THE SOCIETY OF RHEOLOGY

72ND ANNUAL MEETING PROGRAM AND ABSTRACTS

Westin Resort
Hilton Head Island, South Carolina
February 11-15, 2001

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Meeting Schedule

Monday, February 12, 2001

8:30	L. Leibler (PL1)			
9:20	Coffee			
9:45	PF1	RT1	CG1	BC1
10:10	PF2	RT2	CG2	BC2
10:35	PF3	RT3	CG3	BC3
11:00	PF4	RT4	CG4	BC4
11:25	PF5	RT5	CG5	BC5
11:50	Lunch			
1:30	EF1	RT6	CG6	BC6
1:55	EF2	RT7	CG7	BC7
2:20	EF3	RT8	CG8	BC8
2:45	EF4	RT9	CG9	BC9
3:10	Coffee			
3:35	EF5	RT10	CG10	SC1
4:00	EF6	RT11	CG11	SC2
4:25	EF7	RT12	CG12	SC3
4:50	EF8	RT13	CG13	SC4
5:15	End			
5:30	Poster Session & Refreshments			
7:00	Society Reception			

Tuesday, February 13, 2001

8:30	L. G. Leal (PL2)			
9:20	Coffee			
9:45	PF6	RT14	FD1	SC5
10:10	PF7	RT15	FD2	SC6
10:35	PF8	RT16	FD3	SC7
11:00	PF9	RT17	FD4	SC8
11:25	PF10	RT18	FD5	SC9
11:50	Lunch			
1:30	EA1	RT19	FD6	SC10
1:55	EA2	RT20	FD7	SC11
2:20	EA3	RT21	FD8	SC12
2:45	EA4	RT22	FD9	SC13
3:10	Coffee			
3:35	EA5	AS1	FD10	SC14
4:00	EA6	AS2	FD11	SC15
4:25	EA7	AS3	FD12	SC16
4:50	EA8	AS4	FD13	SC17
5:15	End			
5:30	Business Meeting			
7:00	Awards Reception			
8:00	Awards Banquet			

Wednesday, February 14, 2001

8:30	R. K. Prud'homme (PL3)			
9:20	Coffee			
9:45	FB1	AS5	FD14	SC18
10:10	FB2	AS6	FD15	SC19
10:35	FB3	AS7	FD16	SC20
11:00	FB4	AS8	FD17	SC21
11:25	FB5	AS9	FD18	SC22
11:50	Lunch			
1:30	FB6	AS10	MS1	SC23
1:55	FB7	AS11	MS2	SC24
2:20	FB8	AS12	MS3	SC25
2:45	FB9	AS13	MS4	SC26
3:10	Coffee			
3:35	FB10	AS14	MS5	SC27
4:00	FB11	AS15	MS6	SC28
4:25	FB12	AS16	MS7	SC29
4:50	FB13	AS17	MS8	SC30
5:15	End			

Thursday, February 15, 2001

8:05	LC1	AS18	MS9	MR1
8:30	LC2	AS19	MS10	MR2
8:55	LC3	AS20	MS11	MR3
9:20	LC4	AS21	MS12	MR4
9:45	Coffee			
10:10	LC5	AS22	MS13	MR5
10:35	LC6	AS23	MS14	MR6
11:00	LC7	AS24	MS15	MR7
11:25	LC8	AS25	MS16	MR8
11:50	LC9	AS26	MS17	MR9
12:15	End			

Session Codes

AS = Associating Polymers and Surfactant Systems
BC = Blends and Co-polymers
CG = Rheology in Confined Geometries and Microfluidic Applications
EA = Elastomers, Adhesives & Soft Solids
EF = Extensional Flow & Extensional Rheometry

FB = Food and Biopolymers
FD = Non-Newtonian Fluid Dynamics & Flow Stability
LC = Liquid Crystalline Systems
MR = Microscopic Rheology & Single Chain Dynamics: Experiments & Analysis
MS = Polymer Melts and Solutions

PF = Rheology in Processing Flows
PL = Plenary Lectures
RT = Rheology & Topology
SC = Suspensions and Colloidal Systems

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Monday Morning

Symposium PL
Plenary Lectures

Monday   8:30   Archer   PL1
YIELD, SLIP & AGING: THE FATE OF SOFT DISPERSIONS
<u>Ludwik Leibler</u>
CNRS/ATOFINA, Levallois Perret, France

We will present our recent investigations of concentrated dispersions made of soft polyelectrolyte microgel particles. The flow properties of these systems can be nicely tuned by changing the molecular parameters and environmental conditions. Our studies bring a new insight to the relation between the local microstructure and the macroscopic rheological behavior. We have observed intriguing yield, slip and physical aging phenomena which seem to be quite universal. It is thus tempting to argue that the lessons learned from microgel pastes can be relevant to other concentrated dispersions.

Symposium PF
Rheology in Processing Flows

Organizers: William H. Hartt and Michael E. Mackay

Monday   9:45   Lady Davis   PF1
MAKING MICROPOROUS SEMICRYSTALLINE POLYMERS BY A MELT EXTRUSION PROCESS
Matthew Johnson, Jiannong Xu, and <u>Garth L. Wilkes</u>
Chemical Engineering, Virginia Polytechnic Institute & State University, Blacksburg, VA 24061

In this paper, we address the features of a given crystallizable polymer to be able to promote a microporus morphology through use of a melt extrusion/annealing/stretching process. While this process has been utilized to promote such microporous films using linear high density polyethylene and isotactic polypropylene, we extend our investigations to include isotactic poly-1-butene, isotactic poly-4-methyl-1-pentene, polyoxymethylene and polyvinylidene fluoride. We conclude that in addition to certain required features of the melt process itself, the polymer in turn most also possess certain characteristics for achieving the desired microporosity.

Monday   10:10   Lady Davis   PF2
SHEAR INDUCED PE ALIGNMENT IN THE TLCP/PE BLEND SYSTEM
<u>Chi-Kwong Chan</u> and Ping Gao
Department of Chemical Engineering, Hong Kong University of Science and Technology, Hong Kong

A thermotropic copolyester containing p -hydroxybenzoic acid, hydroquinone and sebacic acid (HBA/HQ/SA), denoted as TLCP 3, has been found to be as an outstanding processing aid for high molecular mass polyethylene. By adding 1wt% of TLCP 3, a bulk apparent shear viscosity reduction of 95% is observed. Such a drastic viscosity reduction effects have been found to be caused by the strong interaction between the highly aligned TLCP molecules within the dispersed phase and those PE molecules close to their vicinity. The interaction between TLCP and PE

under the shear flow was studied by means of X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM) and rheological measurements. The X-ray diffraction revealed that shear flow produces strong TLCP alignment along flow direction when embedded in a molten PE matrix. In the steady shear optical studies, the induction time for PE crystallization is much shorter when they were close to highly aligned TLCP3 phase. Capillary rheometry measurements of flow curves show a strong hysteresis effect, where the apparent shear viscosity is much lower when measured in decreasing shear rate direction. SEM micrographs of blend extrudates show strong PE alignment on the surface with PE lamella crystal surfaces parallel to flow axis. In conclusion, the viscosity reduction effects induced by a small amount of TLCP 3 inclusion may be attributed to the alignment induced mesophase formation within PE phase caused by the strong interaction between the two phases at high shear stresses.

Monday   10:35   Lady Davis   PF3
FLOW VISUALIZATION OF DROP DEFORMATION IN A 3D MIXING CAVITY
Dennis J. Ternet, Olexei S. Galaktionov, Patrick Anderson, Gerrit Peters, and Han Meijer
Materials Technology, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands

An understanding of the mixing process is fundamental to the successful use of polymer blending as an economical means of producing polymers with customized properties. Using a front tracking method, we have simulated drop deformation in a 3D mixing cavity and shown the existence of periodic structures (regions of very poor mixing) for a given mixing protocol. This tracking method is computationally expensive even for a simple geometry such as a cube so a mapping approach was developed which successfully matches the more rigorous tracking method while allowing mixing efficiencies, for a given mixing protocol, to be calculated in a matter of minutes instead of days. The link between our simulations and experiments has yet to be verified and that is the goal of this work.

We present new flow visualization experiments with a 3D mixing cavity consisting of a 5x5x5 cm cube in which two of the opposing faces are glass plates attached to stepper motors allowing movement in the x and y directions. This setup allows us to experimentally duplicate the mixing protocols used in the simulations. The initial experiments are aimed at reproducing the qualitative features of the simulations, namely the existence of periodic structures or islands in which the material points periodically return to their original position after n periods. Later, we make quantitative comparisons between the drop deformation predicted by the simulations and that visualized in the experimental mixing cavity.

Monday   11:00   Lady Davis   PF4
PARALLEL VISCOELASTIC SIMULATIONS OF CYLINDRICAL DOUGH MIXING FLOWS
Ahsanullah Baloch, Phil W. Grant, and Mike F. Webster
Institue of non-Newtonian Fluid Mechanics, Computer Science, University of Wales Swansea, Swansea SA2 8PP, Wales, United Kingdom

Simulations of two-dimensional incompressible complex flows of viscoelastic fluids are presented. The context is one of food mixing within a cylindrical vessel, where stirrers are located on the lid of the vessel. Here, the motion is considered as driven by the rotation of the outer vessel, with various stirrer locations. With a single stirrer, both a concentric and an eccentric configuration are adopted. An eccentric case with two stirrers is also contrasted against the above, where a symmetrical arrangement is assumed. The numerical method is based on a finite element semi-implicit time-stepping Taylor-Galerkin/Pressure-Correction scheme, posed in a cylindrical polar coordinate system. Simulations are conducted via distributed parallel processing using PVM. For viscoelastic fluids, a constant viscosity Oldroyd-B and two shear-thinning Phan-Thien/Tanner constitutive models are employed, of linear and exponential form. Comparisons are made for various rheological properties and their respective influences analysed upon the flow. Variation with increasing speed of mix and change in mixer geometry are investigated, with respect to the flow kinematics and stress fields produced.

Monday   11:25   Lady Davis   PF5
PRESSURE DROP OF VISCOELASTIC FLUIDS FLOWING THROUGH POROUS MEDIA
Wolfgang Gleissle
Chemieingenieurwesen, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

Porous media are systems of single flow channels with periodicaly changing cross-sectional areas. So, the pressure drop of a viscoelastic fluid flowing through a porous system is a combination of viscous and elastic effects. Assuming that the entrance pressure loss of a contraction is proportional to the first normal stress difference N1 (as the Bagley-correction term), the total pressure drop of an average channel should be a simple superposition of viscous pressure drop (which is proportional to the length of the channel) and the elastic pressure drop (which should be proportional to the number of contractions). Applying the concept of the shear stress equivalent inner shear rate, the change of the inner hydrodynamics of a package with respect to a simple cylindrical tube can be characterized by a single number (independent of the flow function of the fluid). So, the average inner shear stress and the average inner normal stress difference can be defined for a given volume flow rate. For viscoelastic fluids with known shear and normal stress functions the pressure drop over a model package, a glass bead and quartz particle package, could be predicted over a range of 5 decades of volume rates. Average size of the beads and the length of the packages have been varied. At high volume rates the pressure drop generated from the elastic fluid properties is as high as the pressure drop generated from the viscosity alone.

Symposium RT
Rheology & Topology

Organizers: Jay Janzen and Tom C. B. McLeish

Monday   9:45   Drayton   RT1
INFLUENCE OF LONG-CHAIN BRANCHING ON LINEAR VISCOELASTIC PROPERTIES OF POLYETHYLENE MELTS
Claus Gabriel and **Helmut Münstedt**
Institute of Polymer Materials, University of Erlangen-Nürnberg, Erlangen, Bavaria 91058, Germany

This contribution intends to present a survey on the influence of long-chain branching on linear viscoelastic properties of polyethylene melts. The materials chosen are linear and slightly long-chain branched, metallocene-catalyzed polyethylenes of narrow molecular mass distribution as well as linear and highly long-chain branched polyethylenes of broad molecular mass distribution. The molecular characterization of the polyethylenes is performed by size exclusion chromatography coupled with light scattering for the determination of the radius of gyration, which allows for the qualitative comparison of the degrees of branching of the polyethylenes investigated. The linear viscoelastic properties zero shear rate viscosity and steady-state recoverable compliance are determined in shear creep recovery by a magnetic bearing torsional creep apparatus. The slightly long-chain branched polyethylenes exhibit a surprisingly high zero shear rate viscosity in comparison to linear polyethylene whereas the highly branched polyethylenes have a much lower viscosity compared to linear samples. The investigation of the influence of long-chain branching on steady-state compliance leads to new insights. Slightly long-chain branched polyethylenes have got a higher elasticity in comparison to linear products of similar polydispersity, whereas the highly long-chain branched polyethylenes of broad molecular mass distribution exhibit a surprisingly low elasticity. The dependence of zero shear rate viscosity and steady state compliance on the degree and structure of long-chain branching and molecular mass will be interpreted by comparison with rheological results from literature on model branched polymers of different molecular topography and chemical composition. This comparison suggests a more generalized view on the influence of long-chain branching on linear viscoelastic properties of polymer melts, which is based on the branching structure, the molecular mass and the entanglement densities of different types of polymers.

Monday   10:10   Drayton   RT2

MICRORHEOLOGY OF STAR/LINEAR POLYMER BLENDS

Jung-Hun Lee[1] and Lynden A. Archer[2]
[1]Chemical Engineering Department, Texas A&M University, College Station, TX 77843-3122;
[2]Cornell University, Ithaca, NY

Blends of linear and star-like macromolecules have long been recognized as useful model systems for investigating the effects of tethering on polymer relaxation dynamics. More recently, these systems have been observed to provide an important means of evaluating molecular theories for branched polymer rheology. We report results from a detailed study of linear and nonlinear shear rheological properties of narrow molecular weight distribution blends of well-entangled linear and six-arm star 1,4-polybutadiene melts. It is shown that the star arm contribution to terminal blend properties is well described by a constraint release dynamic process even at relatively high star compositions, where entanglements between star arms are important. In steady shear flow, early power-law deviations from Newtonian fluid response are also discussed in terms of constraint release dynamics and arm/arm entanglements in quiescent star/linear polymer blends. A detailed comparison of frequency-dependent star/linear blend properties in oscillatory shear flow with predictions from molecular theories suggest that the Rouse hopping time Te of entanglement points in the blends is not universal, but rather depends sensitively on the blend composition and star arm molecular weight. This observation is discussed in terms of the effect of chain ends on the segmental jump time in the blends. Our results also underscore the need for more detailed knowledge of the molecular weight and composition dependencies of the constraint release relaxation time as a prerequisite for reasonable theoretical predictions of linear/branched polymer blend rheology.

Monday   10:35   Drayton   RT3

SHEAR AND EXTENTENSIONAL PROPERTIES OF STAR POLYSTYRENE SOLUTIONS

Xiangnan Ye and Tam Sridhar
Chemical Engineering, Monash University, Melbourne, Victoria, Australia

The rheological properties of star polystyrene solutions are investigated at 3 different concentrations from 10% to 20%. The arm retraction model of Milner and McLeish are used to model the dynamic data for these solutions.The model is able to describe the data very well and enables the relaxation time of an entanglement segment to be obtained.

The same solutions were examined in the filament stretching rheometer. Over a range of strain rates, a steady state in extension was achieved. The data show some remarkable similarity to the extensional viscosity of linear polystyrenes. However, significant differences remain and are analysed using the time scales obtained from the dynamic data.

Monday   11:00   Drayton   RT4

STRESS RELAXATION IN STAR POLYMER MELTS

Daniel A. Vega, John M. Sebastian, William B. Russel, and Richard A. Register
Department of Chemical Engineering, Princeton University, Princeton, NJ 08544

Recently, Milner and McLeish [*Macromolecules*, **30**, 2159 (1997)] have presented a parameter-free theory for the stress relaxation of low-functionality star polymer melts. This theory, based on the concepts of arm retraction and dynamic dilution, achieves very good agreement with dynamic rheological measurements of low-functionality star polymer melts. In the Milner-McLeish (MM) theory, the dynamic moduli are determined through an approximation of the first passage-time (FPT), which is related to the time required for each arm to escape from its original tube. Although the approximation is valid only for stars where the arms participate in a high number of entanglements, this theory has been applied successfully to systems that clearly do not satisfy this assumption. In this work we calculate the FPT exactly and determine the corresponding dynamic and relaxation moduli. Comparing the MM results with our solution indicates the range of applicability of the MM approximations. In addition, our exact expression for the FPT allows us to analyze several viscoelastic properties: the terminal relaxation time, the steady-state recoverable compliance, the zero-shear viscosity and the scaling of the characteristic frequency obtained from the maximum in the loss modulus with the arm molecular weight.

Monday 11:25 Drayton RT5

RHEOLOGY OF THREE-ARM ASYMMETRIC STAR POLYMERS
Amalie Frischknecht[1], Scott T. Milner[1], Rhoda M. Hawkins[2], Tom McLeish[2], Ron N. Young[3], and Andrew Pryke[3]
[1]Research and Engineering Co., ExxonMobil, Annandale, NJ; [2]Polymer IRC, University of Leeds, Leeds, United Kingdom; [3]Department of Chemistry, University of Sheffield, Sheffield, United Kingdom

We present experimental and theoretical results for the linear rheology of melts of entangled, three-arm asymmetric polyisoprenestars. Asymmetric three-arm stars, in which two arms have the samelength and the third is shorter, cross over from star-like to linear-like stress relaxation as the length of the third arm varies. We combine recent theories of stress relaxation in symmetric stars and in linear melts to predict the dynamic modulus of the asymmetricstars. Our theory underestimates the effective drag caused by the short arm by a factor of about 100, even when polydispersity effectsare included. This unexplained discrepancy does not appear in a recent comparison of a related theory with measurements on polyisoprene H-polymers.

Symposium CG
Rheology in Confined Geometries and Microfluidic Applications

Organizers: Andrea Chow and Ronald G. Larson

Monday 9:45 Elliott CG1

LATERAL DISPERSION OF PARTICLES AND MAMMALIAN CELLS IN MICROCHANNELS
Ben Wang, Andrea W. Chow, and Michael Spaid
Caliper Technologies Corp., Mountain View, CA 94043

We are developing microfluidic devices to perform a variety of biochemical assays using minute quantities of reagents and with faster analysis times. In many applications, biological molecules such as proteins and nucleic acids are dissolved homogeneously in aqueous buffers flowing in microchannels. Other applications require transport of suspended particles such as mammalian cells in microchannels. In certain cases, it is useful to focus the cells into a narrow region of a microchannel to study the characteristics of one entity at a time. During hydrodynamic focusing of particles in microfabricated channels using pressure-driven flow, we observe that particles initially focused into one region of a microchannel tend to disperse laterally with time. The particles are non-Brownian, with diameters of about 5 to 20 micrometers. The flows are characterized by a low Reynolds number (0.1 to 0.01); the observed lateral dispersion is thus unlikely to be due to inertia. The dispersion rate, measured by video imaging and analysis of a large population of particles or cells, is a strong function of particle concentration. In this paper, we will present experimental measurements of dispersion rate of hard spheres and slightly deformable mammalian cells. We will also discuss possible mechanisms causing the lateral dispersion.

Monday 10:10 Elliott CG2

MICROCHANNELS FOR THE STUDY OF POLYMER SOLUTIONS
Bruce B. Caswell, Kenneth S. Breuer, and Peter D. Richardson
Division of Engineering, Brown University, Providence, RI 02912

The design and construction of micro-channels with gaps of 10 to 50 microns will be presented. The channels are intended for the study of both steady and unsteady flows of biopolymers. The instrumentation of such channels for measurement of bulk flow rate, pressure loss and local velocities will be discussed. Fabrication by Thermal oxide growth for very small gaps, or the Silicon-on-wafer(SOI) process for the larger ones, guarantees dimensional uniformity of the gaps and smoothness of the crystalline, flat surfaces which define the channels. Designs which effectively eliminate edge- and end-effects can easily be achieved due to the very small gaps. The scale of the gaps suggests that polymer solutions flowing in such channels will exhibit wall slip. Experiments are being carried out with polymer solutions known to exhibit slip in macro-scale equipment, such as those of Cohen & Metzner(J. Rheol. 29, 67(1985). Their data of have been used to estimate slip effects in the microchannels.

Monday   10:35   Elliott   CG3
RHEOLOGY OF PERFLUOROPOLYETHERS WITH POLAR END GROUPS

Tom E. Karis and Bruno Marchon
ARC, IBM, San Jose, CA 95120-6099

Perfluoropolyethers offer a wide range of physical properties suitable for tribological applications. Low temperature rheological measurements were done on representative samples of commercially available perfluoropolyethers: Fomblin Z, Demnum, and Krytox with and without polar end groups. Viscoelastic master curves of bulk perfluoropolyethers derived from measurements cover the range of reduced frequency from the terminal region through the rubbery plateau. The cooperative flow model of Adam and Gibbs, in conjunction with the WLF equation, provides a relationship between the fluid relaxation times and the configurational entropy. This relationship predicts a dramatic lengthening of relaxation times for molecularly thin films on surfaces due to their loss of configurational entropy. These bulk rheological measurements provide insight into the dynamic response of thin perfluoropolyether films in elastohydrodynamic lubrication and magnetic recording.

