reducers remains a problem for their practical use. We compared drag reducing effectiveness and mechanical degradation of several blood soluble DRPs. The tested polymers included PEO, PAM, and an aloe vera plant derived DRP which was discovered in our laboratory. In

Blood-soluble drag-reducing polymers (DRPs) were demonstrated to have the ability to significantly increase blood flow and tissue oxygenation with no direct effect on vessel tone when injected at nanomolar concentrations in animals with normal and pathological circulation. Several DRPs, including several high molecular weight polyethylene oxides (PEO), polyacrylamides (PAM), and plant-derived polysaccharides were applied in previous in vivo studies. However, the search continues for new DRPs that would be more biocompatible and mechanically stable than the synthetic DRPs and better defined and reproducible during preparation than the natural DRPs. In addition, mechanical instability of the best drag reducers remains a problem for their practical use. We compared drag reducing effectiveness and mechanical degradation of several blood soluble DRPs. The tested polymers included PEO, PAM, and an aloe vera plant derived DRP which was discovered in our laboratory. In
addition, we synthesized a new candidate for a biocompatible blood soluble DRP, high molecular weight poly(N-vinylformamide) (PNVF). Since PNVF is known to have no toxicity and is more easily manufactured than natural polymers, it is worth investigating this polymer for potential clinical use. We also compared physico-chemical and rheological characteristics, including molecular weight, intrinsic viscosity, molecular size, polydispersity, viscosity, elasticity, and relaxation time, of these polymers. All of the tested DRPs proved to be effective in reducing resistance to turbulent flow in vitro. The aloe derived DRP was most efficient drag reducer followed by PAM, PEO, and PNVF. Studies of the polymer mechanical degradation caused by high shear stresses showed that the aloe DRP molecules were most resistant to mechanical stress followed by PAM, PNVF, and PEO. The tested DRPs had molecular weights greater than 1 x 10^5 Da, relatively large intrinsic viscosities and hydrodynamic radii, and concentrated solutions exhibited non-Newtonian behavior.

**Wednesday 6:00 Salon A**

**PO42 Structure and rheology of composite cytoskeletal networks**

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The cytoskeleton determines shape and mechanics of living cells. It is composed of three different types of filaments: F-actin, microtubules, and intermediate filaments. While entangled and crosslinked actin networks have been studied extensively in recent years, much less is known about composite networks, where different cytoskeletal polymers can interact with each other. Actin and intermediate filaments belong to the unique class of semiflexible polymers. While actin has a persistence length (lp) of about 15 µm, neurofilaments (NF) have a persistence length of about 500nm. Neurofilaments (NF) are the most abundant cytoskeletal filaments in axons. They fill most of the volume and are thought to provide structural stability. NF are formed by 3 different protein monomers: NF-H (heavy), NF-M (medium) and NF-L (light). In-vivo NF proteins are bundled into filaments, where the alpha-coil parts of the NF proteins form a semi flexible backbone (lp ≈ 500 nm) and the C-terminal ends of the NF-H and NF-M stick out as highly charged unfolded side arms with a length of about 70 nm. In-vitro networks of neurofilaments from pig spinal cord were characterised with rheological methods and TEM imaging. The elastic plateau modulus increases with increasing neurofilament concentration c7/5, which is consistent with a behaviour observed for entangled semiflexible polymer networks. Rheological properties of composite networks with varying ratios of F-actin and neurofilaments were measured. We studied the linear viscoelastic properties of composite networks and compared them with the mechanical properties of the pure networks. The results show that the storage moduli of the composite networks do not result from a linear superposition of the pure components – as expected from the concentration dependence of semiflexible polymers. The nonlinear behaviour is different for all studied networks: purely entangled actin networks fail at much lower stresses than pure NF networks; the composite networks fail at intermediate stresses.

**Wednesday 6:00 Salon A**

**PO43 Drag reducing polymers as a potential treatment for microvascular impairment in diabetes**

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Diabetes affects more than 18 million people in the US and produces a generalized affliction of the cardiovascular system in these individuals. This affliction results in a microvascular disorder that affects the eyes, kidneys, and nervous system. Current therapies can at best delay the onset of these complications. It has been previously shown that the addition of minute concentrations of blood soluble drag reducing polymers (DRPs) to blood increases microcirculatory flow and reduces vascular resistance without affecting vascular tone. We studied the potential of DRPs as a treatment for the microvascular dysfunction associated with diabetes using a streptozotocin (STZ) animal model of this disease. Diabetes was induced in rats using STZ and characterized by blood glucose levels above 300 mg/dl (~100 mg/dl in normal rats). After at least 15 weeks of hyperglycemia, animals were taken in acute experiments and, after collection of baseline hemodynamic data, injected via the jugular vein with polyethylene oxide (PEO, MW 4500 kDa) at 1 ppm. The DRP effects on normal and diabetic animal hemodynamics were evaluated by blood pressure, tissue perfusion (plantar surface of both hind paws - relative changes compared to baseline) using laser Doppler flowmetry, and heart rate recorded during a baseline period and after infusion of the DRP (saline in control). Body weight, tissue perfusion (TP), and heart rate were significantly lower and vascular resistance and hematocrit were both significantly higher in diabetic animals. The DRP injection increased TP by ~20% in both control and diabetic rats with no significant change in MAP. Potential mechanisms of the DRP effects on TP include their ability to reduce flow separations at vessel bifurcations causing an increase in precapillary pressure and, thus, an increase in functioning capillary density. This study demonstrated that DRPs were able to improve impaired TP in diabetic animals and may represent a new rheological method for the treatment of impaired microcirculation in diabetes.

**Wednesday 6:00 Salon A**

**PO44 Nonlinear model for blood behavior: Application for sedentary and athletic mammals**

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It is generally accepted that blood is a non-Newtonian fluid with complex rheological properties. Theoretical models to explain adequately the behavior of mammals’ blood are still missing. Based on the viscous and elastic properties of blood and on the observation that the aggregation of RBC has been shown to influence the viscosity at low shear rates and deformability at high shear rates we proposed a model in which we consider the dynamic viscosity as a complex quantity. The experimental data from literature support our choice for the dynamic viscosity and the constitutive equations that we propose are in concordance with blood behavior for sedentary and athletic animals.
In this work, solvent-induced sol-gel transition in lysozyme/TMU/water systems was investigated as a function of temperature and ionic strength by means of rheology, infra-red spectroscopy (FTIR) and microcalorimetric techniques. Gel points displayed an exponential decay in the presence of salt with both protein and TMU concentrations and with temperature. Activation energy decreased linearly with TMU mass fraction ($w_{TMU}$). FTIR analysis revealed a strongly enhanced β sheet content and reduced α helix in the gels with the increase in TMU concentration. Differential scanning calorimetry indicated an inverse linear dependence of lysozyme denaturation temperature on $w_{TMU}$ in the 0.1 < $w_{TMU}$ < 0.6 range, beyond which no denaturation signal could be detected.

Gelation kinetics observed for heat-set TMU/water lysozyme gels presented similar behavior to that verified for sol-gel transitions solely induced by solvent. FT-IR spectroscopy showed that both gelation processes involve partial disruption of the protein secondary structure leading to an increase in β sheet content at the expense of α helices. TMU reduced lysozyme denaturation temperature, thus allowing heat-induced gelation to take place at milder conditions.

The addition of a co-solvent to the system opens new possibilities of modulation of protein stability in liquid media. Although it adds new parameters to an already complex situation, it also allows introduction of controlled perturbations as a tool for the investigation of the forces involved in protein stabilization.

Acknowledgements: M.A. da Silva and E.P.G. Arêas thank CNPq, CAPES and FAPESP (Brazil).

Wednesday 6:00 Salon A

**PO46**

**P-V-T properties of glass and crystal polymers and their compositions with nanofillers**

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The transition temperatures, the specific volume and the thermal expansion coefficient of styrene/acrylonitrile copolymer (SAN) and polypropylene (PP), containing up to 25% of the nanofiller (lathed silicate on the base of Na-montmorillonite) at pressure 100 MPa and temperatures up to 250°C were studied. It was shown that addition of the filler leads to linear reduction of the specific volume of compositions of both polymers in solid and melt conditions owing to the more high density of the filler. At high concentrations of the filler (20-25%) the increase of the glass temperature of SAN and the decrease of the melt temperature of PP was observed. The first effect is stipulated by the interaction of SAN with filler and by the increase of the copolymer packing density in solid state. The second effect is determined by the formation of small crystal structure of PP at presence of the filler Na-montmorillonite. On base the result received the thermal expansion coefficient for the studied systems was calculated. It was shown that introduction of filler did not influence significantly the value of thermal expansion coefficient when the polymers are in melt state. However, in the case of solid state of the compositions the high filler concentrations change significantly the temperature dependence of the thermal expansion coefficient in comparison with the one of unfilled SAN and PP. P-V-T characteristics of the examined systems was describe quantitatively with the use Spenser-Gilmore equation. This equation is widely use for the prognosis of conditions of processing polymer materials and allow the prediction of their thermal shrinkage.