Monday   11:00   Elliott   CG4
SURFACE RHEOLOGY OF MONOLAYERS OF PHYSICAL NETWORK-FORMING PEG LIPOPOLYMERS AT THE AIR-WATER INTERFACE: A STUDY ABOUT MOLECULAR WEIGHT AND TIME DEPENDENCE OF RHEOLOGICAL PROPERTIES

John P. Coffman and **Christoph A. Naumann**
Chemistry, Indiana University Purdue University Indianapolis, Indianapolis, IN 46202-3274

We will present recent surface-rheology experiments on amphiphilic PEG lipopolymers, which have been reported to form two-dimensional physical networks at the air-water interface [1]. Our experiments focus on two new aspects of surface rheological properties in the postgel region: (1) their molecular weight dependence over a larger range (MW of the polymer chains used: 550, 750, 1000, 2000, 3000, 5000) and (2) their time dependence. In the first case, we found that the storage moduli show a power law-like behavior with their scaling exponents being independent of the molecular weights investigated and with their absolute values (for a given area per molecule) being dependent on molecular weight. In the second case, the study of time-dependent rheological properties in the postgel region, we observed a significantly different behavior between lipopolymers with shorter (MW: 550-1000) and longer (MW: 2000-5000) polymer chains. This observation can be attributed to the various competing interactions acting upon the physical network. In order to obtain a more complete model of the interactions involved in this gelation process, we also performed temperature and shear-amplitude-dependent experiments.

[1] Naumann, C.A., Brooks, C.F., Fuller, G.G, Knoll, W., Frank, C.W. (1999) Langmuir 15, 7752.

Monday   11:25   Elliott   CG5
DIRECT MEASUREMENT OF APPARENT SLIP IN SHEAR-THICKENING WORMY MICELLE SOLUTIONS

Hua Hu and Ronald G. Larson
Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109

The rheological behaviors of low-concentration solutions of wormy micelles are characterized by shear-thickening behavior apparently due to the formation of shear-induced structures (SIS) and by a gap-dependent shear viscosity (Hu et al. 1998), indicative of a layered flow. Here, the rheological properties of a surfactant solution (CTAB/NaSal) are measured in a cone-plate rheometer, and again, both shear thickening and gap-dependent rheology are observed. In order to examine whether the shear-thickening behaviors are due to the stratification of flow, particle image velocimetry is developed and applied to measure the velocity profile in a plate-plate flow cell. We note that the velocity profiles at different shear rates show two clear layers with different shear rates, with the high-shear rate ¡°slip¡± layer closest to the moving surface. The thickness of slip layer does not change with shear rate increasing for a given gap and it is also independent of the gap, i.e., the thickness of slip layer does not vary with the gap varying. The results obtained by microscopy show that the transition shear rate for shear thickening is close to the measurements by rheometer. We find that small-amplitude vibrations in the motion of the moving surface are enormously amplified in the resulting velocity field of the wormy micellar solution, in contrast to Newtonian fluids,

which damp these vibrations. The large-amplitude velocity fluctuations in the wormy micellar solution can be eliminated only by careful smoothing of the motion of the motor driving the rotating plate.

Hu, Y.T, P. Boltenhagen, E. Matthys, D.J. Pine, J. Rheology 42, 1209-1226 (1998)

Symposium BC
Blends and Co-polymers

Organizers: Nitash Balsara and Ramanan Krishnamoorti

Monday   9:45   Heyward   BC1
RHEOLOGICAL BEHAVIOR OF MODEL IMMISCIBLE POLYMER BLENDS. PREDICTION OF COMPONENT AND INTERFACIAL CONTRIBUTIONS
Thomas Jansseune, Paula Moldenaers, and Jan Mewis
Department of Chemical Engineering, K.U. Leuven, Leuven 3001, Belgium

The rheological behavior of immiscible blends during certain well-defined flow histories can be modeled quite accurately. Earlier studies mainly focused on the evolution of the contribution of the interface to the stress tensor during transient flows as relaxation after steady state shear flow and start-up flows at high capillary numbers. This is extended here to include the detailed rheology at low capillary numbers and the direct contribution of the components to the stress. Based on the morphology evolution proposed by Maffettone and Minale for single droplets the interface contribution to the stress of dilute blends can be calculated. From stress relaxation measurements this interface contribution can be deduced independently, without assuming any mixing rule to account for the component contribution to the stress. Experimental data for start-up and steady state shear flow and for the relaxation of stresses afterwards compare quite well with model predictions. the effect of important morphology changes on the component contribution, as e.g. during a sudden start-up of flow, was evaluated. For blends with Newtonian components, experimental evidence seems to indicate that the effect is rather small.

Monday   10:10   Heyward   BC2
MEASUREMENTS OF THE INTERFACIAL TENSION IN NON-NEWTONIAN BLENDS BY RHEO-OPTICAL TECHNIQUES
Francesco Greco[1], Manlio Tassieri[2], and Nino Grizzuti[2]
[1]Istituto per la Tecnologia dei Materiali Compositi ITMC-CNR, Napoli 80125, Italy;
[2]Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli Federico II, Napoli 80125, Italy

The measurement of interfacial tension in polymer blends is a difficult task. This is especially true for non-Newtonian fluids, and when the presence of elasticity may produce a "dynamic" interfacial tension which is different from the corresponding "static" value. In this work, we present an original method to determine the interfacial tension through rheo-optical measurements of flow-induced drop distortions. We use drops of a polyacrilamide aqueous solution (a highly elastic, shear thinning liquid) immersed in a polyisobutylene matrix.

A counter-rotating shearing device with transparent plates is used to measure drop distortions by means of an image acquisition and analysis system. The cell geometry allows for a "top view" of the deforming drop, i.e., along the velocity gradient direction. Two different quantities are monitored, namely, the drop axis in the vorticity direction, and the rotation period of the drop surface.

The experimental results are interpreted in terms of perturbative theories, where the small deformation perturbation parameter is the Capillary number. Since Taylor first order theory cannot predict the observed behaviour, higher order models are considered. If an appropriate viscosity ratio is chosen, which accounts for the shear thinning behaviour of the drop phase, good agreement is found between measurements and theoretical predictions. As a result, a robust estimate of the blend interfacial tension is obtained.

Monday   10:35   Heyward   BC3

APPLICATIONS OF A CONSTITUTIVE MODEL FOR DISPERSIVE MIXTURES

Patrick Anderson[1], Rich Schiek[2], Gerrit Peters[2], and Han Meijer[1]
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Two problems are central in the engineering of dispersions. One considers the influence of dispersed phase microstructure on material properties. The other addresses achieving a particular morphology. The morphology in a blend results from the interaction between a frequently complex or chaotic flow, and coalescence and breakup. The mixing is crucial, and , in some cases, it is possible to tailor a morphology with a flow. However, the modeling of this process is incomplete. Presently, no model can fully predict the spatial statistics of dispersed phase morphology. A further complication is that the dispersed phase influences the macroscopic rheology of the blend. Einstein first demonstrated this behavior by showing that the effective viscosity of a system increased with dispersed phase volume fraction of solids. Later, Taylor extended Einstein's results to allow for a dispersed phase of spherical liquid droplets. Recent developments in this area, allow for larger deformations, and coalescence and breakup. However, this area is relatively new with many inconsistencies in the literature. Furthermore, these newer phenomenological models contain a variety of adjustable parameters. The two interrelated goals of our work are a model for the spatial evolution of dispersed phase microstructure, and a rheological description of liquid-liquid systems. The former is accomplished by coupling pre-existing models of coalescence and breakup with the kinematics of mixing processes. We develop the latter by unifying the theory of the present phenomenological models for rheology, and by applying the description of the dispersed phase microstructure provided by our model to remove the adjustable parameters presently in the rheology models. A DEVSS-DG finite element implementation of the model is presented and results are shown for steady shear flow and the flow between two eccentric cylinders.

Monday   11:00   Heyward   BC4

THE INFLUENCE OF ELASTICITY ON THE DISPERSED-PHASE DROPLET SIZE OF HDPE/PS BLENDS

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The influence of elasticity of the blend constituent components on the size and size distribution of dispersed phase droplets is investigated for blends of polystyrene and high density polyethylene under a simple shearing flow. The elasticities of the blend components are characterized by their first normal stress differences. The role played by the ratio of drop to matrix elasticity at fixed viscosity ratio was examined by using high molecular weight polymer melts, HDPE and PS, at temperatures at which the viscosities matched, or differed by a factor of close to two. The experiments were conducted by using a cone-and-plate rheometer. The resulting ensemble mean averages and volume-mean averages of droplet diameter at steady-state morphology were determined. Compared with Newtonian systems, the viscoelastic drops are more difficult to break than the Newtonian drops. From the steady-state dispersed-phase droplet diameters, the steady-state capillary numbers, Ca, defined as the ratio of the viscous shearing stress over the interfacial tension stress were calculated. The resulting steady-state capillary numbers were determined as a function of the drop/matrix first normal stress difference ratio. For the blend systems with viscosity ratio 0.5, 1 and 2, the values of steady-state capillary number were found to increase with the first normal stress difference ratio and followed a power law with scaling exponents between 1.7 - 1.9 .

References

1. Taylor GI *Proc. R. Soc. London, Ser A* 1934, **146**, 501.

2. Wu S *Polymer. Eng. Sci.* 1987, **27**, 335.

3. Sundararaj U, Macosko CW *Macromolecules* 1995, **32**, 1814.

4. Mighri F, Carreau PJ, and Ajji A *J Rheol* 1998, **42**, 1477.

Monday   11:25   Heyward   BC5
COALESCENCE IN COMPATIBILIZED POLYMER BLENDS
Peter Van Puyvelde, Sachin Velankar, Jan Mewis, and Paula Moldenaers
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Block copolymers are commonly used to stabilize the morphology in polymer blends. The conventional view of the role of block copolymers in promoting emulsification is that they reduce interfacial tension and facilitate droplet break-up. However, recent experiments (e.g. Macosko et al., 1996; Hu et al., 2000) have challenged this long-standing idea by suggesting that an additional effect of copolymers is to inhibit coalescence. In this paper, systematic coalescence experiments are reported on a model blend consisting of PIB/PDMS, with and without the addition of a PIB/PDMS block copolymer as compatibilizer. Relevant parameters such as block copolymer concentration and shear rate have been varied which resulted in a detailed kinematic study of the coalescence process. It is shown that a mere reduction in interfacial tension is not able to explain the kinetics of the coalescence process. Moreover, it has been demonstrated that the presence of block copolymer has a significant effect on the initial coalescence rate and that in the presence of a compatibilizer, the coalescence process is blocked. A possible mechanism for the evolution of the droplet size during coalescence is proposed based on the existence of Marangoni stresses on the drop surface.

References

Macosko, C.W., Guegan, P. Khandpur, A., Nakayama, A., Marechal, P. and Inoue, I., Compatibilizers for melt blending: premade block copolymers, Macromolecules, 29, 5590-5598, 1996.

Hu, Y.T., Pine, D.J. and Leal, L.G., Drop deformation, breakup and coalescence with compatibilizers, Phys. Fluids, 12, 484-489, 2000.

Monday Afternoon

Symposium EF
Extensional Flow & Extensional Rheometry

Organizers: Shelley L. Anna and Kurt W. Koelling

Monday   1:30   Lady Davis   EF1
TRANSIENT EXTENSIONAL RHEOLOGY AND ELONGATIONAL FLOW INSTABILITIES OF POLYMER SOLUTIONS: ROLE OF POLYMER CONCENTRATION AND MOLECULAR WEIGHT

Octavia F. Brauner[1] and **Gareth H. McKinley**[2]
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[2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 01239

We investigate the influence of molecular weight and concentration on the transient extensional properties of a wide range of polystyrene solutions. In addition to monitoring the evolution of the tensile stress in a filament extensional rheometer (FiSER), the temporal evolution of the filament's spatial profile can be used to differentiate between the extensional response of dilute and concentrated polymer solutions. We summarize the results of filament stretching experiments on dilute, semi-dilute and concentrated entangled fluids over a spectrum of strain rates (0.1 to 7 s^{-1}) and Hencky strains (up to 6).

The correlation between the linear viscoelastic behavior and the composition of polymer solutions can be summarized in a Graessley diagram; i.e. a plot of molecular weight versus polymer concentration that shows criteria such as chain overlap (c*) and onset of molecular entanglement (Me). By varying the physical composition of solutions tested in the extensional rheometer we can probe the role of different molecular mechanisms in the growth of tensile stresses for each of the five regions identified in the Graessley diagram. The high viscosity of concentrated entangled fluids results in a close-to-ideal filament stretching behavior that is almost unaffected by gravitational sagging. However, little strain-hardening is obtained and observations show that the filament fails at moderate strains by a necking instability. By contrast, chain stretching and pronounced strain-hardening are observed in all the unentangled fluids which prevents filament necking, but ultimately leads to an elastic endplate instability. The onset of chain stretching in semi-dilute and concentrated entangled polymer solutions occurs at very high deformation rates and can be identified by the onset of strain-hardening and by the visual detection of transition from necking failure to elastic end-plate instability. These experimental trends are in agreement with the predictions of the Doi-Edwards-Marrucci-Grizzuti model.

Monday   1:55   Lady Davis   EF2
A TECHNIQUE FOR CHARACTERIZING COMPLEX POLYMER SOLUTIONS IN EXTENSIONAL FLOWS

Gavin Braithwaite and **Stephen H. Spiegelberg**
Cambridge Polymer Group, Somerville, MA 02143

Associative polymers are a class of copolymers that contain blocks of varying water solubility. The more hydrophobic blocks often try to associate to minimize their exposure to water. If the concentration is high enough, the polymer chains form a dynamic network that is subject to breaking and reforming under deformation and thermal effects, resulting in a range of rheological behavior. These materials are widely used as rheology modifiers in industrial chemical and medical applications, and the prevalence of extensional flows in these processes results in a need to observe the response of these complex materials to extensional deformation.

We present a technique for characterizing the behavior of associative polymer solutions when they are subjected to an extensional flow. Based on the work of Rozhkov and Entov (1996), we have constructed an extensional rheometer that rapidly stretches a small cylindrical fluid sample at a known rate. The instrument then monitors the breakup kinetics of the formed polymer filament as it "necks" under the combined effects of surface tension, viscoelasticity, and gravity. Measurements were made on a variety of complex solutions. We demonstrate that the shape and subsequent necking process of the formed filaments depends on the rate of deformation, a behavior not observed in simple fluids. This dependence is believed to be related to the association time scale of the materials. This technique permits the straight-forward examination of the extensional properties of the fluid, and allows determination of processing conditions that will lead to the formation of stable, reproducible filaments. This information is not obtainable from simple shear experiments, which were also performed as part of this study.

Monday   2:20   Lady Davis   EF3

ELONGATIONAL RELAXATION TIMES OF ELASTIC FLUIDS MEASURED BY MICRO-FILAMENT RHEOMETRY AND AXISYMMETRIC CONTRACTION FLOWS

Geoffrey M. Wise and **Geoffrey W. Reynolds**
Procter & Gamble, West Chester, OH 45069

Predicting the strain rate for the onset of strain-hardening or "stringy" behavior is of critical importance in liquid processing operations such as spraying, adhesive transfer, bottle filling, and spinning. In this work, we present the measured relaxation times of model fluids using different techniques: steady-shear rheometry, micro-filament rheometry, and both single-stage and two-stage axisymmetric contraction flows. The model elastic fluids used are semi-dilute solutions of polyacrylamide (M~300,000) in a honey-water solution. Each solution has a zero-shear viscosity approximately twice that of its high-shear-rate value, enabling a simple estimation of relaxation time from the transition in the steady-shear viscosity curve. The micro-filament rheometry setup used is similar to that described by Basilevskii and coworkers (ref. 1) and analyzed by Entov and Hinch (ref. 2). The single-stage contraction flow method is modeled on Collier's non-lubricated method (ref. 3), while the two-stage device is a novel combination of two contractions, with a higher strain rate in the downstream section. Good agreement is found among the extensional methods of determining relaxation time, but the shear rheometry results differ by about an order of magnitude. This disparity may be a result of the polydispersity in the polyacrylamide; the shear method gives more weight to the shorter polymers, while the extensional methods are more sensitive to the longest relaxation times in the samples.

References:

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#2: Entov-VM, Hinch-EJ, "Effect of a spectrum of relaxation times on the capillary thinning of a filament of elastic liquid" J. Non-Newtonian Fluid Mech. v.72 (1997) pp.31-53.

#3: Collier J.R., Romanoschi O., Petrovan S., "Elongational rheology of polymer melts and solutions", J Appl Polym Sci 69(12) 2357-2367 (1998).

Monday   2:45   Lady Davis   EF4

SPRAY DROP BREAKUP AND ELONGATIONAL VISCOSITY MEASUREMNTS OF DILUTE POLYMER SOLUTIONS

Robert K. Prud'homme[1], **Vera Smith-Romanogli**[1], and **Robin Dexter**[2]
[1]Department of Chemical Engineering, Princeton University, Princeton, NJ 08544; [2]Agricultural Products, BASF, Princeton, NJ 08540

Elongational viscosity plays a major role in the formation of drift-prone aerosols in agricultural pesticide and herbicide spraying applications. We will present data on the role of elasticity on the breakup of drops in highspeed air flows that simulate spraying from aircraft and the role of emulsion droplets on breakup of fan sprays. Instruments for measuring the elongational viscosity of dilute solutions have problems either imposing known kinematics of with Lagrangian unsteady deformations on the polymers. We will present data and discuss elongational viscosity measurements on an opposing jet viscometer (Rheometric RFX) and on a screen viscometer. The simplicity of the

screen viscometer makes it an attractive instrument for measuring elongational properties of dilute polymer solutions.

Monday   3:35   Lady Davis   EF5

STEADY UNIAXIAL ELONGATIONAL FLOWS: THE ROLES OF INTRAMOLECULAR POTENTIALS

Anand S. Bhandar and <u>John M. Wiest</u>

Department of Chemical Engineering, University of Alabama, Tuscaloosa, AL 35487

We examine the roles of several types of intramolecular interactions in the behavior of the steady elongational flow properties of infinitely dilute polymer solutions. In particular, bond stretching, bond bending, bond torsion, and non-bonded intramolecular interactions are included. Geometric and rheological properties are calculated using Monte Carlo integration. We observe that bond bending and non-bonded interactions result in significant changes over the traditional bond stretching predictions, but bond torsion plays only a minor role. Bond bending results in more abrupt chain expansion with increasing elongation rate, and the corresponding increase in the elongational viscosity is also more steep. Non-bonded interactions cause the chain to be more spheroidal at lower elongation rates, and they result in a minimum in the elongational viscosity at an intermediate elongation rate - presumably as a result of excluded volume effects causing the chain to be slightly more expanded.

Monday   4:00   Lady Davis   EF6

POLYMER DYNAMICS IN SEMI-DILUTE DNA SOLUTIONS IN A PLANAR EXTENSIONAL FLOW

<u>Charles M. Schroeder</u>[1], Hazen Babcock[2], Joe S. Hur[1], Steve Chu[2], and Eric S. G. Shaqfeh[1]

[1]Department of Chemical Engineering, Stanford University, Stanford, CA 94305; [2]Physics Department, Stanford University, Stanford, CA 94305

The dynamic behavior of polymers in solution has been an area of research for many years. DeGennes (*J. Chem. Phys.*, 1974) predicted that an abrupt coil to stretch transition would occur for polymer chains in dilute solution in an extensional flow above a critical value of the strain rate; herein, we seek to determine whether an abrupt transition exists in a semi-dilute polymer environment. Relying on recent advances in experimental procedures allowing for the observation of single molecules, we employ fluorescence microscopy to investigate the dynamics of stained lambda-phage DNA in semi-dilute solutions. We present data obtained from a flow cell with a cross-slot geometry necessary to generate a planar extensional flow. After properly characterizing the polymer relaxation time in a high-viscosity, semi-dilute polymer chain environment, we examine the steady-state chain extension versus dimensionless strain rate. Interestingly, we find that upon rescaling the dimensionless strain rate with the longest polymer relaxation time, the semi-dilute steady extension data is quantitatively similar to steady dilute solution extension results. The unraveling dynamics of single DNA chains is also investigated by taking transient measurements of extension versus fluid strain for several molecules at various strain rates; further anaylsis of this data reveals molecular conformation and probability distribution function extension data at different accumulated fluid strains and strain rate values, which is compared to dilute solution results.