Wednesday 6:00 Salon A

**PO47**

**Rheology of thermoplastic elastomer nanocomposites**

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The rheological properties of thermoplastic elastomer nanocomposites (TPV) based on dynamically vulcanized PP/EPDM with three propolylenes of different viscosities and different levels of nanoclay content were studied and compared with similar but unfilled samples. Nanocomposite samples were prepared in a laboratory mixer (Rhemix 600) where EPDM was cured with polypropylene and different nanoclay content under shear with efficient sulfuric curing system. Nanocomposites based on low viscosity of PP showed a more significant enhancement of the storage modulus in comparison with the one of unfilled SAN and PP. P-V-T characteristics of the examined systems was describe quantitatively with the use Spenser-Gilmore equation. This equation is widely used for the prognosis of conditions of processing polymer materials and allow the prediction of their thermal shrinkage.
Electrical, rheological, and dynamic mechanical properties of polycarbonate and carbon nanotube composites
Yu-taek Sung1, Chong Koo Kum2, Heon Sang Lee2, and Woo Nyon Kim1
1Chemical and Biological Engineering, Applied Rheology Center, Korea University, Seoul 136-701, Republic of Korea; 2Tech Center, LG Chemical Ltd., Daejeon 305-343, Republic of Korea

Electrical, rheological, and dynamic mechanical properties of the polycarbonate (PC)/multi-walled carbon nanotube (MWNT) composites were studied by electrical conductivity, dynamic rheological, and dynamic mechanical thermal measurements, respectively. PC/MWNT composites were prepared by dilution of a masterbatch using the melt extrusion. From the results of electrical conductivity and rheological measurements, the electrical and rheological percolation threshold of the composites showed at 1.5 wt% MWNT content. The measured EMI shielding efficiency of the composites showed 15.9 dB (1.2 GHz) at 7.0 wt% MWNT content. From the results of dynamic mechanical properties, PC/MWNT composites showed different behavior of glass transition temperature (Tg) with the MWNT content. For the PC/MWNT composites containing the high content of the MWNT (> 7.0 wt%), double Tg peaks were observed, which could be explained by the phase separation morphology model.

Wednesday 6:00 Salon A

Rheology of highly filled propylene/ethylene copolymers
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A new family of propylene/ethylene (P/E) copolymers has a unique chain microstructure and an excellent balance of product performance properties. They feature narrow molecular weight distribution and broad crystallinity distribution. The unique molecular architecture offers the distinguishing feature of allowing exceptionally high filler loadings (even higher than 80 wt%) yet maintaining good processability. Our goal is to thoroughly characterize the rheological behavior and the interfacial phenomena to provide a fundamental understanding of the unexpectedly low viscosity exhibited by these materials when filled with particulates. Such a fundamental understanding is necessary for the design of other new resins with a better capacity for incorporating particles and for the development of optimum processing conditions for the composites. In this work, the rheological properties of P/E copolymers filled with calcium carbonate were studied. Steady shear and dynamic measurements on composites with different loadings (0-80 wt%) were carried out. The steady state shear viscosity increased dramatically with increasing filler loading. The dynamic measurements indicated time-dependent rheological behavior. Due to the particle motion, filled systems with different loadings have different time dependency. At high filler loading, yielding behavior was obtained with samples not previously sheared. To minimize/prevent bulk slip, rough plates were used for the samples with 80 wt% loading. Contact angle measurements were carried out to investigate the interfacial phenomena. The layer coated with calcium stearate decreases the adhesion of the polymer to the filler surface which perhaps results in particle-matrix interfacial slip.