Monday   4:25   Lady Davis   EF7

BIREFRINGENCE MEASUREMENTS ON POLYMER MELTS IN AN AXISYMMETRIC FLOWCELL

<u>Philip Harrison</u>[1], Luc J. Janssen[1], Vincent Navez[2], Gerrit Peters[1], and Frank Baaijens[1]

[1]Materials Technology, Technische Universiteit Eindhoven, Eindhoven NL-5600 MB, The Netherlands; [2]NMC, Raeren, Belgium

The stress-optic rule relates birefringence to stress. Consequently, measurement of flow birefringence provides a non-intrusive technique of measuring stresses in complex flows. In this investigation we explore the use of an axisymmetric geometry to create a uniaxial elongational flow in polymer melts. In axisymmetric flows both birefringence and orientation angle change continuously along the path of the propagating light. Because polarimetry measurements provide the cumulative influence of the material's optical properties along the light's integrated path, this makes determination of local birefringence in the melt impossible. One can nevertheless use

experimentally determined birefringence measurements to compare with predictions from computer simulations as a means of evaluating the materials' governing constitutive stress equations. More specifically, in this investigation we compare the light intensity transmitted through the experimental set-up, with the theoretically calculated transmitted intensity as a means of comparing experiment and simulation. The main complication in our experiments is the use of a flowcell that necessarily consists of materials of different refractive indices. This introduces refraction and reflection effects that must be modelled before experimental results can be correctly interpreted. We describe how these effects are taken into account and test the accuracy of predictions against experiments. In addition, the high temperatures required to investigate polymer melts, mean that a further complication is introduced by thermal stresses present in the flowcell glass. These thermal-stresses are incorporated in the simulations. Finally, we present a few preliminary results and evaluate the success of the overall method.

Monday   4:50   Lady Davis   EF8
SYNERGISTIC EFFECT OF STRAIN HARDENING IN HDPE/PS BLENDS

Kyung H. Ahn, **Jung S. Hong, Seung J. Baik, and Seung J. Lee**
School of Chemical Engineering, Seoul National University, Seoul, Seoul 151-744, Republic of Korea

One of the hot issues in polymer industry is the development of new materials, which show the strain hardening behavior in elongational flow field. Branched polymers normally show this behavior, and some linear polymers with modification or high molecular weight tail also show the same behavior. Due to recent advances in metallocene catalysts, the interest on this issue is growing very fast. In this talk, we will present the synergistic effect of strain hardening in HDPE/PS blends. In the HDPE matrix that shows strain hardening, small amount of PS is blended and dispersed. Under specific conditions, the strain hardening behavior becomes more pronounced. SEM photographs during the morphology evolution in the elongation experiments will also be presented. By comparing the blends whose matrix shows strain hardening and whose does not, a hint on the role of strain hardening in elongational flow field will be suggested.

Symposium RT
Rheology & Topology

Organizers: Jay Janzen and Tom C. B. McLeish

Monday   1:30   Drayton   RT6
COMPARISON OF RHEOLOGICAL PROPERTIES OF LONG-CHAIN BRANCHED POLYETHYLENES AND LONG-CHAIN BRANCHED POLYSTYRENES

Helmut Münstedt, **Claus Gabriel, and Jens Hepperle**
Institute of Polymer Materials, University of Erlangen-Nürnberg, Erlangen, Bavaria 91058, Germany

The intention of this paper is to compare the influence of long-chain branches on the rheological properties of polymers of different chemical structure. For the investigation metallocene-catalyzed polyethylenes and model-comb polystyrenes are used. The materials chosen have a similar polydispersity (Mw/Mn of about two), and the degree of long-chain branching is on the average one long-chain branch per molecule. This information results from size exclusion chromatography and online light scattering for the polyethylenes. The polystyrenes are synthesized using the macromonomer technique which allows to control the length of the side branches and their average number per molecule. For both types of polymers a distribution of branches as a function of molecular mass has to be taken into account. The viscosity function in shear is strongly influenced by long-chain branching in the case of polyethylene melts, whereas only a small change is observed for the polystyrenes. Similar observations have been made for elastic properties. The zero shear rate viscosity of the long-chain branched polymers in comparison to linear ones is found to be higher for the polyethylenes and lower for the polystyrenes. The flow activation energy of polyethylene is strongly increased by long-chain branching, whereas the temperature dependence of the shift factor of linear and long-chain branched polystyrenes is the same. The different molecular processes governing the temperature dependence of melts of amorphous and semicrystalline polymers are regarded to be the reason for the

observed difference. The non-linear properties in elongational flow are drastically changed by long-chain branches. For both types of polymers an increase in strain hardening is observed. The specific influence of branches on rheological properties will be discussed in the light of entanglement molecular weight Me and entanglement density Mw/Me.

Monday   1:55   Drayton   RT7
DYNAMICS OF TOPOLOGICAL MIXTURES

Emmanuel Stiakakis[1], Dimitris Vlassopoulos[2], George Fytas[3], and Jacques Roovers[4]
[1]Institute of Electronic Structure and Laser, FORTH, Heraklion, Crete 71110, Greece; [2]Institute of Electronic Structure and Laser, FORTH, Heraklion, Crete, Greece; [3]Institute of Electronic Structure and Laser, FORTH, Heraklion, Crete 71110, Greece; [4]Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, Ontario, Canada

Taking advantage of recent advances in the understanding of the structure and dynamics of multiarm star polymers, as well as in the theory of star-star and star-linear blends based on the tube model, we investigate the dynamic properties of topological mixtures. In particular, we study mixtures of different hyperstars or hyperstars and linear chains. In the latter case, if the linear chains are small compared to the arm size, they penetrate into the star; on the other hand, if they are large, they can be depleted. We explore the consequences of this on the linear rheological behavior, as well as on the observed thermal gelation properties of such blend solutions. A comparison against pure component properties suggests ways for controlling the dynamics of hyperstar polymers.

Monday   2:20   Drayton   RT8
LINEAR AND NONLINEAR RELAXATION DYNAMICS OF ENTANGLED MULTIARM POLYMERS

J Juliani[1], Mohammad T. Islam[1], and Lynden A. Archer[2]
[1]Chemical Engineering, Texas A&M University, College Station, TX 77843-3122; [2]Cornell University, Ithaca, NY

Rheological behavior of model entangled six-arm (A3-A-A3) and eight arm (A3-A-A2-A-A3) polybutadiene melts investigated using low amplitude oscillatory shear, step shear strain, and plane-Couette steady shear flow measurements. In oscillatory shear, the effect of variable arm and cross-bar molecular weight on plateau and terminal material properties are studied in detail. A second low-frequency plateau in storage modulus is observed in both cases and the corresponding plateau modulus found to depend on crossbar volume fraction in a manner consistent with a picture of cross-bar constraints diluted by relaxed arms. Zero shear viscosity and terminal relaxation time, reveal higher than expected dependences on cross-bar molecular weight, even when results are presented in terms of the diluted cross-bar entanglement density. Our results suggest a greater role of contour length fluctuation effects in branched polymer relaxation dynamics. In step shear experiments, two regimes are apparent in shear damping functions. At low strains, the shear damping function of the multiarm polymers is less strain softening than those observed for entangled linear polymers. At strains above a critical value, strain softening behavior manifested by multiarm materials is rather similar to that seen in the entangled linear polymers. The dependence of this critical strain on arm and cross-bar molecular weight as well as on the architecture of the branched polymers is investigated in detail. Our results show, for example, that the strain at which the transition in damping properties is observed is an explicit function of the number of arms and the ratio of cross-bar to arm molecular weight. Implications of branch point withdrawal on the validity of the empirical Cox-Merz rule are also discussed in detail.

Monday   2:45   Drayton   RT9

INFLUENCE OF THE CHAIN LENGTH BETWEEN BRANCH POINTS ON RANDOMLY BRANCHED POLYMER STRUCTURE AND RHEOLOGY

Charles P. Lusignan[1], Thomas H. Mourey[1], John C. Wilson[2], and Ralph H. Colby[3]
[1]Imaging Materials & Media Research & Development, Eastman Kodak Company, Rochester, NY 14650-2109; [2]Heidelberg Digital, LLC, Rochester, NY 14650-2129; [3]Materials Science and Engineering, Penn State University, University Park, PA 16802

The structural and rheological properties of randomly branched polymers in the molten state are studied as the chain length N between branch points is varied below the gel point. Measurements of oscillatory shear modulus, viscosity, recoverable compliance, and molar mass distribution are presented for polyester systems with N = 2, 20, and 900. Data from the literature for systems with other N values are also discussed. Power law relationships between the measured quantities are observed, and the static scaling exponents depend on N as predicted by the Ginzburg criterion. We demonstrate that dynamic scaling holds in systems with N < 50, and find that the branched polymer Rouse theory is the only model to correctly predict the rheological response for systems in this class. In the vulcanization limit, N >> 50, the Rouse model does not describe the rheological properties. Its failure is attributed to entanglements in the long linear chains between branch points. The dynamic scaling relation u = t / (s + t) seems to apply in systems with N > 50, but the values of the observed dynamic exponents vary systematically with N.

Monday   3:35   Drayton   RT10

DETECTING LONG-CHAIN BRANCHING USING LINEAR VISCOELASTICITY

Ronald G. Larson[1] and Cattaleeya Pattamaprom[2]
[1]Chemical Engineering, University of Michigan, Ann Arbor, MI 48109; [2]Chemical Engineering, University of Michigan, Ann Arbor, MI, MI 48109

Recent theoretical advances open the possibility of developing theories for the linear viscoelasticity of linear and branched polymers that are general enough to be applied to commercial melts, including ones with long-chain branching (LCB). For branched polymers, a first step is simply to detect unambiguously the presence of LCB from measurements of linear rheology. In principle, this can be done using the "double reptation" theory of des Cloizeaux, Tuminello, and Tsenoglou, which has been shown to predict successfully the linear viscoelasticity of polydisperse linear polymers, and so indicates the presence of LCB when the predictions of the theory deviate from experimental measurements. Unfortunately, however, polydispersity can masquerade as LCB, and double reptation may not always be reliable in distinguishing LCB from polydispersity, since the phenomenological constant "K" of the double reptation theory is found to be dependent on the width of the molecular weight distribution. Here, we describe a refinement of the "dual constraint model" of Mead, Van Dyke, et al. that includes additional physics that permit it not only to describe polydisperse linear polymers more accurately, but also to make predictions for star-branched polymers. The predictions of the dual constraint model are shown for polydisperse linear polymers and for star-branched polymers, and compared to literature data, including data for both polystyrene and commercial polyethylene. We find that excellent predictions of the linear viscoelasticity of commercial linear polyethylenes can be obtained without adjustable parameters, but that accurate predictions of rheology of star-branched polyethylenes require as yet incompletely explained adjustments to both the entanglement spacing and the plateau modulus.

Monday   4:00   Drayton   RT11

CHARACTERIZATION OF LONG-CHAIN BRANCHING EFFECTS IN LINEAR RHEOLOGY

Wolfgang B. Thimm, Christian Friedrich, Tobias Roths, Stefan Trinkle, and Josef Honerkamp
Freiburger Materialforschungszentrum, Albert-Ludwigs-University Freiburg, Freiburg i. Brsg. D-79104, Germany

The central quantity in linear rheology is the relaxation time spectrum. We discuss that once this quantity is estimated from the measured data, using a regularization procedure, one obtains a mighty tool to characterize homopolymers. Starting from some mixing rules based on reptation and Rouse concepts, we derived an analytical relation between the relaxation time spectrum and the molecular weight distribution, which allows a robust and fast determination of the latter quantity [1,2].

We discuss that a comparison of the molecular weight distribution determined this way with the related size-exclusion chromatography determined molecular weight distribution provides also a tool to characterize long-chain branching effects using linear rheology.

Monomodal samples which contain long-chain branches will show two relaxation processes in the rheological examination, which are converted to two peaks in a corresponding molecular weight distribution. But these samples will show only one peak in a molecular weight distribution determined by size-exclusion chromatography. This difference can be used to characterize long-chain branching, as will be discussed regarding model H-polymers. Limitations to the method due to a limited relaxation time window will be discussed.

[1] Thimm et al., J.Rheol. 43, 1663 (1999)

[2] Thimm et al., J.Rheol. 44, 429 (2000)

Monday   4:25   Drayton   RT12
THE RHEOLOGY OF BRANCHED POLYISOBUTYLENE AND 1,4-POLYISOPRENE
Patrick G. Santangelo[1], Chris G. Robertson[1], C. Michael Roland[1], and Judith E. Puskas[2]
[1]Chemistry, US Naval Research Laboratory, Washington, D.C. 20375; [2]Chemistry & Biochemical Engineering, University of Western Ontario, London Ontario N6A 5B9, Canada

The effect of long chain branching on the rheology of entangled polymers has been studied for polyisobutylene (PIB) and 1,4-polyisoprene (PI). Since terminal relaxation involves motion of the entire molecule and well-entangled arms suppress longitudinal motion, another mechanism is needed to allow translation of a branched molecule. Arm retraction of all branches to a transient, more compact structure has been proposed as such a mechanism. Such an arm retraction would alter the distribution of rotational states, causing a change in the temperature dependence of both the zero-shear viscosity and the diffusion constant. Polyisobutylene presents an interesting case since the gauche and trans conformational energies are essentially equal. The rheology of high molecular weight, six-arm star polyisobutylenes (PIB) was measured and compared to the behavior of linear PIB. The star and linear PIBs had equivalent plateau moduli, and conformed well in the terminal zone to the time-temperature superposition principle. Moreover, the temperature coefficients of the terminal relaxation times were identical for the star and linear polymers. The absence of enhanced temperature sensitivity in star PIB, as well as the thermorheological simplicity, are consistent with an interpretation of the rheology of branched polymers based on an arm retraction mechanism.

In the case of 1,4-polyisoprene (PI), the gauche conformers are *lower* energy than the trans and hence the branched PI should be less affected by temperature than linear PI (smaller temperature coefficient). Nevertheless, the presence of long chain branches in star PI was shown to increase the sensitivity to temperature of the terminal relaxation. The excess activation energy associated with branching increased in proportion to the molecular weight of the branches. In these respects, the reptation-based arm retraction interpretation of the temperature-dependence of branched PI fails.

Monday   4:50   Drayton   RT13
ENTANGLED SOLUTION RHEOLOGY DETECTION OF LCB
Tom McLeish[1], Bryan J. Crosby[1], Rob Daniels[1], Marc Mangnus[2], and Sjoerd de Vries[2]
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We present a new and very sensitive method to detect the presence of LCB in a polymer melt. The linear rheology of the melt is compared to marginally-diluted solutions. The tube model predicts that relaxation times of LCB melts are shifted exponentially further on dilution than linear melts. The theory is tested quantitatively in the case of monodisperse linear, star and H-polymers, then applied to a range of industrial branched resins including LDPE and metallocene LCB grades. The method gives a "fingerprint" dilution-curve, sensitive to different degrees of LCB. The sensitivity of the method actually increases as the LCB/ 100C reduces until only a small minority of molecules have any branches at all, so compliments dilute solution techniques. An additional advantage is that no other molecular characterisation or text-book data is required - a melt is compared with itself.

Symposium CG
Rheology in Confined Geometries and Microfluidic Applications

Organizers: Andrea Chow and Ronald G. Larson

Monday   1:30   Elliott   CG6
2D ELECTROPHORESIS AND FLOW OF DNA CHAINS
Gerald G. Fuller, David J. Olson, and Ed Stancik
Chemical Engineering, Stanford University, Stanford, CA 94305-5025

The attachment of DNA chains onto mobile, supported membranes forms the basis for 2D electrophoretic motion that can ultimately be used to separate chains on a surface. In addition, this system serves as model for rheologically complex interfaces encountered when emulsions are stabilized through the addition of certain surfactants, and for processes such as transvection in gene therapy. In this paper the dynamics and conformation of labelled DNA chains are monitored as they are propelled across supported, cationic lipid bilayers by either electric or hydrodynamic fields. It is found that most supported membranes, which are formed by the process of vescicle fusion, present a sparse obstacle course for the DNA chains to negotiate. However, the two fields (which can be applied simultaneously) operate on the system in qualitatively different ways. When electric fields are applied the obstacles (which are most likely unfused vescicles lying on top of the membranes) are stationary and the DNA chains become temporarily trapped and obtain hairpain conformations. The application of flow fields, on the other hand, cause the obstacles to translate along with the chains. In the presence of flow, the chains become much more elongated compared to the case of electric fields and can be ripped from the surface. Strategies to use this system for the purpose of separation are discussed.

Monday   1:55   Elliott   CG7
MAGNETOSENSITIVE SELF-ORGANIZING ARRAYS FOR DNA SEPARATIONS
Patrick S. Doyle[1], Jerome Bibette[2], Bendicte Deminiere[3], and Jean-Louis Viovy[4]
[1]Department of Chemical Engineering, M.I.T., Cambridge, MA 02139-4307; [2]CRPP, Bordeaux, France; [3]ADEMTECH, Bordeaux, France; [4]Institut Curie-PCC, Paris, France

The separation of large DNA fragments is a crucial step in DNA mapping and fingerprinting. Traditionally, large DNA molecules are separated using polymer gels. This process is cumbersome, slow (taking 24-48 hours), and can not be easily incorporated into Lab-on-a-Chip devices. We have developed a new method to separate kilobase-size DNA molecules. The separation medium consists of a ferrofluid emulsion which organizes into an array of regularly spaced columns upon application of a magnetic field. The DNA are driven by an electric field through this obstacle course and collide with the columns, leading to size fractionation. Microscopic observations of the DNA dynamics, the separating ability of the matrix and an elastomer microchip device for these separations will be discussed.

Monday   2:20   Elliott   CG8
BROWNIAN DYNAMICS SIMULATIONS OF POLYMER MOLECULES IN SHEAR FLOW CONFINED BETWEEN PARALLEL ADSORBING WALLS
Manish Chopra and Ronald G. Larson
University of Michigan, Ann Arbor, Ann Arbor, MI

We report an attempt to understand the micro-dynamics of a single semi-flexible polymer molecule in solution confined between two parallel hard walls under the influence of steady shear flow. In the past, Brownian Dynamics simulations have been shown to give accurate predictions of microscopic observations of single molecules (DNA in particular) in shear and extensional flow [1,2]. Here, we present results of extending these simulation methods to a long-standing problem in polymer dynamics, namely that of interactions of polymers with solid surfaces at equilibrium and during flow. For the case of equilibrium, in the presence of a non-adsorbing wall, the conformation of the polymer chain is in basic agreement with known analytic solutions derived from an analogy with the heat equation, except for finite-bead-number effects. For irreversible adsorption from quiescent solution, the chain conformation, as expected, is a simple two-dimensional random walk. For nonadsorbing chains under flow, there is a depletion layer near the wall whose thickness decreases with increasing Weissenberg number, in qualitative

agreement with a scaling law derived by Hur et al. [2] for simple shearing flows. For the most interesting case of irreversible adsorption during flow, the adsorbed polymer conformation has a bimodal distribution, with chains adsorbing both in a coiled state and in an extended state. The degree of stretch and the percentage of extended conformations both increase with increasing Weissenberg number. These results are analyzed in terms of the sequence by which different parts of the chain adsorb to the wall.

[1] T.T. Perkins, D.E. Smith, R.G. Larson, S.Chu, Science 268, 83 (1995).

[2] J.S. Hur, E.S.G. Shaqfeh, R.G. Larson, J. Rheol. 44, 713 (2000).

Monday   2:45   Elliott   CG9

THE CONFORMATIONS OF A DNA MOLECULE NEAR A GLASS SURFACE

Lei Li, Hua Hu, and Ronald G. Larson

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

DNA molecular stretching in an evaporating droplet has potential applications for high throughput gene optical mapping analysis. In this study, we used a fluorescent microscope to observe the configurations of DNA molecules close to a substrate both in a flow induced by droplet evaporation and in a simple parallel-disk shearing flow. The statistical results obtained from image processing after rewetting the dried out droplet show that the DNA molecules are stretched along the radial direction and their conformation and length distribution vary along the radial direction. There are several factors which affect the distributions of DNA molecules on the glass surface, including evaporation rate and surface adsorption characteristics. In order to decouple the flow and the surface effects, we also studied the DNA near a glass surface under steady simple parallel-disk shearing flow. The molecular conformation, length, and orientation distributions were measured at different shear rates, and compared for surfaces with different chemical treatments. The differences between surface and bulk behaviors will also be discussed.

Monday   3:35   Elliott   CG10

"SUPERSTRINGS" IN SHEARED POLYMER BLENDS: THE INFLUENCE OF COALESCENCE, BREAKUP AND FINITE SIZE

K B. Migler

Polymers Division, NIST, Gaithersburg, MD 20899-8544

We have discovered a droplet-string transition in concentrated polymer blends which occurs when the size of the dispersed droplets becomes comparable to the gap width between the shearing surfaces. The transition is abrupt and proceeds via the coalescence of droplets in a four stage kinetic process. Once formed, the strings are stable and exhibit pronounced hysteresis. The string state is stabilized by a suppression of the Rayleigh-Tomatika instability due to both finite size effects and to the shear induced advection of small amplitude disturbances.

Monday   4:00   Elliott   CG11

DISPERSION VISUALIZATION UNDER HIGH SHEAR RATE IN A TRANSPARENT COUETTE FLOW CELL

Frej Mighri and Michel A. Huneault

Materials and Processes, Polymer Materials Engineering, Industrial Materials Institute, National Research Council, Boucherville, Quebec J4B 6Y4, Canada

Dispersion mechanisms in model fluid systems of different viscosity ratios under high shear stress were studied in transparent Couette flow-cell. The originality of this new setup is that visualization can be made at high shear rates without any secondary flow effects. Elastic drops (Boger fluids) and Newtonian drops (high viscosity PDMS fluids), deformed at low shear rates in a Newtonian matrix (low viscosity PDMS fluid),oriented along the flow field and drop deformation increased with increasing shear rate as expected. Surprisingly however, for each viscoelastic drop/matrix system studied, the deformed drops elongated along the vorticity axis when a critical shear stress, characteristic of the fuid system used, was reached. When increasing the shear stress over this critical value (but still in the non-breakup region), drop contraction along flow direction continued and was accompagned by an increase of elongation along the vorticity axis. This is most probably related to normal force development. It was put in evidence by comparing the drop deformation kinetics to that of normal force development. The breakup mechanism at high stress was also very different from that expected for Newtonian fluids. Because droplets become highly

elongated perpendicular to the flow direction, small rocking instabilities (in the velocity gradient direction) result in large velocity difference between one end of the droplet and the other. Therefore when this rocking motion sets in, quick elongation of the drop tears it apart in two or more daughter droplets. The kinetics of drop deformation along vorticity direction corresponded to that of normal force development, which also puts in evidence that drop elasticity helps vorticity alignment.

Monday   4:25   Elliott   CG12
VIRTUAL GAP RHEOMETRY: DETERMINING THE RELAXATION SPECTRUM FROM WAVE DISPERSION DATA
Russell Davies[1], **Dafydd Morgan**[1], **and Rhodri Williams**[2]
[1]Depart,ment of Mathematics, University of Wales, Aberystwyth SY23 3BZ, United Kingdom;
[2]Department of Chemical and Biological Process Engineering, University of Wales, Swansea SA2 8PP, United Kingdom

Viscoelastic systems display anomalous dispersion of high frequency shear waves, in which the phase velocity, v, is exceeded by the group velocity, U, where $v < U < 2v$. A dimensionless wave number, $y = (U-v)/v$, viewed as a function of frequency, has been suggested by P.R.Williams and S.Ravji (J. Phys. D: Appl. Phys. 32(1999)1750-1758) as an alternative measure of relaxation properties of a viscoelastic medium, in contrast to the more traditional relaxation spectrum of relaxation times for the medium. The wave number and its derivatives are easily calculated from direct measurement of U and v in a Virtual Gap Rheometer (VGR). The purpose of this paper is to develop, and then exploit, new mathematical relationships which connect the traditional relaxation spectrum to the wave number and its derivatives. The use of the VGR as a differential spectrometer in this context is advantageous in collecting highly accurate data, which in turn enables the calculation of high order derivatives without excessive filtering of noise. These new relationships take the form of a sequence of Fredholm integral equation of the first kind. As we progress along the sequence, the degree of ill-posedness associated with each equation decreases, and we are able to obtain sequentially better resolved estimates of the relaxation spectrum. We can relate resolution directly to the sampling interval in log-frequency and to noise levels in the data. It is shown that the each Fredholm equation is sequentially less ill-posed than traditional integral equations relating the spectrum to dynamical measurements. The paper will be illustrated with several numerical examples.

Monday   4:50   Elliott   CG13
NANO-SCALE AND MACRO-SCALE STUDIES OF THE DYNAMIC TENSILE STRENGTH OF COMPLEX FLUIDS
Rhodri Williams, Nidal Hilal, and Richard Bowen
Department of Chemical and Biological Process Engineering, University of Wales, Swansea SA2 8PP, United Kingdom

We report work in which cavitation is provoked in liquids which undergo rapid stretching in two different experiments. In the first of these, tension is produced within nanometre-scale liquid filaments and films which undergo stretching within a modified Atomic Force Microscope (AFM): in the second experiment, a one-metre long column of liquid is subjected to dynamic tension using an improved version of the Bullet - Piston (B - P) pulse reflection apparatus. Although very different in terms of the lengthscales involved, the two experiments are shown to highy complementary. In both experiments the rate of development of tension within the newtonian and non-newtonian fluids considered is typically 1 bar per microsecond: the non-newtonian fluids include dilute aqueous solutions of a high molecular weight polymer (polyacrylamide). The values of effective tensile strength obtained from the B - P experiments provide an important guide to the stability of the stretching filaments in AFM work, particularly in their early stages of development. We show how the response of the AFM's cantilever during the stretching of a liquid provides information on cavitation bubble dynamics within the confined stretching fluid and the relevance of this work to various problems in engineering, bio-engineering and the Life-sciences is discussed.

Symposium BC
Blends and Co-polymers

Organizers: Nitash Balsara and Ramanan Krishnamoorti

Monday   1:30   Heyward   BC6

RHEOLOGY AND PHASE BEHAVIOR OF A BICONTINUOUS POLYMER MICROEMULSION UNDER SHEAR

Wesley R. Burghardt[1], Kasiraman Krishnan[2], Timothy P. Lodge[2], Frank S. Bates[2], and Franklin E. Caputo[1]

[1]Chemical Engineering Department, Northwestern University, Evanston, IL 60208; [2]University of Minnesota, Minneapolis, MN

An equilibrium bicontinuous microemulsion phase may be formed in ternary blends of immiscible homopolymers mixed with the corresponding diblock copolymer. The sample studied here consists of a symmetric blend of poly(dimethyl siloxane) (PDMS), poly(ethyl ethylene) (PEE) and their diblock copolymer. In small ampliude oscillatory shear, the microemulsion exhibits considerable viscoelasticity associated with the deformation and relaxation of the interface; the relative strength of the elastic response increases as temperature is lowered and the system becomes more strongly segregated. Steady viscosity shows four distinct regimes: Newtonian at low rates, shear thinning at moderate rates, a shear stress plateau at higher rates, and finally a high rate regime where shear stress increases further. The origin of this behavior is explored using in situ structural probes. Small angle neutron and x-ray scattering during shear reveal flow-induced anisotropy in the microemulsion structure is responsible for the initial shear thinning. The shear stress plateau corresponds to the development of flow-induced macroscopic phase separation, studied both by in situ optical microscopy and small angle light scattering. Flow inception experiments in this regime show transient stresses that are direct signatures of the initial microemulsion distortion and the subsequent onset of phase separation. The sample is still phase separated, and highly turbid, in the highest shear rate regime. However, structural relaxation in this regime occurs via a very different mechanism than in the stress plateau regime.

Monday   1:55   Heyward   BC7

POLYMER SURFACE FUNCTIONALIZATION BY FIELD-INDUCED MIGRATION OF COPOLYMER ADDITIVES

Ho-Jun Lee[1] and Lynden A. Archer[2]

[1]Texas A&M University, College Station, TX 77843; [2]Cornell University, Ithaca, NY

Field-induced migration of low surface energy (polystyrene-b-polydimethyl siloxane, PS-b-PDMS) and moderate surface energy (polystyrene-b-polymethylmethacrylate, PS-b-PMMA), block copolymer additives in polystyrene (PS) hosts was investigated. Dynamic Contact Angle analysis and Attenuated Total Reflection Fourier Transform Infrared spectroscopy measurements were used to characterize surface properties of polymer/additive blends created by solvent casting, precipitation, and melt annealing processes. Experiments covering a range of copolymer concentration, matrix polymer molecular weights Mw, and annealing temperatures were performed to determine the effect of additive and interface physical chemistry on surface composition of polymer/additive mixtures. For PS-b-PDMS additives, selective DMS enrichment of the air/polymer interface was observed for all matrix polymer molecular weights. A scaling relationship between surface excess DMS groups, DfDMS, and host polymer Mw could be defined, DfDMS ~ Mw,PSa; where the scaling exponent a is less than 0.25 for blends where the host and additive molecular weights are of the same order. In blends where these molecular weights are substantially different, a values of 0.5 and higher are observed. In PS-b-PMMA/PS blends, a similar scaling relationship between surface excess MMA groups and host polymer molecular weight is observed. In this case, however, the scaling exponent a is 0.5 and larger over a much broader range of host polymer and copolymer additive molecular weights. We discuss both observations in terms of competitive enthalpic and entropic driving mechanisms for surface transport of additives in polymers. Finally, we discuss results from extrusion studies of enhancement of additive concentration in polymer/copolymer additive blends subject to shear fields. Specifically, we consider the roles played by non-zero first normal stress differences and shear stress gradients on surface migration of copolymer additives in polymer liquids extruded through long capillaries.

Monday 2:20 Heyward BC8

ORIENTATIONAL PROLIFERATION AND SUCCESSIVE TWINNING FROM THERMOREVERSIBLE HEX-BCC TRANSITIONS

Hee Hyun Lee[1], Julie A. Kornfield[1], Zhen-Gang Wang[1], Jin Kon Kim[2], and Shuyan Qi[3]
[1]Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125; [2]Chemical Engineering, Pohang University of Science and Technology, Pohang, Kyungbuk 790-784, Republic of Korea; [3]Chemical Engineering, UC Berkeley, Berkeley, CA 94720

The formation of degenerate hexagonally packed cylinders (HEX) from the twinned body centered cubic (BCC) phase is investigated by synchrotron SAXS and rheo-optical methods for di- and triblock copolymers of styrene and isoprene (SI and SIS). Repeated heating and cooling cycles starting from an initially aligned HEX, produce a proliferation of cylinder orientations from successively twinned BCC states. The evolution of the orientation distribution of HEX cylinders produces a decrease in the birefringence and increase in the modulus with each successive ¡°generation¡±. The cylinder axis directions of the degenerate HEX¡¯s coincide with the directions of the twinned BCC due to the epitaxial growth of cylinders from the twinned BCC. The distribution of the cylinder axes of the degenerate HEX among the directions of the twinned BCC is found to be affected by memory of the prior HEX state, which decays with annealing time in the BCC state.

Monday 2:45 Heyward BC9

DOUBLE REPTATION PREDICTIONS OF THE LINEAR VISCOELASTICITY OF MISCIBLE POLYMER BLENDS

Jai A. Pathak, Sanat K. Kumar, and Ralph H. Colby
Materials Science & Engineering, Penn. State Univ., Univ. Park, PA 16802

We present results of an experimental study of segmental (local) and terminal (chain end-to-end) dynamics in miscible binary polymer blends and their constituent homopolymers. The blends have been carefully chosen, in order to systematically tailor the blend thermodynamics, and the intrinsic differences in the local dynamics of the components (reflected in their individual glass transitions). This allows us to elucidate the combined influence of these two important factors on anomalous dynamic phenomena (e.g. broadening of the calorimetric glass transition and failure of time-temperature superposition) observed in many miscible polymer blends. The average longest segmental relaxation time, calculated from a concentration fluctuation model for segmental dynamics in miscible blends, is used as a monomer relaxation time of the tube model. We use the component monomer relaxation times to determine their terminal relaxation times, and then calculate the blend complex modulus using the double reptation *ansatz*. These predictions are then compared to experimental data for a model polyolefin blend at different blend compositions, and reveal that the complex modulus of miscible blends can currently be predicted in a *qualitative* fashion. Thermorheological complexity is predicted for blends with sufficiently large composition fluctuations and differences in component local dynamics.

Symposium SC
Suspensions and Colloidal Systems

Organizers: Daniel De Kee and Robert Lionberger

Monday 3:35 Heyward SC1

THE ROLE OF REPULSIVE INTERPARTICLE FORCES ON SUSPENSION RHEOLOGY

J. Bergenholtz[1], John F. Brady[2], and Michael Vicic[3]
[1]Department of Physical Chemistry, Goteborg University, Goteborg, Sweden; [2]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125; [3]Cyrano Sciences, Inc., Pasadena, CA

The effect of excluded volume interactions on the structure and rheology of colloidal dispersions is studied. The two-particle Smoluchowski equation, which governs the colloidal microstructure, is solved numerically for simple

shear flow at arbitrary Peclet number (Pe, dimensionless shear rate). The calculations confirm the formation of a boundary layer along the compressive axis at high Pe observed in previous computer simulations and analytical treatments. The boundary layer concentrates stress in a small region of the flow and is of singular importance for the rheological behavior at high Pe. It leads to a number of important results, such as an increasing shear viscosity with increasing Pe (shear thickening) when the interaction is sufficiently hard sphere-like, as well as maxima and minima in the first and second normal stress differences as functions of Pe. The theoretical predictions from the dilute model are used with a simple scaling theory to predict the viscosity and normal stress differences in concentrated colloidal dispersions, and comparison with Stokesian Dynamics simulation is found to be very good over the full range of Peclet numbers.

Monday   4:00   Heyward   SC2
THE THEORY UNDERLYING THE RHEOLOGY OF COLLOIDAL DISPERSIONS: A GENERIC APPROACH
Norman J. Wagner
Chemical Engineering, University of Delaware, Newark, DE 19716

The rheology of concentrated colloidal dispersions has been described by particle-level theories starting with the work of Einstein (1912) and Smoluchowski (1912), and continuing with the seminal work of Batchelor (1972). Progress to incorporate many body effects has been frustrated by a lack of a coherent, nonequilibrium thermodynamics framework that enables proper incorporation of many-body effects in expressions for the equilibrium and nonequilibrium microstructures and the stress tensor. The GENERIC approach provides such a framework. In this talk, I will overview the approach as applied to colloidal dispersions, analyze current microstructural theories for colloidal rheology for thermodynamic consistency, and comment on their ability to accurately model the rheology of concentrated (i.e. interacting) colloidal dispersions. Further, a complete and consistent set of transport equations will be presented. The results of this investigation provide pathways forward for improving particle-level theories of suspension rheology

Monday   4:25   Heyward   SC3
DYNAMIC SIMULATION OF CONCENTRATED COLLOIDAL SUSPENSIONS
Kevin R. Hase and Robert L. Powell
Chemical Engineering and Material Science, University of California—Davis, Davis, CA 95616-5294

Dynamic simulation of colloidal monodisperse, bimodal and polydisperse suspensions of spherical particles subjected to shearing flow. Dispersed hard spherical particles suspended in a Newtonian fluid experience hydrodynamic interactions, Brownian forces, and DLVO forces; these colloidal interactions are considered in the suspension model. DLVO type force contributions include electrostatic and van der Waals forces, which are dependent on the absolute particle size. The particles experience far field many body interactions and near field interactions. The near field interactions include hydrodynamic lubrication as well as electrostatic and van der Waals forces. The convergence of the far-field interactions is accelerated by means of Ewald summation calculated for arbitrarily sized particles. This model is used to examine the microstructure of colloidal suspensions, and to determine the effective dynamic and time averaged viscosity of sheared suspensions. The microstructure is determined by projecting the pair distribution function onto the vorticity-velocity gradient plane. Variation in Péclet number produces a shift in the structure of the suspended particles from ordered at low Pe, to disordered at moderate Pe, to ordered at high Pe. The Péclet number is defined as the shear rate times the square of the characteristic length divided by the diffusivity of an isolated particle. The Stokes-Einstein diffusivity relation for an isolated particle is $kT/6\pi\mu a$ where kT is the fluid thermal energy and μ is the fluid viscosity. Transport properties of the suspension are found such as the relative viscosity, the hydraulic permeability, and particle diffusivities.

Monday   4:50   Heyward   **SC4**
SHEAR FLOW OF A MONOLAYER OF ROUGH SPHERES
Helen J. Wilson
Department of Applied Mathematics, University of Leeds, Leeds, United Kingdom

The viscosity of a dilute suspension of solid spheres in a shear flow cannot be calculated beyond $O(c)$ in the small volume concentration c. This is because the $O(c^2)$ term involves the interaction between pairs of particles, and the pair distribution function is undefined because of closed orbiting pairs of particles.

We consider particles with microscopic surface roughness such that they can come into contact and when they do, an irreversible interaction occurs (using the model of Davis '92). This does not solve the problem of closed orbits for a general suspension, but in the case of a monolayer the closed orbits have a distance of closest approach which is much smaller than the size of typical surface roughness elements (Rampall, Smart and Leighton '97) and so all closed orbits will be broken by the roughness. This allows us to calculate the particle pair distribution function.

We consider a monolayer of spheres lying in the plane of shear and find the theoretical form for the viscosity of this model suspension. The method also gives us an insight into the microstructure of the suspension. We also give numerical values for both the viscosity and the normal stresses as a function of the two model parameters, roughness height and friction coefficient.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday   8:30   Archer   PL2

THE MICRODYNAMICS OF DROP BREAKUP AND COALESCENCE IN FLOW

L. Gary Leal

Chemical Engineering, University of California, Santa Barbara, CA 93106

In this talk, I review work from my research group on the dynamics of drop deformation, breakup and coalescence, beginning in the mid-80s with the invention of the computer controlled four-roll mill, and continuing to our current studies of polymeric fluids with "co-polymer" compatibilizer. The combination of novel experiments and boundary integral techniques for numerical simulation has led to a reasonably complete understanding of drop breakup at modest capillary numbers for two Newtonian fluids with a clean interface. However, there is still much that we do not understand about drop breakup when the fluids become viscoelastic or surfactant/compatibilizer is added to the interface. The problem of coalescence is less well understood and is currently the subject of intensive experimental investigation in our group.

Symposium PF
Rheology in Processing Flows

Organizers: William H. Hartt and Michael E. Mackay

Tuesday   9:45   Lady Davis   PF6

THE MYSTERY OF THE MECHANISM OF SHARKSKIN: CASE CLOSED?

K B. Migler, F Qiao, and K Flynn

Polymers Division, NIST, Gaithersburg, MD 20899-8544

We utilize in-situ optical measurements in the exit region of a transparent sapphire capillary tube to determine the mechanism of sharkskin during extrusion. Upstream of the die exit, the polymer, a linear low density polyethylene (LLDPE), sticks at the wall-acceleration occurs in the last 25 microns from the exit. Downstream of the exit, high-speed video-microscopy reveals the existence of cohesive failure; the material splits into a surface layer and a core region. The material from the surface layer cyclically accumulates near the exit wall and then peels off via adhesive detachment. We also utilize polymer process additives which modify the surface and allows the polyethylene to slip, delaying the onset of sharkskin to higher flow rates. Comparing the modified and unmodified surfaces, we quantitatively assess the numerous suggested causes for sharkskin. We propose that the extensional deformation rate is the controlling parameter for the onset of sharkskin.

Tuesday   10:10   Lady Davis   PF7
NUMERICAL STABILITY ANALYSIS OF INJECTION MOLDING FLOW
Anne Grillet, Arjen Bogaerds, Gerrit Peters, and Frank Baaijens
Mechanical Engineering, Eindhoven University of Technology, Eindhoven 5600 MB, The
Netherlands

Flow instabilities during injection molding can cause non-uniform surface reflectivity on the plastic product. Our research focuses on a specific surface defect characterized by alternating shiny bands perpendicular to the flow direction which are referred to as `flow marks', `tiger stripes' or `ice lines'. One proposed theory is that an instability at the stagnation point in the fountain flow disrupts the steady flow resulting in the surface defects. However, a definitive mechanism for such a stagnation point instability which is able to clarify the full range of observed effects has remained elusive. We examine the stability of several constitutive models for polymer melts in plane Poiseuille flow using a Chebyshev-Tau spectral method. We also present finite element results in steady injection molding flow using both the Phan-Thien-Tanner model and the Giesekus model to examine the effect of extensional viscosity on the steady flow. Linear stability analyses are performed for several extensional rheologies using a transient finite element method incorporating fully implicit time integration. The most unstable eigenmode is found to be a swirling flow near the free surface which is in qualitative agreement with experimental results and consistent with the stagnation point instability theory.