Wednesday 6:00 Salon A

Extension-induced dispersion of carbon nanotube suspensions
Joung Sook Hong, Yang Soo Son, and Chongyoup KIM

Almost all the carbon nanotubes (CNTs) are not straight and remain in entangled aggregates. These aggregated clumps cluster to form large, weakly bound agglomerates with diameters up to millimeters. The dispersion of CNT into individual nanotube is difficult because of strong entanglement and van der Waals force between tubes. In this study CNT dispersion was subject to a continuous extensional flow to disentangle the tubes from agglomerates. Then the morphological and rheological behavior of dispersion was compared before and after the imposition of the continuous extensional flow. It has been observed that the zero shear viscosity of treated dispersion increased dramatically from the untreated dispersion. Also the treated dispersion showed highly shear thinning behavior and the viscosity at large shear rate approached to the viscosity of dispersing medium. The observations are quite similar to the rheological behavior of long fiber suspension. Therefore the rheological properties suggest that the nanotubes should be disentangled from agglomerates.

Wednesday 6:00 Salon A

Case study 2: Vane rheometry superiority over smooth geometry in evaluating solids-filled asphalt emulsions for cold-patch sealants
David J. Moonay and Brendan T. Sullivan
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A crumb-rubber-filled asphalt emulsion was prepared by a customer to a specification of 2,500-20,000 mPa·s as measured by Brookfield RVT viscometer with RV-6 disk-shaped spindle at 10 rpm. However, similarly-specified materials didn’t properly pump from delivery trucks at the jobsite. We, therefore, analyzed the new material by various methods, to find better procedures providing more meaningful data. All tests were at 20-23 °C. RVDV-III+ rheometer measurements with RV-6 and RV-4 spindles at 10 rpm gave mean average maximum apparent viscosities of \( \eta_{am} = 9,036 \pm 2,313 \) and \( 5,560 \pm 559 \) mPa·s, respectively. \( \eta_{am} = 26,745 \pm 1,098 \) mPa·s measured by HBDV-III+ with V-71 vane spindle at 1
rpm, immediately after stirring each sample. In contrast, $\eta_{am} = 197,653 \pm 23,454$ mPa·s, after standing quiescently for 48 h. $\eta_{am}$ was on the order of 50,000 mPa·s as measured by LVDV-III+ with Helipath and T-C spindle at 1 rpm. The average yield stress, for samples stirred immediately before each trial, measured with HBYR-1 Yield Rheometer and V-71 spindle at 1 rpm, was $\tau_{y,ave} = 6.54 \pm 0.71$ Pa. In conclusion: (1) Vane rheometry methods are superior to the specification's procedure in analyzing solids-filled asphalt emulsions because vane spindles test the whole material, whereas smooth geometries primarily test the liquid portion of the colloidal suspension, (2) vane-method viscosities, approximately four times higher for pre-stirred and eight times higher for settled samples, compared to viscosities measured with the specified method, far more realistically describe the material's behavior, and (3) the specification's method does not quantify the significant yield stress of the multiphase sample. We therefore recommend that vane-rheometry data, for both settled and well-mixed samples, be used in designing appropriate delivery systems.

### Wednesday 6:00 Salon A

#### PO52

**Evaluation of two techniques for testing of polyethylene film resins**

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The processability of a resin in film blowing is strongly influenced by its flow behavior in extension. In this study, the suitability of the Sentmanat Extensional Rheometer (SER) and of a novel tester for polyethylene film resins was evaluated. The SER, which subjects the resin to simple extension, is simple and fast to use, requires a small quantity of sample and gives reliable data that can be used to detect differences in molecular weight, molecular weight distribution and levels of long-chain branching. The data are also related to the stability of the bubble in film blowing. The tester, on the other hand, is a simple device that generates biaxial extension by inflating a sheet into a bubble. The resulting pressure traces from this empirical test were found capable of differentiating resins on the basis of their flow in biaxial extension.

#### PO53

**Using nanoindentation to measure viscoelastic properties of soft materials**

**Paula M. Wood-Adams, Arkadz Fatseyeu, and Luminita Ionescu**

*Mechanical and Industrial Engineering, Concordia University, Montreal, Quebec, Canada*

Nanoindentation is an experimental technique for measuring mechanical properties of materials using indenters of a very small size (down to a few dozen nanometers). Up to now nanoindentation has primarily been applied for the testing of very stiff, solid materials. We apply it to soft, viscoelastic materials and attempt to overcome experimental and other difficulties resulting from the small size and the complex deformation field. Experimental studies were performed on an un-modified polybutadiene and a cross-linked silicone rubber. An approximate technique was developed for extracting material functions of viscoelastic liquids from nanoindentation results. Size and/or surface effects were observed with the polybutadiene that remain unexplained. Material functions for the viscoelastic solid are extracted from nanoindentation data using the classical solutions derived from simple elastic indentation using the inverse Laplace Transform. Using this approach we find that the average local response is equal to the bulk in the case of the viscoelastic solid.