Tuesday   10:35   Lady Davis   PF8
**AN INVESTIGATION OF THE CAUSES OF SURFACE ROUGHNESS AND HAZE IN
POLYETHYLENE BLOWN FILMS**
Ashish Sukhadia[1], David C. Rohlfing[1], Matthew Johnson[2], and Garth L. Wilkes[2]
[1]Phillips Petroleum, Bartlesville, OK 74004; [2]Chemical Engineering, Virginia Polytechnic
Institute & State University, Blacksburg, VA 24061

In this paper we report on some recent studies regarding the factors (structural & rheological) affecting the optical (haze) properties of polyethylene films. The principal contribution to the total haze in the blown and cast films investigated resulted from surface roughness in contrast to the smaller contribution arising from bulk scattering. Using both structural and rheological characterization methods we found that for low elasticity melts, such as often seen for metallocene based resins, the origin of the haze arose from surface roughness caused by the nucleation and growth of spherulitic-like superstructures. In contrast, for high elasticity melts, such superstructures are absent but surface roughness arises from melt elastic effects. An intermediate region of melt elasticity promotes high optically clear films due to the promotion of more fibril-nucleated morphologies that possess a relatively smooth surface.

Tuesday   11:00   Lady Davis   PF9
FORCED WETTING OF NEMATIC FLUIDS ON FIBERS
Jung O. Park[1], Mohan Srinivasarao[1], and Alejandro D. Rey[2]
[1]School of Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295; [2]Chemical Engineering, McGill University, Montreal, Quebec/ Canada H3A2B2, Canada

In many industrial applications it is necessary to coat a solid substrate with a fluid. This is usually accomplished by dragging the solid object through the fluid of interest. Here we refer to such processes as forced wetting of the solid substrate, irrespective of whether the fluid is a wetting or a nonwetting fluid for the substrate. In such a process it is obvious that the thickness of the fluid coating will depend on the velocity at which the solid substrate is withdrawn. At zero velocity the film thickness is zero (where we ignore the possibility of a thin wetting film) and at infinite velocity it will be zero as well, since the fluid does not have enough time to form a coating. Thus a maximum wetting speed naturally enters the problem of forced wetting, as has been discussed in the literature. In this talk we are interested in addressing the issue of forced wetting of fluids where the fluids are complex fluids. In particular, we confine our attention to the special case of the solid substrate having a cylindrical geometry (fibers) and where the fluid is an anisotropic fluid with long range orientational order. We consider the case of a nematic fluid and a polymer solution whose concentration is above the overlap concentration being coated onto a polypropylene fiber. In both cases the initial thickness of the fluid film coated on the fiber is proportional to the capillary number, Ca

(defined as the ratio of the viscous forces to those due to surface tension), to the first power. We present a model to account for the observed thickness dependence on the capillary number.

Tuesday   11:25   Lady Davis   PF10
FILM: "NON-NEWTONIAN FLUIDS"
Ken Walters[1], <u>Mike F. Webster</u>[2], and Rhodri Williams[3]

[1]University of Wales Swansea, Swansea, United Kingdom; [2]Institute of Non-Newtonian Fluid Mechanics, University of Wales Swansea, Swansea, West Glamorgan SA2 8PP, United Kingdom; [3]Department of Chemical and Biological Process Engineering, University of Wales, Swansea SA2 8PP, United Kingdom

The presentation is associated with the production and remake of a film by the University of Wales Institute of Non-Newtonian Fluid Mechanics on the topic of NON-NEWTONIAN FLUIDS. Following the success of the previous version of this film, the Institute launches an updated version that may prove to be a valuable teaching tool. The new release will be available in both CD-ROM and VHS format, and will include fresh features using high-quality computer graphics and updated experimental sequences. The presentation introduces the viewer to the basic science of rheology and highlights various rheological phenomena, typically as they arise in everyday situations. The topics covered include: Introduction to Rheology, Viscometry, Rheometry, Extensional Flow, Normal Stress Effects, Other Rheological Effects (including Sharkskin and Melt Fracture).

Symposium RT
Rheology & Topology

Organizers: Jay Janzen and Tom C. B. McLeish

Tuesday   9:45   Drayton   RT14
THE EXTENDED POM-POM CONSTITUTIVE EQUATION FOR COMPLEX POLYMER MELT FLOWS: A QUANTITATIVE DESCRIPTION
<u>Wilco Verbeeten</u>, Gerrit Peters, and Frank Baaijens

Materials Technology, Technische Universiteit Eindhoven, Eindhoven NL-5600 MB, The Netherlands

In general, visco-elastic fluids are characterised in shear, and, to a lesser extent, also in elongation. To discriminate between different constitutive equations, predictive capabilities for shear (viscosity and first normal stress coefficient) and elongation (planar, uniaxial and equibiaxial), both in steady state and transient behaviour, have to be investigated simultaneously.

A new molecular constitutive equation for a class of branched polymers has been introduced by McLeish and Larson (J.Rheol. 42(1), 1998), the Pom-Pom model. If the multi-mode differential form of the model is taken, including local branch-point displacement introduced by Blackwell *et al.* (J.Rheol. 44(1), 2000), three problems can be detected. First, solutions in steady state elongation still show discontinuities because of the maximum stretch condition. Second, the equation for orientation is UCM-like, which means that it is unbounded for high strain rates. And third, the model does not have a second normal stress difference in shear. We take a Giesekus-like equation for the orientation and don't incorporate the maximum stretch condition. Furthermore, we write the equations for stretch and orientation in a closed differential form for the stress tensor, resulting in a generalised differential constitutive equation. We call this new form the Extended Pom-Pom model. It doesn't show the three problems as seen for the original differential Pom-Pom model.

By fitting the linear parameters to dynamic measurements, and most of the non-linear parameters to the transient uniaxial or planar elongational data, a good quantitative agreement is obtained for both shear and elongation, transient and steady state data, including reversed flow.

For the Extended Pom-Pom model, several complex flows are investigated. All complex flow calculations show a quantitative agreement with experimental data.

Tuesday   10:10   Drayton   RT15
USING THE POM-POM EQUATIONS TO ANALYZE POLYMER MELTS IN EXPONENTIAL SHEAR
Richard S. Graham[1], Tom McLeish[1], and Oliver G. Harlen[2]
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Exponential shear flows of polymer melts are investigated. These flows are of interest because they share some properties of both planar extension and simple, constant rate, shear flows. In particular embedded points separate exponentially in time, like extensional flows, yet the flow direction and velocity gradient are perpendicular, as for all shear deformations. A comparison between the predictions of the pom-pom molecular model of McLeish and Larson (J. Rheol. 42(1):81-110, 1998) in exponential shear and experimental data is presented. The solutions in exponential shear are used to contrast this flow with simple shear and extensional flows and the physical processes driving the solutions are analyzed in each of the three flow geometries. Accurate quantitative predictions are made using the multimode approach and the possibility of using exponential shear to obtain the multimode non-linear spectrum of a melt is explored. It is concluded that, although exponential shear is less effective than extensional flows at exposing the influence of the non-linear parameters of a melt, there are still situations where it is a useful flow for obtaining these parameters.

Tuesday   10:35   Drayton   RT16
BRANCHING STRUCTURE AND RHEOLOGICAL BEHAVIOR OF METALLOCENE POLYETHYLENE
Stephane Costeux, Paula M. Wood-Adams, and Daryoosh Beigzedeh
Department of Chemical Engineering, McGill University, Montreal, Quebec, Canada

Constrained Geometry metallocene catalysts make it possible to control independently various molecular characteristics. The polyethylene produced with these catalysts is of great interest commercially and in terms of providing an opportunity for the systematic study of the effects of various molecular characteristics on material properties. We have made use of Monte Carlo simulations based upon the assumption that long chain branches (LCB) result from the incorporation of macromonomers to predict the detailed branching structure of four polyethylenes. These materials have approximately the same molecular weight distributions and varying levels of LCB and they had previously been submitted to a thorough rheological characterization including both shear and extensional flows. We then used the predicted branching structure to explain the observed rheological behaviors.

Tuesday   11:00   Drayton   RT17
MOLECULAR RHEOLOGY AND STATISTICS OF LONG-CHAIN-BRANCHED METALLOCENE-CATALYSED POLYOLEFINS
Daniel J. Read[1] and Tom McLeish[2]
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We derive the rheologically relevant "priority" and "seniority" distributions of entangled segment topology from a kinetic model of long chain branch formation in metallocene catalysed polyolefins. For the model considered, the chemistry results in a two-parameter family of molecular distributions; convenient parameters are the typical strand molecular weight between crosslinks and a branching probability. Only the branching probability controls the chain topologies. We comment on the different nature of the metallocene ensemble from the usual gellation ensemble that is a candidate for standard low density polyethylene. We calculate the extensional rheology of a model system within a decoupling approximation that permits a partial mapping onto the "multi-mode pom-pom" constitutive scheme.

Tuesday   11:25   Drayton   RT18
THE EFFECTS OF ENTANGLEMENT ON ATTEMPTS TO OBTAIN MOLECULAR ARCHITECTURE INFORMATION FROM POLYETHYLENE VISCOSITIES

David C. Rohlfing
Polymer Physics, Technology Department, Chevron Phillips Chemical Company, Bartlesville, OK 74004

There are many examples in the literature of attempts to extract molecular architecture information for a polymer from rheological measurements of the polymer melt. The main efforts are in trying to determine the molecular weight distribution (MWD) of a polymer from the complex shear viscosity vs. oscillatory shear frequency and in trying to obtain information about the amount of long-chain branching (LCB) present in a given polymer.

This paper presents results of complex viscosity measurements on different entanglement states of polyethylene as expressed by stabilized nascent reactor product (fluff), extruded pellets produced from such fluff, and solvent-treated fluff and pellets. These results show that the complex viscosities can be greatly affected by the degree of physical entanglement of the molecules in the polymer melt. Consequently, what one may calculate for a MWD or amount of LCB may be very different depending on the state of physical entanglement, even though the polymer remains unchanged chemically.

This is illustrated by calculating the amount of LCB present using the Janzen-Colby model for several polymers in these different entanglement states. The results show that when attempting to extract molecular architectural information one must take great care to insure that the rheology measurements are performed on samples in suitably entangled reference states.

Symposium FD
Non-Newtonian Fluid Dynamics & Flow Stability

Organizers: Dilip Rajagopalan and Yuriko Renardy

Tuesday   9:45   Elliott   FD1
THE EFFECT OF VISCOUS HEATING ON ELASTIC INSTABILITIES IN TORSIONAL FLOWS OF POLYMERIC LIQUIDS

Jonathan P. Rothstein and Gareth H. McKinley
Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 01239

The combination of streamwise curvature and elastic normal stresses can lead to the onset of elastic flow instabilities. Torsional shear flows of elastic fluids with closed streamlines can accumulate heat from viscous dissipation resulting in spatial nonuniformities in the temperature profile and nonlinearities in viscometric properties. Recently, it has been shown by Al-Mubaiyedh et al.(1999) that the inclusion of energetics in the linear stability analysis of viscoelastic Taylor-Couette flow can change the mode of the elastic instability. The work to be presented is a detailed experimental study of the effect of viscous heating on the steady shearing of elastic fluids between a rotating cone-and-plate and two coaxial parallel-plates. The relative importance of viscous heating (Nahme number, Na) and elasticity (Deborah number, De) can be quantified by a new dimensionless thermoelastic parameter, $\Theta = Na^{1/2} / De$, which is a fluid material property, independent of the rate of deformation, and is a function of polymer molecular weight, flow geometry and fluid temperature. By utilizing this thermoelastic number, experimental observations of viscoelastic flow stability in three different polystyrene solutions and two different geometries over a range of temperatures can be rationalized and the critical conditions unified into a single flow stability diagram. The thermoelastic number can be systematically varied by altering the temperature of the test fluid. When the timescale for viscous heating is much longer than the relaxation time of the fluid the critical conditions for the onset of the elastic instability are in good agreement with the predictions of isothermal linear stability analyses. As the thermoelastic number increases, strong temperature gradients induced by viscous heating reduce the elasticity of the test fluid and delay the onset of the instability. At even larger values of the thermoelastic number, the flow is stabilizes completely.

Tuesday   10:10   Elliott   FD2

TIME SCALES AND DESTABILIZATION OF NEWTONIAN AND VISCOELASTIC TAYLOR-COUETTE FLOWS CAUSED BY VISCOUS HEATING

James M. White and Susan J. Muller

Department of Chemical Engineering, University of California - Berkeley, Berkeley, CA 94720

The effects of viscous heating on the stability of Newtonian and viscoelastic fluid flow between concentric, rotating cylinders (Taylor-Couette flow) were investigated. It has been established that viscous heating, when coupled with the destabilizing influences of elasticity or inertia, produces instabilities at lower values of the destabilizing parameter (De or Re, respectively). Viscous heating also leads to secondary flows with different temporal symmetry than isothermal instabilities. We present detailed experimental results regarding the time scales and the stability boundaries for the Newtonian instability, and compare the results with the linear and non-linear stability predictions of Al-Mubaiyedh, Sureshkumar, and Khomami. We extend the experimental techniques to viscoelastic fluids, where elasticity rather than inertia is the destabilizing influence. Viscous heating effects appear to explain the long-standing discrepancies between experiments and predictions for critical conditions and the form of the disturbance flow for viscoelastic instabilities. The extraordinarily long time scales for the onset of instability in viscoelastic fluids, however, may require a more detailed explanation.

Tuesday   10:35   Elliott   FD3

ENERGETIC EFFECTS ON THE STABILITY AND DYNAMICS OF VISCOUS AND VISCOELASTIC TAYLOR-COUETTE FLOWS

Usamah A. Al-Mubaiyedh, Radhakrishna Sureshkumar, and Bamin Khomami

Chemical Engineering, Washington University, St. Louis, MO 63130

We have investigated the influence of thermal gradients caused by viscous heating on the stability and nonlinear dynamics of viscous and viscoelastic Taylor-Couette flows. Linear stability analysis predicts that under experimental operating conditions, viscous heating destabilizes the Newtonian and viscoelastic Taylor-Couette flows [1, 2]. Moreover, the secondary flow structures of the non-isothermal flows correspond to new modes of instabilities with different temporal and spatial symmetries as compared to the isothermal Taylor-Couette flow. In this work, we have performed nonlinear stability analysis using time-dependent simulations to investigate the bifurcation structures of the non-isothermal instabilities. Our results indicate that depending on the temperature boundary conditions, a subcritical Hopf bifurcation could result in the Newtonian flow, whereas the viscoelastic flow undergoes a supercritical pitchfork bifurcation. The theoretical predictions have been compared with the experimental findings of White and Muller [3, 4]. A good agreement between theory and experiments is observed for both Newtonian and viscoelastic flows over a wide range of parameter space.

[1] Al-Mubaiyedh, U. A., R. Sureshkumar, and B. Khomami, "Influence of Energetics on the Stability of Viscoelastic Taylor-Couette Flow" Phys. Fluids, 11, 3217-3226 (1999).

[2] Al-Mubaiyedh, U. A., R. Sureshkumar, and B. Khomami, "Linear stability of viscoelastic Taylor-Couette flow: influence of fluid rheology and energetics" J. Rheol., 44, 1121-1138 (2000).

[3] White J.M. and S. J. Muller, "Viscous heating and the stability of Newtonian and viscoelastic Taylor-Couette flows" Phys. Rev. Letters, 84, 5130-5133 (2000).

[4] White J.M. and S. J. Muller, personal communication (2000).

Tuesday   11:00   Elliott   FD4

POLYMER/SURFACTANT-INDUCED EFFECTS ON THE STABILITY OF WALL-BOUNDED SHEAR FLOWS

B. Sadanandan[1] and Radhakrishna Sureshkumar[2]

[1]Washington University, St. Louis, MO; [2]Chemical Engineering, Washington University, Saint Louis, MO 63130

Dissolution of certain polymers or surfactants to wall-bounded shear-dominated flows of Newtonian liquids significantly modifies their stability characteristics. Specifically, viscoelasticity has been shown to have a non-monotonic effect on the critical parameters and/or turbulence intensities. For plane channel flow, both linear and

nonlinear stability analyses have predicted that the critical Reynolds number Rec first decreases with increasing flow elasticity E, defined as the ratio of fluid relaxation time to a time scale of viscous diffusion, until a critical value E = E* is reached and increases back again for E > E*. We show that in the plane Poiseuille flow of an Oldroyd-B liquid, the minimum in the Rec - E curve arises due to two competing contributions to the perturbation vorticity transport in the shear layer: an elastic shear stress contribution that decreases with increasing E and an elastic normal stress contribution that increases with increasing E. When a Deborah number based on the time scale of the critical disturbance becomes O(1) (1.6$\pm$ 0.1), irrespective of the solvent viscosity ratio), the normal stress contribution becomes dominant. The elasticity value at which this occurs, say EC, is found to be very similar to E*. Moreover, both E* and EC exhibit similar asymptotic dependence on the solvent to total viscosity ratio. Furthermore, E* and EC are of the same order of magnitude as the elasticity values at which onset of polymer-induced drag reduction was observed in direct numerical simulations. A similar mechanism surfaces based on the analysis of perturbation kinetic energy transport as well. Finally, we show that the perturbation velocity vector aligns progressively closer with the base flow velocity as E is increased for E < E*, contributing to the initial destabilization. We also investigate the existence of similar mechanisms in more complex shear layers, e.g., in the periodic channel flow.

Tuesday   11:25   Elliott   FD5
STABILITY ANALYSIS OF POLYMER MELT FLOWS USING THE POM-POM MODEL
Arjen Bogaerds, Anne Grillet, Gerrit Peters, and Frank Baaijens
Materials Technology, Technische Universiteit Eindhoven, Eindhoven NL-5600 MB, The Netherlands

Unstable flow conditions can cause severe problems for the processing of polymer products as well as for the final product itself. In order to be able to deal with these difficulties, one of the major issues that needs to be addressed is the dependence of instability on the fluid rheology. This immediately implies that any constitutive model that is used to determine the critical conditions for the onset of instability has to be able to predict the necessary physics of the polymer melt flow. For this, we use the recently proposed pom-pom model which was shown to be able to capture both the steady and the transient behavior of viscometric polymer melt flows.

Essential for the assessment of critical flow conditions is the reaction of the flow to small disturbances. Two different strategies can be followed. First, we will expand the imposed perturbation into normal modes and solve the Generalized Eigenvalue Problem (GEVP). Second, we perform direct time integration of the linearized perturbed flow using viscoelastic Finite Element (FE) calculations. We compute the full eigenspectrum of 1-dimensional flow problems like the planar Couette flow and the pressure driven channel flow and show that these flows remain stable. Also, a comparison will be made between these results and transient FE computations. We show that both numerical methods are consistent and move on to FE computations of more complex flow problems which have more practical relevance.

Symposium SC
Suspensions and Colloidal Systems

Organizers: Daniel De Kee and Robert Lionberger

Tuesday   9:45   Heyward   SC5
SHEAR RESPONSE OF LAYERED SILICATE NANOCOMPOSITES
Ramanan Krishnamoorti and Jiaxiang Ren
Chemical Engineering, University of Houston, Houston, TX 77204-4792

The melt-state linear and non-linear shear viscoelastic properties for a series of intercalated layered-silicate based nanocomposites are studied. The nanocomposites are based on monodisperse polystyrene (30 - 300K) and an organically modified montmorillonite. Both the linear and non-linear viscoelastic properties are closely related to the mesoscale structure and the ability of shear to align the structure. The shear viscoelasticity suggests a high shear rate viscosity and first normal stress difference that are virtually identical to that of the unfilled polymer, suggesting the

ability of shear to orient the layers. On the other hand, at low shear rates the nanocomposites exhibit enhanced viscosity and for samples with ~ 5 wt. % or higher silicate loading the presence of a yield stress. The structural inferences from the viscoelastic measurements are also in good agreement with electron microscopy and small angle neutron and x-ray scattering.

Tuesday   10:10   Heyward   SC6

RHEOLOGICAL SWING TEST TO PREDICT THE TEMPERATURE STABILITY OF COSMETIC EMULSIONS

Rüdiger Brummer, Martin Griebenow, Frank Hetzel, and Rüdiger Uhlmann

4235 Rheology / Thermal Analysis, Beiersdorf AG, Hamburg, Hamburg 20245, Germany

Conventional methods for characterising the stability of cosmetic emulsions are time- consuming and in many cases subjective. To obtain reproducible data about the physical behaviour of cosmetic emulsions a special rheological method was developed. This consisted of a dynamic four cycle mechanical temperature range test. The "rheological swing test" for cosmetic emulsions was performed with parallel plates at constant frequency in the linear viscoelastic range. During the four cycles the temperature was varied from -10°C to 50°C with a programmed constant temperature gradient. Every 10s the amplitude ratio and phase shift was determined and used to calculate the storage modulus G´ and the loss modulus G". Cosmetic emulsions of the types oil-in-water and water-in-oil were freshly prepared and conditioned for 48h at RT (relaxation phenomena) before starting the first test. The rheological swing test was performed with an ARES System after preparation in the first, second, third, fourth and eighth week. Stable formulations show no changes in the storage modulus G´ and loss modulus G" over several cycles at corresponding temperatures. No change is detectable in the shape of curves and in the extreme absolute values. During the storage time no significant changes were detectable. Unstable formulations however show changes in the position of the minimum and maximum values of G´ and G" at the highest and lowest temperatures of -10°C and 50°C. The difference between G´ and G" is less than in the stable formulation. The shape of the curves changes with the cycle time. It is possible to identify the temperature range where the emulsion becomes unstable. Once an instability in a special temperature range has been detected, it is found in all subsequent measurements. This test allows pre-diction of temperature stability of cosmetic emulsions.

Tuesday   10:35   Heyward   SC7

RHEOLOGY OF COLLOIDAL PARTICLES IN CONCENTRATED POLYMER SOLUTIONS

Eugene E. Pashkovski, Lori Szeles, and James G. Masters

Colgate-Palmolive Co., Piscataway, NJ 08855-1343

Rheology of colloidal suspensions is commonly described in terms of interactions between colloidal particles and their volume fraction. Properties of the continuous phase are considered to play a significant role only if they affect interparticle forces. For example, the addition of small amount of a non-interacting polymer may cause flocculation of colloidal particles. At higher polymer concentrations, rheological properties of the continuous phase may play a significant role. In this paper, we discuss influence of viscoelasticity of the continuous phase on mobility and rheology of dispersed colloidal particles in polymer solutions. For weakly viscoelastic polymer solutions, the behavior of colloidal particles and viscoelasticity of the system is controlled by colloidal aggregation. If the viscoelasticity of the continuous phase increases, the aggregation behavior of the colloidal particles changes dramatically. Rheological response of the system can be understood as a combination of contributions from the colloidal and polymer networks.

Tuesday   11:00   Heyward   SC8

A MODEL RELATING STRUCTURE OF COLLOIDAL GELS TO THEIR ELASTIC PROPERTIES

Hua Wu and Massimo Morbidelli

Laboratorium fuer Technische Chemie, ETH Zurich, Zurich, CH- 8092, Switzerland

A new scaling model has been developed to relate the microscopic structure parameters of colloidal gels to their macroscopic elastic properties (storage modulus and limit of linearity). The model, by introducing an appropriate effective microscopic elastic constant, accounts for the elastic contributions of both inter- and intra-floc links. It contains a new parameter, alpha in the range [0, 1], which indicates the relative importance of the two contributions

and allows one to identify the gelation regime prevailing in the system. For extreme values of alpha, the new model correctly reproduces the strong-link (alpha=0) and weak-link (alpha=1) regimes described by Shih et al (1990). Transition regimes are obtained for alpha in the range (0, 1).

The use of the model is twofold. (1) From storage modulus and limit of linearity, one can estimate directly the fractal dimension, df, and an auxiliary parameter, beta. Therefore, one can estimate the fractal dimension in any gelation regime, purely based on rheological properties. (2) In addition, from the estimated value of the auxiliary parameter, beta=1+(2+x)(1-alpha), and assuming the backbone fractal dimension, x in the range [1, 1.3], one can compute the alpha value and identify the gelation regime prevailing in the system.

The developed model has been applied to 12 gelation systems reported in the literature. These systems can be well classified into the three (strong-link, weak-link and transition) regimes. For x in the range [1, 1.3], the estimated alpha values are in [0.98, 1.06] (very close to 1) for the weak-link regime, and in [-0.136, 0.06] (very close to 0) for the strong-link regime. In both situations, the present and the Shih models give the same values of the fractal dimension. For the transition regime corresponding to alpha in (0.4, 0.7), however, only the developed model provides physically consistent results.

Shih, W. H. et al. Phys. Rev. A 1990, 42, 4772.

Tuesday   11:25   Heyward   SC9
RHEOLOGICAL SIMPLE BEHAVIOUR: THE STRESS EQUIVALENT SHEAR RATE, A CONCEPT TO SOLVE COMPLEX FLOW PROBLEMS
Wolfgang Gleissle
Chemieingenieurwesen, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

The flow behaviour of liquid-solid suspensions is normally described by the relative viscosity, the ratio between the suspension and the matrix liquid viscosities. For the dependence of this relative viscosity on the suspension parameters, such as solid fraction, solid particle size and aspect ratio, one finds numerous equations in the literature. For suspensions based on non-Newtonian matrix liquids the relative viscosity is additionally a function of the shear rate and hence not the appropriate value to describe the influence of the solid fraction parameters. Comparing the flow functions of suspensions and the clear matrix liquid at the same shear stress one finds a parameter B describing the effect of the solid fraction on the flow function independent of the shear rate, a rheological simple behaviour. Parameter B is a measure of the increase of the inner shear rate because of the presence of rigid particles. With the flow function of the matrix liquid and parameter B, which is a function of the solid fraction only, the flow function of the suspension is known. By means of B one can define a shear stress equivalent inner shear rate. Taking the same particles but different matrix liquids one gets the same parameter B as a function of the solid fraction. Hence, B is property of the solid only and independent of the flow function of the matrix liquid (and has to be measured for one single liquid). With the concept of the shear stress equivalent shear rate; the transient viscosity, the complex viscosity in oscillation and the flow resistance of porous media, can be described. The same concept gives a tool to separate hydrodynamic forces from other particle-particle intreacting forces e.g. in suspensions.

Tuesday Afternoon

Symposium EA
Elastomers, Adhesives & Soft Solids

Organizers: Jean-Michel Piau, Garth L. Wilkes and David J. Yarusso

Tuesday 1:30 Lady Davis   EA1

STRUCTURING DURING HOT-MELT PROCESSING OF BLOCK-COPOLYMER–BASED PRESSURE-SENSITIVE ADHESIVES

Adrienne E. O'Connor and Christopher W. Macosko

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

The goal of this work is to investigate how the variables in the hot-melt coating process affect the microstructure and properties of pressure-sensitive adhesives based on styrene-isoprene-styrene triblock copolymers. Traditionally, pressure-sensitive adhesives have been coated in solution. Hot-melt coating eliminates solvent emissions and simplifies processing. However, the properties of pressure-sensitive tape are dependent on the coating method used.

Adhesive tape samples have been made through hot-melt and solvent coating methods using materials with the same thermal history. Properties depend on the time scales of application and debonding, as revealed by rheological measurements and performance tests used to capture the various responses. Solvent-coated tape has superior shear strength, while hot-melt coatings display higher tack and peel strength.

Understanding the behavior of an adhesive below its order-disorder transition temperature is necessary for predicting its microstructure and properties. Below this temperature, the microphase separation in the PSA results in nonlinear rheological behavior, even at very small strains. The time required for the adhesive to achieve an ordered state after cooling below the order-disorder transition will determine the degree of phase separation in a hot-melt adhesive, which cools quickly after being coated and may not have enough time to reach equilibrium. Room temperature SAXS shows a narrower primary peak for a solvent-cast sample when compared with a hot-melt-pressed sample, indicating that more order is present. Dynamic measurements during annealing of a hot-melt-pressed sample between the glass transition of the polystyrene phase and the order-disorder transition reveal a transition to an ordered structure marked by an increase in the level of the storage modulus and a decrease in the loss modulus. SAXS indicates that this transition corresponds to the arrangement of the polystyrene spheres onto a body-centered cubic lattice.

Tuesday 1:55 Lady Davis   EA2

THEORY AND ANALYSIS OF PSA PEELING

Jean-Michel Piau[1] and Claude Verdier[2]

[1]UJF-INPG-CNRS, Laboratoire de Rhéologie, Grenoble cedex 9 38041, France; [2]Laboratoire de Rhéologie, Grenoble cedex 9, France

Pressure sensitive adhesives are frequently investigated using peeling tests. However the force necessary to pull the adhesive away from the substrate results from a combination of the material properties, the process characteristics, and stability. It is very important to identify experimentally the specific mechanisms of the various 2D and 3D peeling regimes observed. The elongational viscosity has been found to be one of the key parameters. This allows to review and extend the simplified theories of peeling.

Tuesday   2:20   Lady Davis   EA3
FINITE ELEMENT MODELING OF PSA PEEL USING A STORED ELASTIC ENERGY
DENSITY FAILURE CRITERION
David D. Lindeman and <u>David J. Yarusso</u>
SEMS Technology Center, 3M Company, St. Paul, MN 55144-1000

To correctly simulate the response of a pressure-sensitive adhesive (PSA), both the mechanical behavior and failure mechanisms of the adhesive must be represented. The mechanical behavior of the PSA is generally well-represented by the viscoelastic models implemented in most commercial finite element programs. However, the failure mechanisms are not well-represented by the standard stress-based criteria implemented in the contact surface algorithms of many codes. In addition, fracture mechanics methods, although available, are computationally expensive, and require a detailed representation of the peel front. Strain and energy based criteria, such as those proposed by David Yarusso (Yarusso, D.J. 1999. Quantifying the Relationship Between Peel and Rheology for Pressure Sensitive Adhesives. Journal of Adhesion 70, pp. 299-320), predict the onset of both interfacial and cohesive failures reasonably well, and are well-suited for use in the finite element method.

This paper describes the implementation of the Yarusso PSA model in the general purpose finite element code ABAQUS(TM). In this implementation, the PSA is represented as a viscoelastic solid that is tied to the adherend using multi-point constraints. Debonding - the selective release of the multi-point constraints - is controlled by comparing the local strain and strain-energy density levels in the PSA layer to the limiting values. Finite element simulations of a 180 degree peel test indicate that the model correctly predicts the transition from cohesive to interfacial failures as the peel rate is increased. The predicted steady-state peel forces agree with those reported by Yarusso, but the limit values for strain and strain-energy density must be adjusted to account for differences between the uniaxial stress state assumed by Yarusso, and the multi-axial stress state calculated using the finite element method.

Tuesday   2:45   Lady Davis   EA4
A VISCO-ELASTO-PLASTIC MODEL FOR MATERIALS WITH YIELD STRESS
CHARACTERISTICS
<u>Gareth H. McKinley</u>
Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 01239

We present a new phenomenological constitutive model that describes the time-dependent deformation characteristics of gels and other soft solids exhibiting yield-stress characteristics. The model is inspired by recent developments in the modeling of the flow of granular solids and the creep of amorphous metals and plastics. The internal structure of the material is characterized by a single scalar variable representing the number of binary interaction sites between the molecules, solid filler particles, micelles or other additives which lead to the apparent yield-stress phenomena. The evolution equation for this parameter is nonlinear and depends on the initial conditions, the state of stress and the rate of mechanical work imparted to the system. Below the yield point the system becomes 'jammed'; after an initial transient creep-like response the parameter reaches a constant value and the material does not flow but acts as a nonlinear viscoelastic solid. Beyond a critical stress, however, the number of binary interaction sites decreases and the system 'flows' as a visco-plastic liquid. The onset of flow occurs over a very narrow range of imposed stress; however, the material response is inherently time-dependent, as is the perception of an apparent yield stress. The model only requires determination of three material parameters; a modulus, a relaxation time and a critical stress or 'yield stress'. The model predictions in steady simple shear, small amplitude oscillatory shear flow and in creep/recoil tests accurately capture typical experimental observations. Unlike purely viscoplastic models such as the Bingham plastic, the model does not exhibit discontinuities in the rheological properties and is amenable to numerical computation. We demonstrate this by considering the start-up of rectilinear motion in a pipe.

Tuesday   3:35   Lady Davis   EA5

VISCOELASTICITY OF EPOXY NANOCOMPOSITE GLASSES

Andre Lee[1], Rusty L. Blanski[2], and Shawn H. Phillips[2]
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There is much interest in the dynamics of glass-forming systems above the glass transition temperature. However, in many applications the behavior of the systems needs to be understood in the glass-transition range and particularly in the non-equilibrium state. It has been suggested that the polymer property in the glassy state can influenced by the surrounding environment (topological constraints) and the chain architecture (internal constraints). Using model epoxy systems modified either by the well-dispersed, non-functionalized nanoscopic polyhedral oligomeric silsesquioxane (POSS) macromers (topologlical constraints) or epoxy functionalized POSS macromers (internal constrains), we investigate these effects on the kinetics and nonlinearity of the structural recovery in the glassy state and their impacts on the mechanical response.

Tuesday   4:00   Lady Davis   EA6

ENERGY RELEASE RATE FOR A CRACK IN A TILTED BLOCK

Alan N. Gent and Mehdi Razzaghi-Kashani
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Approximate relations were obtained previously for the tilting stiffness of a rubber block bonded between two rigid plates, assuming linear elastic behavior. They take into account restrictions placed on the deformation by the bonded surfaces, a feature that becomes extremely important for thin blocks of an incompressible material. Results are reviewed here for two special cases: an infinitely wide or a relatively narrow block. In both cases the length and width are assumed to be large compared to the block thickness. Approximate values are then derived for the energy release rate G for a relatively deep crack running into the block on the tension side, parallel to the bonded surface. Values for tilting stiffness and energy release rate have also been calculated by FEA for slightly compressible rubber blocks, with Poisson's ratio in the range: 0.49 to 0.5, and for blocks of various thicknesses. Good agreement is obtained with the approximate theory for deep cracks, when the assumptions on which the theory is based are more likely to be valid. Application of repeated tilting deformations to a bonded rubber block appears to be a simple way of measuring crack growth rates under mechanical fatigue. Moreover, a wide range of energy release rates can be employed using a single specimen.

Tuesday   4:25   Lady Davis   EA7

FORCE TRANSMISSION OF A CONSTRAINED POLYMERIC GEL CYLINDER

Jang-Horng Yu[1], David A. Dillard[1], and Didier R. Lefbvre[2]
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The Poisson's ratio of polymeric gels is somewhat an ambiguous and misunderstood material constant due to the fact that gels exhibit virtually no volume change during deformation. Their Poisson's ratios are very close to 0.5, which is the ratio of a true incompressible material, but are always less than 0.5 because of their slight compressibility. Such deviations, although indeed small, play a significant role in determining the bulk material properties of gels.

In this paper, we study the force transmission of a polymeric gel constrained by and adhesively bonded to a rigid cylinder of finite length. Assuming gels to be purely elastic materials, we have come up with a closed-form solution to calculate the force transmission of the gel cylinder. We find that the force transmission of the gel cylinder is a function of the Poisson's ratio of the gel and the aspect ratio of the cylinder. Notably, a slight change in the Poisson's ratio can have a profound effect on the force transmission of gels. In addition, such analysis can be applied to both elastic and viscoelastic theories.

Based on the analytical study, we develop an experimental technique for measuring the Poisson's ratio by measuring the force transmission of the gel cylinder, but not the volume change. Once the Poisson's ratio is determined, the bulk modulus K can be derived from the elastic modulus E or shear modulus G of gels, which can be measured separately.

The proposed experimental technique will provide crucial experimental data for the bulk material properties of gels. It would also provide essential information for engineers and scientists who use gels as force transmitter, structural components or for biocompatible sensors and actuators.

Tuesday   4:50   Lady Davis   EA8
DYNAMIC NANOSCALE CONTACTS TO ADHESIVE VISCOELASTIC MATERIALS

Manish Giri[1], Douglas Bousfield[1], and William N. Unertl[2]
[1]Chemical Engineering, University of Maine, Orono, ME 04469; [2]LASST, University of Maine, Orono, ME 04469

Dynamic mechanical contacts with nanometer to micrometer dimensions are important in scanned probe microscopy, ultra-low load indentation, microelectromechanical systems, compact discs, etc. These contacts are poorly understood if they involve adhesive viscoelastic materials such as polymers. We have studied contacts to styrene-butadiene latex films with Tg in the range 253-301 K and composite films with polystyrene and CaCo3 pigments. Contact times were in the range 0.01-1000 s and loads were up to 1 mN. Nanoindentation was used, rather than scanned force microscopy, because of its well-defined geometry and capability to control the applied load while simultaneously measuring the displacement. Diamond probes with Berkovich and spherical end shapes were used. Load vs. displacement data showed substantial adhesion hysteresis between the loading and unloading portions. The hysteresis is at least partially due to creep as indicated by the continued increase in penetration after the start of unloading. Works of adhesion were estimated to within 5% by using W as the fitting parameter in modeling the low loading rate adhesion hysteresis curve. The material creep compliance used in this procedure is measured independently. This method is akin to a recent approach suggested by Johnson. Creep tests were carried out under constant load. The model of Hui, Baney, and Kramer (HBK), which predicts the response of an adhesive viscoelastic contact under increasing load, was used to extract a Mode I stress intensity functional. This functional, when normalized by the indentation strain rate, it has a simple universal time-dependence. This result supports the suggestion of HBK that the stress intensity functional may be a simpler alternative to surface energy for characterization of adhesion of viscoelastic materials. For filled anisotropic systems plastic deformation and structure compaction has accounted for.

Symposium RT
Rheology & Topology

Organizers: Jay Janzen and Tom C. B. McLeish

Tuesday   1:30   Drayton   RT19
THE EFFECT OF RANDOM BRANCHING ON THE BALANCE BETWEEN FLOW AND MECHANICAL PROPERTIES OF POLYAMIDE-6

Paul Steeman and Atze Nijenhuis
DSM Research, Geleen NL-6160 MD, The Netherlands

The rheological and mechanical properties of a series of linear and randomly branched polyamide 6 samples, with varying molar mass and varying moderate degree of branching, were investigated.

As expected, it was found that random long-chain branching has a pronounced effect on the rheological behaviour of the materials in both shear and extensional flow. The zero shear viscosity is increased with branching while the flow curve becomes more shear thinning. Randomly branched materials have enhanced melt strength in elongational flow. Although branched, the materials show perfect melt stability in their rheology.

The mechanical properties show minor differences between the linear and the moderately branched samples and are mainly dependent on the weight average molar mass. A small increase in modulus, yield stress and failure stress and a decrease in the strain at break are found, which is probably due to molecular orientation in the plane of injection moulding. The IZOD impact is in agreement with what is normally found for linear polyamide-6, and independent of branching. Also the KIC fracture toughness is not affected by the incorpora-tion of branching. However, it is clearly dependent on the weight average molar mass.

By using branched polyamide-6, molecular weights and related mechanical properties can be obtained that are out of reach for linear polyamide-6.

Tuesday   1:55   Drayton   RT20

THE EFFECT OF BRANCHING ON THE RHEOLOGICAL PROPERTIES OF CONCENTRATED SOLUTIONS OF AB/AB$_2$ ETHERIMIDE COPOLYMERS

Ibrahim Sendijarevic and **Anthony J. McHugh**
Department of Chemical Engineering, University of Illinois, Urbana, IL 61801

In order to study the effects of chain branching on rheological behavior, a series of AB/AB$_2$ etherimide copolymers of essentially constant weight average molecular weight (Mw) and compositions ranging from 0-1 mole fraction AB monomer (x_{AB}) were characterized. Measurements on concentrated solutions, ranging from 0.05 - 0.83 g/ml solids in NMP, showed a slight increase in viscosity with x_{AB} in the composition range of 0 - 0.80 AB, followed by a sharp rise in viscosity at higher x_{AB}. In the dilute regime the viscosity trend correlated directly with the calculated distance between branch points (l_{AB}). Similar behavior was observed for the intrinsic viscosities and Mark-Houwink coefficients. Rheo-optical measurements of dilute solutions indicate negligible birefringence of polymers with $x_{AB} <$ 0.80, followed by a rise in birefringence with x_{AB}. The zero-shear viscosity exhibits a linear dependence on concentration in the dilute regime for the entire series of branched polymers. In the concentrated regime a power law dependence of viscosity on concentration is observed with the power law coefficient increasing with x_{AB}. In steady shear flow the onset of shear thinning occurs at lower shear rates for copolymers with higher fractions of x_{AB}, and the amount of shear thinning increases. Oscillatory experiments indicate increased elasticity with x_{AB}. Mechanical tests show that the strength and toughness of the films increase with x_{AB}.

Tuesday   2:20   Drayton   RT21

RHEOLOGY AND MICROSTRUCTURE OF PDMS-POSS COPOLYMERS

Andre Lee[1], Timothy S. Haddad[2], and Shawn H. Phillips[3]
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Recent advances in the ability to incorporate nanoscopic inorganic polyhedra in organic polymers have provided significant possibilities to produce polymers with enhanced performance. In earlier work, the hybrid polymers were synthesized by copolymerization with monomers containing inorganic polyhedra. Since the polymerization kinetics is affected by the types of monomer used, it is difficult to control the degree of polymerization of these copolymers. However, it is well known that the performance of a linear polymer is strongly influenced by the degree of polymerization. Therefore, it is difficult to access the extend of property enhancement due to the polyhedra incorporation only. In this study, we start with a functional linear polymer, then the inorganic polyhedra were grafted on to the functional group. In this manner, the length of the linear chain is not affected by the amount of polyhedra within the hybrid copolymer. Thus, we separate the effect due to degree of polymerization from the grafting of nanoscopic inorganic polyhedra on the polymer chain. The rheological properties and time-temperature superposition principle of these inorganic-organic hybrid polymers were investigated as a function of amount of polyhedra grafted on to the chain. These results were also compared with the physical blends of polyhedra in the same polymer matrix.