### Wednesday 6:00 Salon A

#### PO54

**A new extreme high-pressure / high-temperature viscometer**

**William Gusler1, Marvin Pless1, Jason E. Maxey1, Patrick Grover1, Jose Perez1, Jeff Moon2, and Todd Boaz2**

1Baker Hughes Drilling Fluids, Houston, TX; 2AMETEK Chandler Engineering, Tulsa, OK 74012

Growing demand for natural gas in North America is driving the gas exploration and production industry to look for new resources in previously unexplored areas. One of these areas is the deep Gulf of Mexico (GOM) Continental Shelf. Several of the current deep shelf high-pressure, high-temperature (HPHT) wells have anticipated bottom-hole fluid conditions that significantly exceed existing HPHT viscometer technology (currently limited to 400°F at 20,000 psig). Conditions towards the bottom of these wells preclude the use of currently available tools for measurement of down-hole annular pressures, placing additional importance on the need for laboratory measured drilling fluid properties at these extreme down-hole temperatures/pressures. The lack of such measured fluid properties could be a major shortfall for hydraulic models used to predict down-hole pressure information.

A new extreme HPHT concentric cylinder viscometer was designed and built to fill this important technology gap for the GOM deep shelf HPHT wells. The instrument is capable of measuring typical drilling fluid viscosities up to 600°F (316°C) and 40,000 psig (276.0 MPa) and is capable of accurately measuring the properties of drilling fluids containing magnetic materials. Verification and validation testing have demonstrated good comparison of the new viscometer data to commercially-available field viscometers and more sophisticated laboratory rheometers. The development of the instrument, automated control system and HS&E issues related to testing drilling fluids at these extreme conditions will be examined.
Rheo-microscopy and Rheo Small Angle Light Scattering (Rheo-SALS) devices for investigations of structure-property relations in complex fluids

Joerg Laeuger and Patrick Heyer
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Rheological methods reveal information on macroscopic material properties. Since the mechanical material properties are strongly dependent on the microstructure, information on the microstructure is often valuable for a better understanding of the rheological behavior. Simultaneous use of rheological and optical techniques is helpful to gain a better understanding of the dependencies between the microstructure and the mechanical properties of complex fluids. Microscopy and Small Angle Light Scattering (SALS) are widely used optical techniques for investigations of micrometer-sized structures. SALS gives information on the structure averaged over the whole scattering volume, whereas a microscopy image shows individual structure elements. On the other hand microscopy displays the structure in the real space, whereas light scattering like other scattering methods measure an intensity distribution in the so-called inverse or momentum space. Although both microscopy and SALS result from density (or orientation) fluctuations they are complementary methods. Both methods have been used frequently in combination with applied flow field to investigate structural changes induced by flow. However, a combination of such setups with a standard rotational research rheometer allows all rheological tests the rheometer can perform simultaneously to the optical measurements. To achieve this goal accessories for Rheo-SALS and Rheo-Microscopy have been developed, which can be easily adapted onto the MCR rheometer platform from Anton Paar. For the SALS module concentric cylinder or parallel-plate geometries can be used. The microscopy setup works for parallel-plate geometries. For both techniques the control of the sample temperature is possible and high temperature versions exist, which facilitate rheo-optical investigations on polymer melts and polymer blends. Details of the new Rheo-SALS and Rheo-Microscopy devices as well as application examples are presented.

Discrepancies in the specified data and presentation of a new data set for NIST Standard Reference Material® SRM 2490