Tuesday   2:45   Drayton   RT22

THE FLOW AND THERMODYNAMIC PROPERTIES OF DENDRITIC POLYMERS

Michael E. Mackay[1], Miyoun Jeong[1], Grant Hay[2], and Craig J. Hawker[3]
[1]Chemical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030; [2]Polymer Materials Laboratory, General Electric Company, Niskayuna, NY 12309; [3]IBM Almaden Research Center, San Jose, CA

Dendritic polymers or dendrimers are highly branched polymers which have a large number of end groups. We have studied these polymers and found them interesting in that they do not seem to exhibit entanglements. The thermodynamic results suggest the dendrimers interpenetrate in the melt, however, the degree of interpenetration is

dependent on their molecular mass or generation number. Despite this effect the intermolecular penetration is low enough for the shear viscosity to be linear with molecular mass. Furthermore, when they are attached to the end of a linear polymer (hybrid copolymer) they seem to create a reduced viscosity compared to the neat polymer. We have recently found the hybrid copolymers can achieve a variety of configurations which can be the cause of this unique effect. Also, this configuration change can cause the glass transition temperature to vary for the hybrid copolymers by up to 30°C.

Symposium AS
Associating Polymers and Surfactant Systems

Organizers: Ralph H. Colby and Andrew M. Howe

Tuesday   3:35   Drayton   AS1
DYNAMICS OF ASSOCIATING POLYMERS

Michael Rubinstein[1] and Alexander N. Semenov[2]
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The process of making and breaking reversible bonds between associating groups (stickers) controls the dynamics of associating polymers. We develop a theory of "sticky reptation" to model the dynamics of entangled solutions of associating polymers with many stickers per chain. At high degree of association there are very few unassociated stickers. It is therefore very difficult for a sticker to find a new partner to associate with after breaking the bond with an old one. Typically a sticker returns to its old partner following an unsuccessful search for a new one, prolonging the effective lifetime of reversible bonds. In the sticky reptation model the search for a new partner is restricted to a part of the tube confining entangled chain. Another important effect is the increase of the fraction of the inter-chain associations at the expense of the intra-chain ones with increasing polymer concentration. The sticky reptation model predicts very strong concentration dependence of viscosity in good agreement with experiments.

Tuesday   4:00   Drayton   AS2
A MODEL FOR THE VISCOELASTIC RESPONSE OF MICELLAR SOLUTIONS OF TELECHELIC POLYMERS

Xiaoxia X. Meng and William B. Russel
Chemical Engineering, Princeton University, Princeton, NJ 08544

We have correlated the viscoelastic response of three model associative polymers, CnHn(EO)m-CnHn with n = 16, 18 and m = 460, 800, with parameters characterizing the micellar structure of the solutions, motivated by the flowerlike micelle theory of Semenov, et al. Relating the micellar radius and the entropic attraction and excluded volume repulsion between micelles to the aggregation number and the association energy to the hydrophobe size leads to quantitative scalings of the high frequency modulus and the relaxation time. These reproduce our experimental data fairly well. Comparisons with data for other compositions, for which aggregation numbers are known is underway, as is an effort to correlate aggregation number with molecular structure.

Tuesday   4:25   Drayton   AS3
GELATION IN PHYSICALLY ASSOCIATING POLYMER SOLUTIONS

Sanat K. Kumar[1] and Jack Douglas[2]
[1]Dept of Materials Science and Engg, Penn State University, University Park, PA 16802; [2]NIST, Gaithersburg, MD

Computer simulations are used to explore the reversible gelation of solutions of associating polymers where sticker pairing energies are comparable to thermal energy (``weak stickers"). Reversible gelation is shown to be a dynamical transition where transport is arrested, as in glass formation. Geometrical percolation, which is a distinct transition occuring at a much higher temperature, is therefore unrelated to gelation. The similarity of polymer physical gelation and vitrification suggests that these phenomena should be describable by a common language.

Tuesday   4:50   Drayton   AS4
**RHEOLOGY AND DYNAMICS OF ASSOCIATIVE POLYMERS IN SHEAR AND
EXTENSION: THEORY AND EXPERIMENTS**

**Anubhav Tripathi[1], Gareth H. McKinley[1], Michael Kam Chiu Tam[2], and Richard D.
Jenkins[3]**

[1]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 01239;
[2]Mechanical & Production Engineering, Nanyang Technological University, Singapore;
[3]Technical Center, Union Carbide Asia Pacific Inc., Singapore 118227, Singapore

We present a systematic study of the shear properties of a series of model hydrophobically modified ethoxylate-urathane (HEUR) polymers with varying degrees of hydrophobicity. The steady shear viscosity exhibits Newtonian behavior at low shear rates, and then exhibits pronounced shear thinning. For a certain intermediate concentration range in the vicinity of 1-4 wt.%, the solutions exhibit considerable shear thickening prior to the onset of shear thinning at shear rates. Linear viscoelastic properties obtained from small amplitude oscillatory shear measurements show that these telechelic polymer systems possess a dual relaxation behavior, which can be well described by a two-mode Maxwell model. The two time constants are related to the Rouse relaxation time tau_R of a polymer chain (~0.003s) and to the network relaxation time tau_N (~ 0.1s). The network relaxation time shows a power law dependence on concentration with code tau_N ~ $c^{2/3}$. A nonlinear network model is described which incorporates appropriate molecular mechanisms for the chain creation and destruction. Like earlier models we model the contributions of both the bridging chains and the dangling chains to the total stress tensor. Both the zero shear viscosity and the network relaxation time show good agreement with experimental results. The model also captures both the shear-thickening and shear-thinning regimes due to the nonlinear forms of the expressions for the collision rate and the ejection rate of hydrophobes. Using a filament rheometer, the HEUR samples were stretched at various strain rates, ranging from 0.1 to 15 1/s, and the critical extensional stress to breakup/rupture was measured. The results from extensional experiments show that the filaments undergo a visco-capillary thinning at low strain rates, however at high strain rates the physical gels exhibit a sudden rupture phenomenon. These critical extensional stresses are an order of magnitude higher than corresponding critical stresses for onset of shear thinning.

Symposium FD
Non-Newtonian Fluid Dynamics & Flow Stability

Organizers: Dilip Rajagopalan and Yuriko Renardy

Tuesday   1:30   Elliott   FD6
BREAKING UP IS HARD TO DO
Yuriko Renardy
Mathematics, Virginia Tech, Blacksburg, VA 24061-0123

Experimental studies of drop deformation and breakup under shear go back to the ancient Babylonians and Egyptians who used emulsions of oil and vinegar to season their salads. The ability to simulate the phenomena involved in emulsification numerically, on the other hand, is a much more recent development. In this talk, I show simulations of the deformation and breakup of a drop surrounded by a matrix fluid under shear. The simulations are based on a volume-of-fluid scheme. I shall discuss the effect of inertia on drop breakup, the size distribution of daughter drops, and the effect of surfactants. The talk features an exciting program of videos and music.

Tuesday   1:55   Elliott   FD7
MAKING BREAKING UP HARDER TO DO
Michael Renardy
Mathematics, Virginia Tech, Blacksburg, VA 24061-0123

Polymer additives are very effective in suppressing the breakup of liquid jets. This was exploited by spiders long before anyone ever heard of the Babylonians and Egyptians. In this lecture, I shall discuss one-dimensional model

equations for slender jets and compare various constitutive theories for Newtonian and viscoelastic fluids. We shall learn about results on breakup or its absence and about similarity solutions which describe the asymptotic approach towards breakup.

Tuesday   2:20   Elliott   FD8

DYNAMICS OF FORMATION OF NON-NEWTONIAN DROPS FROM CAPILLARIES: COMPARISON OF PREDICTIONS MADE WITH GENERALIZED NEWTONIAN AND VISCOELASTIC CONSTITUTIVE EQUATIONS

Ozgur E. Yildirim and Osman A. Basaran
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-1283

Dynamics of drop formation is important in many applications including ink-jet printing, biochip arraying, spray coating, and crop spraying where the working fluid is often non-Newtonian. Whereas a considerable amount of work has been done to date on the formation of drops of Newtonian liquids from a capillary, such studies of non-Newtonian liquids are virtually nonexistent. Here we present a theoretical study of dynamics of formation and breakup of drops of non-Newtonian liquids from capillaries and compare their response to that of drops of Newtonian liquids. Two types of constitutive equations are considered for describing non-Newtonian response. The first is a Carreau type generalized Newtonian fluid model that takes into account both shear thinning and strain hardening effects (see Song & Xia 1994). The second is a FENE-CR model that accounts for fluid viscoelasticity (see Chilcott & Rallison 1988). The mathematical problem is simplified by means of a regular perturbation or slender-jet analysis which reduces the original set of 2-d equations to a set of 1-d equations. The resulting set of transient, nonlinear equations is solved numerically by a method of lines using the Galerkin/finite element method for discretization in space and an adaptive finite difference method for discretization in time. The computations are carried out beyond the instant of first pinchoff to study the dynamics of any satellites that may be formed and interactions between the satellite(s), the primary drop, and the liquid mass hanging from the capillary. The predictions of the 1-d simulations are compared to experimental measurements. Among other things, the constitutive behavior is shown to have a profound effect on the dynamics. An interesting computational result is the occurrence of "bead-on-string" patterns, which are shown to arise when strain-hardening dominates.

Tuesday   2:45   Elliott   FD9

ORIENTATION OF SYMMETRIC BODIES IN A SECOND-ORDER LIQUID AT SMALL AND NONZERO REYNOLDS NUMBER

Giovanni Galdi
Mechanical Engineering, University of Pittsburgh, Pittsburgh, PA 15261

A detailed experimental study of the orientation of long symmetric particles sedimenting in viscoelastic liquids has been recently performed by Liu & Joseph. This work was motivated by the study of aggregation of spheres and, more generally, of flow-induced microstructures, and differs from similar previous experimental studies in that it focuses on the coupled effect of inertia and elasticity on the final orientation of the particles. Let us call Q the tilt angle formed by the long axis of symmetry of the particle with the horizontal, when the body reaches its final equilibrium orientation. Liu & Joseph have found that for squared-off cylinders with flat or round ends Q may vary continuously from 0 to 90 degrees, depending on weight, length and shape of the particle, and on viscosity and polymeric concentration of the liquid . The dimensionless numbers involved in these experiments may be very small. Therefore, the tilt angle phenomenon is a first order effect. In the current literature it is hypothesized that this phenomenon is due to the balance of the competing effect of the inertial and viscoelastic torques. This hypothesis is also supported by a qualitative analysis of the force acting on a particle moving in a second order liquid. Even though this explanation is very plausible and appealing, we show, by a rigorous mathematical analysis, that a long symmetric particle sedimenting in a second-order liquid at small and nonzero Weissenberg and Reynolds numbers can only have Q= 0 or Q=90 . This proves that the competition of inertia and viscoelasticity is not responsible for the tilt angle phenomenon. However, we also show that this competition is responsible for the stability of the two orientations.

Tuesday   3:35   Elliott   FD10
SWIRLING FLOW OF VISCOELASTIC FLUIDS
David V. Boger
Particulate Fluids Processing Centre, The University of Melbourne, Victoria 3010, Australia

A torsional driven cavity consisting of a fully enclosed cylinder with a rotating bottom lid is used to examine the confined swirling flow of constant viscosity elastic liquids (Boger fluids). A wealth of phenomena are observed as the degree of inertia, elasticity and viscous forces are varied by using a range of low to high viscosity flexible polyacrylamide Boger fluids. As the inertia is decreased and elasticity increased the circulation rates for a "Newtonian like" secondary flow decreases until flow reversal occurs due to increasing magnitude of the primary normal stress difference. For each polyacrylamide fluid the flow becomes highly unstable at a critical combination of Reynolds number and Weissenberg number, resulting in a new time dependent elastic instability. Each fluid is characterised by a dimensionless elasticity number and a correlation with Reynolds number is found for the occurrence of the instability. Velocity field data are available on the flow obtained using particle image velocimetry PIV. In addition the fluids are all rheologically well characterised; thus the flow field is available to test numerical simulation methods in non-Newtonian fluid mechanics. A video is used to demonstrate the transition from inertia dominated flows to elasticity dominated flows.

Tuesday   4:00   Elliott   FD11
AXISYMMETRIC FLOW BIREFRINGENCE: EXTENSION TO A TIME-DEPENDENT STAGNATION FLOW
Jason Bryant and Wesley R. Burghardt
Northwestern University, Evaston, IL

Our group has previously developed strategies for flow birefringence studies of complex axisymmetric flows, and applied the method to study axisymmetric stagnation flows of polymer solutions. Access to axisymmetric geometries allows non-invasive probing of stress distributions in flows of greater kinematic complexity than is possible in the planar flow fields more traditionally studied using flow birefringence. Here we report progress on the application of this technique to a time-dependent, axially symmetric stagnation flow, in which fluid is periodically forced back and forth against the end of a cylinder with a hemispherical tip. The geometry closely resembles the one employed in our previous studies, but allows independent variation of Deborah and Weissenberg numbers (through independent control of the amplitude and frequency of the motion), and also imposes periodically reversing kinematics, in which fluid in the stagnation region alternately experiences uniaxial and biaxial extension. This new flow can thus provide tests of viscoelastic fluid models under severe conditions. We will present preliminary data obtained on a concentrated by low MW polystyrene solution, with essentially Newtonian rheology, to demonstrate the principles and capabilities of the experiment.

Tuesday   4:25   Elliott   FD12
DYNAMIC RESPONSE OF A SHEAR STRESS TRANSDUCER
Chanyut Kolitawong and A J. Giacomin
Mechanical Engineering, The University of Wisconsin-Madison, Madison, WI 53706

The damping caused by polymer melt, which commonly gets into the housing of a shear stress transducer, is determined analytically. The analysis employs bipolar coordinates and is applied to Newtonian and then linear viscoelastic fluids. Results are compared with available dynamic calibration measurements, and also with previously used empirical models for the transducer damping. Dimensionless graphs are then provided for estimating transducer attenuation and phase error in oscillatory shear measurements.

Key Words: Sliding Plate Rheometer; Transducer Damping; Shear Stress Transducer; Bipolar Cylindrical Coordinates; Dynamic Transducer Calibration

Tuesday   4:50   Elliott   FD13
CONTRACTION FLOW BEHAVIOR OF METALLOCENE-CATALYZED POLYETHYLENES
Phillip J. Doerpinghaus and **Donald G. Baird**
Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061-0211

The presence of flow contractions in polymer extrusion applications often leads to added pressure drops and may initiate flow instabilities at higher flow rates. The magnitude of the response is generally determined by the rheological characteristics of the melt. The development of metallocene catalysts now provides the ability to tailor polyethylene resins with specific molecular attributes and rheological properties. In the present study, the contraction flow behavior of various conventional and metallocene polyethylene resins has been investigated using abrupt planar and axisymmetric contraction geometries. Pressure measurements combined with full-field flow birefringence observations have been collected for each resin and compared to corresponding numerical simulations.

Symposium SC
Suspensions and Colloidal Systems

Organizers: Daniel De Kee and Robert Lionberger

Tuesday   1:30   Heyward   SC10
DYNAMICS OF CONCENTRATED COLLOIDAL SUSPENSIONS AND GELS
Sara Romer, Hugo Bissig, Anna Stradner, Frank Scheffold, Vladimir Lobaskin, Veronique Trappe, and **Peter Schurtenberger**
Physics Department, University of Fribourg, Fribourg CH-1700, Switzerland

We present a systematic study of the sol-gel transition in concentrated colloidal supensions where we compare results from optical microrheology using diffusing wave spectroscopy (DWS), classical rheology and computer simulations. We demonstrate that concentrated suspensions exhibit universal features during the sol-gel transition. We observe for the local (microscopic) particle dynamics an abrupt transition from free Brownian diffusion to an arrested subdiffusive motion which is clearly related to the corresponding build-up of the elastic properties of the macroscopic particle gel. We demonstrate that we can extract from the DWS data quantitative information about the viscoelastic properties of the suspensions and gels such as the elastic modulus and the frequency dependent storage and loss moduli over an extended range of frequencies, and we compare these data to those directly obtained from rheological measurements

Tuesday   1:55   Heyward   SC11
MECHANICAL DEFORMATION OF 2D AGGREGATED COLLOIDS
Sarunya Promkotra and **Kelly T. Miller**
Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401

The shear and compressive yield stresses of aggregated colloidal particles are strongly dependent upon particle volume fraction, interparticle force, and suspension microstructure. Models to predict these yield stresses, however, are still poorly developed, largely due to lack of understanding of the microscale rearrangement mechanisms which the particles undergo during yield. In this study, we experimentally examine such rearrangement mechanisms in a model two-dimensional aggregated colloid. Aggregated 2D colloids are formed by trapping polystyrene particles at the air-liquid interface of viscous substrates, composed of glycerol-water or sucrose-water solutions. These particle networks are then subjected to large scale mechanical deformations in compression and shear using micromanipulation techniques, and particle movement tracked through digital video microscopy. The mechanisms of particle rearrangement, their frequency, and their dependence upon network structure and volume fraction are systematically investigated.

Tuesday   2:20   Heyward   SC12
THE E-FIRST EFFECT: ELECTRO-RHEOLOGY OF SHEAR THICKENING COLLOIDAL SUSPENSIONS
Sudhir S. Shenoy[1], Norman J. Wagner[1], and Jonathan W. Bender[2]
[1]CMET, Chemical Engineering, University of Delaware, Newark, DE 19716; [2]Analytical Instrumentation Facility, North Carolina State University, Raleigh, NC 27695

External fields have known to significantly alter the rheology of colloidal suspensions. While the field effects on the low shear rheology of dilute to moderately concentrated suspensions have been thoroughly investigated, the effects on the high shear rheology of concentrated suspensions are relatively unexplored. In this work, we present data on the influence of an orthogonal electric field on shear thickening. A concentrated, Brownian-near-hard-sphere suspension of surface-modified Stöber silica in an index-matching medium has been characterized and its electrorheology studied. We find that the E-field significantly affects the onset of shear thickening. This E-FiRST (Electrical Field Responsive Shear Thickening) effect can be rationalized in terms of the electrical polarization of the particles influencing the development of the hydroclusters necessary for shear thickening. The dependence of E-FIRST on electrical frequency dependence is explored and complementary measurements of the frequency dependent dielectric constant enables deconvoluting the relative influence of polariziation versus conduction. This E-FiRST effect may have technological application in control and high shear damping devices.

Tuesday   2:45   Heyward   SC13
CHARACTERIZATION OF ER FLUIDS WITH DYNAMIC DROP VISCOMETRY
Laszlo J. Kecskes
Weapons and Materials Research Directorate, US Army Research Laboratory, APG, MD 21005-5069

Key rheological properties of three commercially available, high shear-strength (σ_y = 4 kPa at 4 kVmm^{-1} and 298 K) electrorheological (ER) fluids have been determined with a new type of constant-stress viscometer. Of primary interest were the effects of the electric field and temperature on the fluid plastic viscosity and yield stress. Concurrent with the evaluation, the current density drawn by each fluid was also measured. The unique design of the device allowed viscosity and shear stress measurements over a range of shear rates of up to 10,000 s^{-1}. The redesigned Stormer viscometer consisted of a dropweight that was connected by a cord to a vertically mounted, free-to-rotate spindle. The spindle's bottom end was fitted with a cup/bob arrangement that held the fluid. In each measurement, the drop-weight was raised, the electric field was applied to the fluid, and the weight was released. Falling under the influence of gravity, the weight caused the spindle to rotate, which, in turn, sheared the fluid in the cup. The ER torque exerted on the shaft increased with increasing fluid activity; correspondingly, the net acceleration of the weight decreased. The viscosity and shear stress of the fluid were obtained by applying a two-parameter curve fit to the overall displacement vs. time trajectory of the falling weight. Details of the technique, data collection, and calibration procedures, as well as the fluid properties, are discussed in this presentation.

Tuesday   3:35   Heyward   SC14
PROBING MOBILITY OF MAGNETIC PARTICLES INSIDE DRYING COATINGS
Andrei Potanin
Data Storage, Imation Corp., Oakdale, MN 55128-3414

Mobility of magnetic particles inside drying coatings is probed with AC and DC magnetic fields. AC susceptibility decay characterizes particles immobilization during drying. Filament coating device is used to study orientation of particles under DC field. A mean-field model relates particle orientation to rheological properties of the drying coating.