Joerg Laeuger¹, Patrick Heyer¹, and Chad R. Snyder²
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A non-Newtonian fluid was introduced in 2001 by the National Institute of Standards and Technology (NIST) as Standard Reference Material(r) SRM 2490 [NIST Special Publication 260-143; 2001]. Recent measurements performed in four different laboratories, on six different rheometers using two different temperature control principles and 3 different bottles of the sample, revealed deviations of up to 20 % at 0 °C in the oscillatory data. The measured viscosity and normal force values show reasonable agreement with the NIST data. A simple calculation of the complex viscosity from the G’ and G” data at small frequencies from NIST and a comparison with the NIST shear viscosity value at low shear rates show the same difference, i.e., the NIST data itself are inconsistent. The comparison with the measured data implies that the published oscillatory data are wrong by up to 20 % at 0 °C. Differences were found in rotational tests as well. Although the zero shear viscosity values at 0 °C agree fairly well, at intermediate shear rates (0.03 s⁻¹ to 0.3 s⁻¹) the certified values are significantly higher than the measurement data. Closer observation of the transient behavior of the viscosity at these shear rates clearly indicates that with the measurement times chosen to produce the certified values, the viscosity is not at a steady state. Extended measurements, both oscillatory and rotational, have been performed at 0 °C, 25 °C, and 50 °C. A new data set for the SRM 2490 is provided for the shear viscosity, the normal force, and G’ and G”, respectively. This allows researchers to still use this excellent sample as a unique non-Newtonian standard material.

Rheological testing of UV curing materials

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The challenge for studying fast changing systems with rheology such as UV initiated polymerization and crosslinking is multifold. These materials react within seconds and the modulus change over 2 to 3 decades. UV light has to irradiate the sample homogeneously over a short time period and fast data acquisition is required for capturing the modulus change during the reaction. An option for UV curing, using parallel plate has been designed for the ARES rheometer. A fast data sampling device with a new correlator has been developed, to provide up to 500 dynamic mechanical data points per second, so the modulus build up can be easily followed. Results are obtained for an acrylate based pressure sensitive adhesive. The curing reaction is being studied as a function of the sample gap, UV intensity and UV exposure time.
Serial rheological characterization of materials represents an unacceptable bottleneck toward research progress, product development, or customer support; however, apparatus for parallel rheological analyses to alleviate this problem have not been developed. In a previous presentation we described a design of a combinatorial squeezing-flow instrumental setup to characterize asphalt. The idea behind this combinatorial rheometer was to characterize the rheological behavior of asphalt under different temperatures and wide shear stresses in a single run. The current implementation of this design comprises a two-dimensional array of nine circular squeezing-flow elements. After pre-conditioning, the specimens are subjected to squeeze flow under vacuum. The changes in the sample diameters are then recorded using a digital camera at desired intervals. We describe here a modified instrument wherein the array features a temperature gradient in one direction and applied stress or material in a Latin-square design along the 2nd dimension. For temperature-gradient control, two constant-temperature circulating baths are connected to coring on each end of the array. Results obtained for selected asphalts will be presented, along with details of the data acquisition and processing. Funding by the UCONN Joint Highway Research Advisory Council and the CT DOT (JH 03-7) is acknowledged.

Are entanglements stable? For how long? What entanglements are we talking about?

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The question is not whether the reptation model-with all its sophisticated ramifications-can describe rheological data well, in several viscoelastic ranges: it does. The question is whether it really describes what entanglements are, and the first question arises from defining the entanglement stability. In the classical view (the reptation model), the longest time for the existence of the tube is of the order of, say, 3 minutes, which characterizes the life-time, or the stability, of entanglements. But for the last 5 years, this author has published more than 20 papers which describe "disentanglement" effects and recovery from disentanglements ("re-sentanglement") which take place in the melt in hours, not minutes. Can the classical view describe the experiments reported on disentanglement and re-entanglement? According to the alternative EKNET model of polymer melt deformation, going from Newtonian to non-Newtonian (shear-thinning) behavior does not need any disentanglement interpretation, is not a non-linear effect (in terms of stability of the entanglements), and there is a true change of the mechanism of deformation from pure diffusion to interactive coupling. In this model, the Newtonian behavior is described by the re-localization of the conformers, without deformation of the potential energy of their interaction, and shear-thinning, is due to the cooperative coupling of the interactions between the polymer macromolecules which form a network, the EKNET network. Disentanglement can be triggered by a mechanism of deformation similar to yielding, but occurring in the molten state, and redefines the structural state of interaction between coupled conformers belonging to adjacent macro-coils. The EKNET statistics describes well the very long relaxation times which define the re-organization of the entanglement state. The EKNET model will be presented and discussed at the meeting.

Effect of non-linear thermal history on the viscosity of polymer melts

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It is well known that the behavior of a polymer melt depends on its previous thermal history. When the polymer melt is slowly deformed, its flow behavior is in the linear (i.e. Newtonian) viscoelastic range, and the Boltzmann superposition principle describes the memory function of the melt, from which the future viscoelastic response can be derived, in particular the melt's viscosity and elasticity. At strain rates that are sufficiently high, non linear effects such as shear thinning are observed for pseudo-plastic melts, and it is more difficult to understand, from a molecular stand point, the effect of previous thermal history. Nevertheless, flow equations exist which describe the rheological properties quite well, for instance viscosity reduction by shear-thinning: a good example is the Carreau equation which calculates the viscosity of a polymeric melt at any temperature T and strain rate. It has now been discovered that it is possible to affect and control the rheological properties of a polymer melt by disentanglement/re-entanglement manipulation methods, applying the combination of longitudinal oscillation, rotational shear and vibration and melt extension coupled with drag flow in the non-linear viscoelastic regime. The method consists in "synthesizing" a given thermal history which influences the melt behavior upon re-heating after cooling. As a consequence, not just one but an infinite number of Carreau's equations apply to describe the melt behavior at various temperature and strain rates. We show that it is possible to render the melt, at will, either more pseudo-plastic, less pseudo-plastic, more viscous, more elastic, less viscous, less elastic, more strain hardening, less strain hardening, at least for a certain time (which describes the stability of the non-equilibrium entanglement state).
Using bead-spring repulsions to model entanglement interactions in Brownian dynamics of bead-spring chains
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We have developed a bead-spring Brownian dynamics simulation method for modeling the interaction between electrophoretically translating DNA strands and an immovable post. The use of a bead-spring approach will allow for the simulation of polymer chains too long to be simulated by bead-rod techniques. Our new method determines the shortest distance between individual springs and the post, calculates a repulsive force inversely related to the distance using an exponential form, and corrects for the rare situation when a spring passes beyond the post. We consider hairpin collisions with a single post in weak electric fields. We use the x-displacement, the spatial separation between a chain that collides with the post and an unhindered molecule translating at the free velocity, as a measure of the influence of the post on chain mobility, and to compare with previous simulations performed using a bead-rod method (Shaqfeh and Patel, 2003). Previously published results show that x-displacement is unchanged by increasing velocity in the limit of high Peclet number (Pe > 1.0). We find that x-displacement linearly increases with increasing velocity in the limit of low Peclet number (Pe < 0.1), and that our low Peclet results are consistent with those for the bead-rod model at Pe > 1.0. Our new method is a general one that allows us to compute the effects of entanglements in systems with rare entanglements and long chains that cannot be simulated by any other method.

Influence of molecular weight on the electrification of extruded linear polyethylene melts
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Contact of dissimilar materials produces an exchange of electric charges that is in general not symmetrical, then, when the materials are separated they become electrified. Electrification is the phenomenon of accumulation of an electric charge in a material. The electrification phenomenon has been lastly observed during the extrusion of linear polyethylene melts under strong slip conditions [Pérez-González, J. J. Rheol. 49, 571-583 (2005)]. In this work we present a study of the influence of molecular weight on the electrification of linear low-density polyethylene under continuous extrusion. The experiments were performed using a single screw extruder with different die materials under slip and no-slip conditions. The use of different die materials and extrusion conditions allowed the identification of two different mechanisms for the electric charge generation, as well as the dependence on processing conditions. It was found that the accumulated electric charge is a function of the shear stress, increases along with the polymer molecular weight, and shows a maximum when the extrusion is carried out under strong slip conditions.
The Society of Rheology 77th Annual Meeting, October 2005

Wednesday 6:00 Salon A

PO64

The effects of supercritical carbon dioxide and pressure on the rheological properties of high density polyethylene

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Supercritical carbon dioxide (SC-CO$_2$) is used as a physical blowing agent in the manufacture of plastic foam and as a plasticizer to reduce melt viscosity during processing. Pressure is also an important variable for processing, and the combined effects of dissolved SC-CO$_2$ and pressure on rheological properties must thus be known to achieve optimum processing conditions. However, until recently there was no method to measure these effects accurately. A high-pressure sliding plate rheometer in which the shear deformation, temperature, pressure, and CO$_2$ concentration are uniform, was used in the present study. Since the shear stress transducer senses the stress in the center of the sample, edge effects are not a problem. The effects of CO$_2$ and pressure on the viscosity, stress growth function, and creep compliance of a high-density polyethylene (HDPE) are presented. To separate the effects of pressure and CO$_2$, samples were first pressurized without CO$_2$, and then pressurized and saturated with CO$_2$. It was possible to use shift factors for pressure and CO$_2$ concentration to obtain a master curve.

Wednesday 6:00 Salon A

PO65

Polymer melt elasticity by rotational and capillary rheometers

Stanley P. Westphal

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The elastic response of commercial polymers is a fundamental characteristic of each material. The polymer processor's normally observe the effect of that elasticity is the die swell observed upon extrusion. However, there are other less obvious effects that occur as a result of differences in elasticity. Increasing melt elasticity causes increases in elongational viscosity which in turn causes a reduction in the maximum spinning speed when making polypropylene face yarn for carpeting. Lower elasticity causes a reduction in the flexural modulus of polypropylene, lower melt strength during film extrusion or blow molding, etc. Many rheologists characterize elasticity dynamically with cone-plate geometry or parallel plate geometry over a range of frequencies and compare the elastic modulus, $G'$, to a constant loss modulus, $G''$. Another technique is to measure the First Normal Stress Difference (N1) in steady shear and as expected at the same shear the relation was independent of material. The purpose of these experiments was to create a simple model to characterize material elasticity and to relate dynamic measurements to steady shear measurements important to processors. Measurements of the steady shear response in a rotational mode are limited to very low shear rates. Comparison of dynamic measurements of $G'$ vs. the Complex Stress yields a unique, pre-exponential number termed the Elastic Index which increases from 10$^{-6}$ for a high molecular weight, newtonian viscosity standard to ca.1 for the most elastic material. Since it is also independent of temperature and material, it is a real material constant. The Elastic Index varies directly with the Area Swell Ratio at constant shear using a L/D=0 capillary with the pre-exponential coefficient varying with shear rate. Since the Elastic Index is a material constant the Area Swell can be predicted as a function of shear rate and capillary L/D at any melt temperature.

Wednesday 6:00 Salon A

PO66

Linear viscoelasticity, extensional rheology and melt fracture of polyethylene blends

Omar Delgadillo-Velazquez$^1$, Savvas G. Hatzikiriakos$^2$, Martin Sentmanat$^1$, and James Feng$^1$

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Two kinds of blends were carried out mixing commercial polyethylenes. A Ziegler Natta, film grade, linear low-density polyethylene (LL3001.32), was blended in each case with a different low-density polyethylene; first, a coating grade (LD200), and second, a film grade (EF606). The weight fraction of the low-density polyethylenes in the blends being from 1%, 5%, 10%, and 20%. Flow curves were done in a flow rate controlled capillary extruder with a die of 0.762 mm diameter, and L/D=32 at 150 °C. The appearance of the extrudates indicate that for both type of the blends, and all their compositions, the onset of sharkskin is not delayed of eliminated, as would be expected, since the LDPE content of the blends, showed that the initial stress growth region is the same, regardless the content of LDPE in the blend. The strain hardening was observed at higher deformation rates and longer times, which suggest the effect of the presence of long chain branching in the blends.
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Plenary Lectures

8:30 AM  Salon 1 & 2

Monday, October 17  Modeling and simulation of dynamics of polymeric solutions: Progress and challenges
Bamin Khomami
Department of Chemical Engineering, Washington University

Tuesday, October 18  Thixotropy or «inelastic» time dependency
Bingham Lecture
Jan Mewis
K. U. Leuven, Belgium

Wednesday, October 19  Some amusing examples of polymer rheology: Knotted DNA and microfluidic logic
Stephen Quake
Bioengineering Department, Stanford University

Social Program

Sunday, October 16  Welcoming Reception
7:00 PM – 9:00 PM  Stanley Park Ballroom
Sponsored by a generous contribution from TA Instruments

Monday, October 17  Awards Reception
7:00 PM  Salon 1 & 2
Sponsored by a generous contribution from Xpansion Instruments

Awards Banquet
7:30 PM  Salon 1 & 2

Tuesday, October 18  Society Business Meeting
5:45 PM  Seymour

Wednesday, October 19  Poster Session Refreshments
6:00 PM – 8:00 PM  Salon A
Sponsored by a generous contribution from Malvern Instruments

The Society gratefully acknowledges the generous contribution from The University of British Columbia – Faculty of Applied Science. The Society also gratefully acknowledges the generous support of the event sponsors.