Tuesday   4:00   Heyward   SC15

RHEOLOGICAL BEHAVIOR AND MICROSTRUCTURE OF MAGNETIC PARTICLE DISPERSIONS DILUTED WITH NONMAGNETIC PARTICLES

Young S. Lee, Byeong S. Chae, and Alan M. Lane
Department of Chemical Engineering and MINT Center, The University of Alabama, Tuscaloosa, AL 35487

The rheological behavior of dispersions containing magnetic Co-γ-Fe$_2$O$_3$ particles diluted with non-magnetic Co-α-Fe$_2$O$_3$ particles was studied. We present the frequency, stress and strain dependence of the dynamic shear storage and loss moduli (G$_¡^-$ and G$_¡\pm$) as magnetic particle content increases. With the stress sweep experiment, the critical stress marking the linear viscoelastic limit for the suspension was almost the same as the apparent yield stress obtained from the steady shear experiment for all magnetic particle concentrations. In the nonlinear region, the storage modulus decreased rapidly while the loss modulus passed through a maximum and then decreased less dramatically than G$_¡^-$. The crossover between G$_¡^-$ and G$_¡\pm$ marks the transition from solid-like behavior to liquid-like behavior. This transition stress as well as the critical stress is shifted to higher stress with increasing magnetic particle fraction. The critical strain at the linear viscoelastic limit was found to have the same value of 0.1 with different magnetic particle fractions. This observation suggests that the mechanism of breakdown of network structure is similar for all samples. At small stresses within the linear viscoelastic regime, the storage shear modulus for mixed magnetic particle dispersions (> 50% magnetic particles) was independent of frequency. This plateau in the storage modulus is evident of a long range network structure. The loss modulus exhibited a minimum at a certain frequency. The linear increase of the loss modulus at high frequency reflects the initial diffusive motion of the particle while at low frequency their motion is constrained by the network structure. The viscosity exhibited double relaxation behavior representing two structures. These may be related to the breakdown of the magnetic particle network and breakdown of small flocs of magnetic particles.

Tuesday   4:25   Heyward   SC16

A SLOTTED PLATE DEVICE FOR MEASURING STATIC YIELD STRESS

Daniel De Kee, Lixuan Zhu, and Kyriakos Papadopoulos
Department of Chemical Engineering, Tulane University, New Orleans, LA 70118

A slotted-plate device was constructed with a balance and a linear-motion platform to directly measure static yield stresses of suspensions by moving the plate in the suspension in a similar mode as is done in the well-known Wilhelmy-plate technique for measuring surface tension. Wall effects associated with our original plate yield-stress instrument were minimized by opening a series of slots on the plates. Yield-stress experiments were conducted on both high-concentration (40, 50, 60 and 70 wt % TiO2) and low-concentration (2, 3 and 5 wt % bentonite) aqueous suspensions. Our new setup avoids the disadvantages of the vane instrument, possible secondary flow between the blades as well as a non-uniform stress distribution along a virtual cylindrical surface. Yield stress values of TiO2 suspensions were compared with the values obtained via a variety of other methods, including indirect extrapolation from steady-shear data, vane creep testing, and vane stress-ramp measurements using an SR-5000 rheometer. Very small yield stress (up to ~10-4 Pa) measurements of low-concentration bentonite suspensions (2, 3, 5 wt %) could be determined only with our slotted-plate device. The vane method could not measure yield stress values of bentonite suspensions of less than 7 wt % concentration. Relaxation tests on high-concentration suspensions indicated that these suspensions may not be purely elastic below yield stress.

Tuesday   4:50   Heyward   SC17

DIRECT MEASUREMENT OF STRONGLY ATTRACTIVE PARTICLE-PARTICLE INTERACTIONS

Kelcey L. Eccleston and Kelly T. Miller
Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401

Direct measurements of strongly attractive particle-particle interactions are performed using a novel micromechanical testing technique. In this technique (adapted from the work of Yeung and Pelton), particles are attached to borosilicate glass microcapillaries, which act as force transducers. These are then repeatedly brought into

contact and subsequently separated using micromanipulators under a light microscope. Interparticle force is determined from the displacement of the microcapillaries, which is measured using digital video microscopy techniques. Two systems are examined and compared as a function of particle size, solution pH, and surface roughness: an aluminosilicate powder with very smooth surfaces and an alpha alumina powder with very rough surfaces.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday   8:30   Archer   PL3
STRUCTURE AND DYNAMICS OF SURFACTANT MESOPHASES
<u>**Robert K. Prud'homme**</u>
Department of Chemical Engineering, Princeton University, Princeton, NJ 08544

The rheology of surfactant solutions provides a rich field for investigation because the length scales of surfactant self-assembled mesophases produces time scales of structural rearrangement comparable to the time scales of flow processes. Subtle changes in surfactant structure, concentration, or solution properties can be used to manipulate self assembly and tune rheological response. We will provide an overview of surfactant rheology beginning with the rheology of solutions of spherical micelles, then moving to rod-like micelle systems, which behave like entangled polymer solutions. Liquid crystalline (lamellar) phases obey rheological rules not unlike those governing liquid crystal polymer solutions. The effect of flow on rheology of surfactant mesophase structure is even more pronounced than the effect of flow of polymeric fluids leading to phase separation and closed vesicle structures. Finally we will point to interesting problems that involve interactions between surfactant mesophases and polymers and particles.

Symposium FB
Food and Biopolymers

Organizers: Jeff Byars, Peter Fischer and Jozef Kokini

Wednesday   9:45   Lady Davis   FB1
GELATION OF GLOBULAR PROTEINS
<u>**Simon B. Ross-Murphy**</u>
Biopolymers Group, Division of Life Sciences, King's College London, London SE1 9NN, United Kingdom

Significant advances in the structure and rheological properties of globular protein gels are described. The kinetics of gelation measured by rheological methods are also discussed, including currently applied models for the gelation time, the gel elastic modulus and the critical gel concentration.

In particular the gelation behaviour of solutions of relatively pure beta-lactoglobulin (under isothermal heating at 80°C) were investigated over a range of concentrations and pH values (7, 3, 2.5 and 2). Both gel time and limiting (extrapolated) long-time modulus data have been measured and considered in the light of currently available models for the gelation process.

While the gel time data was described best by a semi-empirical model, the modulus data could be quite adequately understood in terms of branching theory (cascade theory description) results corresponding well with conclusions from structural studies of the gels using negative-staining electron microscopy. A fractal model, which suggests that the modulus-concentration behaviour can be described by a single power law, was much less successful in this respect. Gel time data, it seems, reflect much more sensitively the details of network assembly in a particular case. Modulus-concentration data, on the other hand, are less determined by gel type and more universal.

Gosal WS, Ross-Murphy SB: Globular protein gels. Current Opinion in Colloid & Interface Science 2000, 5:209-215.

Kavanagh GM, Clark AH, Ross-Murphy SB: Heat-induced gelation of globular proteins: Part 4 Gelation kinetics of low pH beta-lactoglobulin gels. Langmuir 2000, in press

Wednesday   10:10   Lady Davis   FB2

MICROSCOPIC DETERMINATION OF CROSSLINKED STARCH GRANULE STIFFNESS

Julie B. Hirsch[1], <u>Jozef L. Kokini</u>[2], William McConnoughey[3], and Elliot Elson[3]
[1]R&D, Gorton's Seafood, Gloucester, MA 01930; [2]Department of Food Science, Rutgers, The State University of New Jersey, New Brunswick, NJ 08901-8520; [3]Washington University School of Medicine, St. Louis, MO

To fully understand the contribution of crosslinked starch to a food system, it is important to be able to characterize the physical properties of the individual granules. Although bulk property rheological measurements of starches indicate that crosslinking increases the stiffness of starch granules, there is no information in the literature which proves this, specifically addressing the effect of chemical crosslinking at the microscopic level. The objective of this work is to quantify the stiffness of individual starch granules, treated with three different crosslinking agents (phosphorous oxychloride (POCl3), sodium trimetaphosphate (STMP), and epichlorohydrin (EPI)) with microscopic, physical measurements. Using an apparatus called a microscopic cell poker, we have shown that average stiffness of gelatinized swollen starch granules increases with increasing crosslinking agent concentration, with a range of 3.70 to 15.3 dyn/cm^3 for three concentrations of each of these crosslinking agents. Quantification of granule stiffness was achieved using the slope of a force/distance curve generated from the bending of a horizontal beam, which is attached to a glass rod (poker). The poker is programmed to penetrate the granule a certain distance and the resulting magnitude of force is calculated based on the degree of beam bend. When comparing the three agents on a molar concentration basis, STMP granules showed the greatest deformability, then EPI, and POCl3 treatment resulted in the stiffest granules. This research builds on the existing knowledge of starch and may prove useful to better predict the many functional benefits of food starches.

Wednesday   10:35   Lady Davis   FB3

AGGREGATION AND GEL FORMATION IN BIOPOLYMER SOLUTIONS

<u>Anna Stradner</u>, Sara Romer, Claus Urban, and Peter Schurtenberger
Physics Department, University of Fribourg, Fribourg CH-1700, Switzerland

We report on an investigation of the microscopic structure and dynamics of biopolymer gels and relate them to the macroscopic viscoelastic properties of such systems. Biopolymer solutions and gels represent one of the most interesting class of gelling systems since they are of major industrial and scientific interest. Despite the importance of biopolymer gels and the role of the sol-gel transition in this context there have only been a few attempts to link our current understanding of colloidal model systems to 'real world' biopolymer solutions and gels. We have thus performed a systematic study using concentrated solutions of casein micelles which we destabilized and investigated during the process of gelation using dynamic and static light scattering, diffusing wave spectroscopy (DWS) and rheological measurements. An analysis of the light scattering data shows a significant increase in the characteristic decay time of the correlation functions during the sol-gel transition. For the analysis of the DWS data we developed an algorithm which, based on the microrheology approach of Mason et. al. [1], determines the viscoelastic properties G'(w) and G"(w) of the gel. A comparison of the results obtained with DWS and measurements with a rheometer shows excellent agreement of both approaches [2]. We demonstrate that we can clearly link the changes observed in the microscopic dynamics to the formation of a macroscopic gel with drastically modified viscoelastic properties. Our results obtained with casein are also compared with those obtained with colloidal model systems such as concentrated latex suspensions.

[1] T. G. Mason, H. Gang and D. A. Weitz, J. Opt. Soc. Am. A 14 (1997) 139.

[2] C. Urban, S. Romer and P. Schurtenberger In Proceedings of the 2nd International Symposium on Food Rheology and Structure, P. Fischer, I. Marti, E.J. Windhab Eds., Zürich (2000), p. 41-46.

Wednesday   11:00   Lady Davis   FB4

RHEOLOGY OF CONCENTRATED BIOPOLYMER SYSTEMS WITH ELASTIC FILLER PARTICLES

Irene Marti, Peter Fischer, and Erich J. Windhab

Laboratory of Food Process Engineering, ETH Zurich, Zurich 8092, Switzerland

Viscoelastic fluids filled with elastic particles exhibit complex non-Newtonian flow behaviour. Beside the volume fraction occupied by the disperse phase and the shear viscosity of the continuous phase, the viscoelastic properties of both the disperse and the continuous phase, and the interactions between them can not be neglected for a fundamental understanding of the rheological properties of such systems.

A well-described example for filled food biopolymer systems are starch pastes where swollen starch granules act as elastic filler components in a viscoelastic matrix containing solved polysaccharide molecules. For food protein systems extensive research has been done in the analysis of rheology and structure of low dry matter milk protein gels like yoghurt. However, little attention has been given to concentrated milk protein systems (with caseins and whey proteins) where the minor milk protein fraction, the whey proteins, is in the native state and thus able to build up an entangled network whereas the caseins which form submicelles or micelles act as elastic filler particles.

With respect to large deformation processes, the steady-state shear viscosity and first normal stress difference of concentrated milk protein systems are studied by rotational and capillary rheometry. The investigated milk protein systems contain caseins (filler) and whey proteins (matrix) at a weight ratio 8:2. In the investigated concentration and temperature regimes we found a constant zero shear viscosity. First normal stress difference and viscosity functions were quantified in a temperature range of 10 °C to 30 °C at concentrations of 15 % to 30 % dry matter. Related temperature and concentration dependencies are interpreted with respect to microstructure and prossesing.

Wednesday   11:25   Lady Davis   FB5

ENZYMATIC CONTROL OF RHEOLOGY IN MIXED BIOPOLYMER GELS

Vandita B. Pai and Saad A. Khan

Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695

Natural polysaccharides have diverse applications in the food industry as gelling and texture-modifying agents. Our studies on the selective enzymatic hydrolysis of guar galactomannan provides insights into techniques for producing novel biopolymers with enhanced functionality. Highly specific enzymes are used to cleave off the side chains of guar resulting in a range of galactomannans with varying molecular architecture. A rheological investigation into blends containing xanthan and the modified polymer reveals that the extent of synergism illustrated by the dynamic storage modulus G' is proportional to the degree of modification. Ionic strength of xanthan solutions and the blending temperature of the gels are varied to examine the influence of xanthan conformation on the viscoelastic behavior of these systems. At low extents of modification, the blends form weak physical gels whose properties are independent of temperature/ionic strength. When the galactose content is reduced further, an increase in the blending temperature leads to a corresponding increase in the measured storage modulus. However, increasing the ionic strength produces weaker gels. Thus, the rheological characteristics of the mixtures are dictated both by the extent of modification as well as the conformation of the xanthan molecules. As the galactose content of guar progressively decreases, the mixed gel modulus and yield strength passes through a maximum. As more of the mannan backbone is exposed, intermolecular associations between adjacent guar chains assume importance resulting in a transition to softer, synerising gels beyond the maximum. This phenomenon of self-association of modified guar molecules is also evident when guar solutions and the mixed gels are allowed to age. Images obtained from confocal scanning laser microscopy of fluorescently tagged gels provide evidence for self-aggregation which eventually leads to phase separation in the mixed systems.

Symposium AS
Associating Polymers and Surfactant Systems

Organizers: Ralph H. Colby and Andrew M. Howe

Wednesday   9:45   Drayton   AS5
STRUCTURE AND RHEOLOGY OF DIBLOCK POLYELECTROLYTE GELS

Surita R. Bhatia and Ahmed Mourchid
Complex Fluids Laboratory, UMR 166, CNRS/Rhodia, Cranbury, NJ 08512

We present results for aqueous solutions of novel diblock polymers. The hydrophilic block is a polyelectrolyte and the hydrophobic block is glassy at room temperature, leading to the formation of micellar solutions with "frozen" cores. As polymer concentration is increased, the solutions go through a percolation transition, with $G' \sim G'' \sim \omega^{1/2}$ at the gel point. Above the gel point, we observe strain-hardening behavior, which may be related to similar phenomena observed in fractal colloidal gels. The strain at which the gels "rupture", coincident with a sharp downturn in G', moves to lower strains as the polymer concentration increases.

In steady shear experiments, our gels show an instability in the measured stress at two different shear rate regimes. We believe that this may be due to a structural transition triggered by shear. We have performed small-angle neutron scattering under shear to determine the effect of shear on the microstructure. In addition, we have used optical microscopy to visualize the flow and solution structure on larger length scales.

Finally, we have used two different methods of tuning the solution interactions, and thus the rheological properties. The first is to decrease the number of associative groups per chain through the use of a simple post-polymerization reaction. The second method is to screen the associative groups through the use of a surfactant. In both cases, the effect on the rheology is the same: the gel becomes weaker, and eventually the systems undergo a gel-to-liquid transition, similar to what is seen as the polymer concentration is decreased.

Wednesday   10:10   Drayton   AS6
ORDERING TRANSITION OF PEGS MODIFIED WITH FLUOROCARBON AT BOTH ENDS: RHEOLOGY AND SANS

Giyoong Tae[1], Julie A. Kornfield[1], Jeffrey A. Hubbell[2], and Jyotsana Lal[3]
[1]Chemical Engineering, California Institute of Technology, Pasadena, CA 91125; [2]Institute for Biomedical Engineering and Dept. of Materials, Swiss Federal Institute of Technology (ETH) Zurich, Zurich CH-8044, Switzerland; [3]IPNS, Argonne National Laboratory, Argonne, IL 60439

Aqueous solutions of associative polymers, consisting of PEG modified with perfluorocarbon groups at both ends, exhibit ordering transitions with increasing concentration. The hydrophobic micelle-like aggregates order into a body-centered-cubic (BCC) structure, observed by SANS. The micelle packing effect (excluded volume interaction) that is responsible for this ordering transition is also manifested in changes in the viscoelastic properties from single-relaxation behavior to the appearance of a new low frequency elastic plateau in the dynamic moduli, and from a linear response to a yielding behavior in creep . The effect of PEG midblock length and hydrophobicity of the end groups on the ordering and the aggregation state of the hydrophobic end groups will be described.

Wednesday   10:35   Drayton   AS7
NONLINEAR CHAIN STRETCHING AND FRACTURE IN TRANSIENT NETWORKS UNDER SHEAR

Jean-François Berret[1] and Yaelle Séréro[2]
[1]Université de Montpellier 2, CNRS, Montpellier 34095, France; [2]FOM-Institute for Atomic and Molecular Physics, Amsterdam 1098, The Netherlands

We report on telechelic associating polymers in aqueous solutions that self-assemble into star-like flowers in the dilute regime and develop a fully connected network of flowers above some threshold concentration (~ 1% by weight). Small-angle neutron scattering has been used to investigate the form and structure factors of the star-like

aggregates and linear rheology was performed in order to identify the viscoelastic features of the physically cross-linked network. Taking advantage of the long network relaxation times (the end-groups are partially fluorinated), we use step-stain experiments to explore the linear and nonlinear regime of shear deformations. In the linear regime, the stress relaxation function is well described by a stretched exponential with an exponent 0.8. With increasing deformations, the elastic modulus is found to increase (strain hardening) while simultaneously the viscoelastic relaxation time decreases. From the results on the structure of the network, we could interpret the strain hardening in terms of nonlinear stretching of the elastically active chains. Using particle tracking experiments, we show that under steady shear, the shear-thinning regime is associated to a mechanical fracture of the viscoelastic fluid.

Wednesday   11:00   Drayton   AS8
SCALING OF THE MATERIAL FUNCTIONS IN HASE ASSOCIATIVE POLYMERS - EFFECT OF MACROMONOMER TYPE AND CONSTITUTION

Andrew Hirst[1] and Robert English[2]
[1]Department of Colour Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom;
[2]Centre for Water Soluble Polymers, North East Wales Institute of Higher Education, Wrexham LL11 2AW, United Kingdom

HASE associative polymers are complex terpolymers of ethyl acrylate, methacrylic acid and an associative macromer. Associative macromers were made by functionalising linear alcohol ethoxylates with m-TMI isocyanate. Model HASE polymers were prepared with different types and concentrations of macromer. Macromers bearing both nC16 and nC18 hydrophobes and mean degree of ethoxylation from 2 to 100 have been used. The amount of macromer used in the polymer syntheses was varied between 0.25% and 1.5 mole%. Following purification by dialysis, the polymers were freeze dried and characterised by 1H NMR and GPC. Rheological data from steady shear and dynamic experiments will be presented and discussed in terms of the differences in polymer architecture. In each case, the concentration dependence of the material functions was described by a simple power law scaling relationship. Within the concentration regime examined, the temperature dependence of the material functions was Arrhenius-like. In dynamic shear, the polymer solutions behaved as a reversible network, indicating the presence of relatively small amount of microgel fraction. However, in steady shear, the solutions did not show the apparent "shear banding", or flow at constant shear stress, as previously observed in solutions of HASE polymers bearing hydrophobes of high molar volume. The exact influence of the macromer type and amount is difficult to ascertain. Polymers based on macromers with a mean degree of ethoxylation of ~10 appeared to provide the most efficient structuring in aqueous media, whilst those with a degree of ethoxylation of ~2 were weak viscosifiers. Preliminary NMR studies suggested that the most hydrophobic macromers show a lower level of incorporation in the polymer, attributed to poor mass transport properties during emulsion polymerisation. Although HASE polymers are used widely in industry, their microstructural variation, compositional heterogeneity and polydispersity make them poor candidates as model comb associative polymers.

Wednesday   11:25   Drayton   AS9
SOLUTION RHEOLOGY OF A MODEL HASE POLYMER: SOLVENT QUALITY AND HYDROPHOBIC INTERACTION

Ahmed A. Abdala[1], Keith Olesen[2], David R. Bassett[2], and Saad A. Khan[3]
[1]Fiber and Polymer Science Program, North Carolina State University, Raleigh, NC 27606;
[2]UCAR Emulsion Systems, Union Carbide Corporations, Cary, NC 27511; [3]Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695

The effect of the solvent solubility parameter on the association behavior of a model hydrophobically modified alkali soluble emulsion (HASE) polymer, comprising of random copolymer of methacrylic acid (MAA), ethylacrylate (EA) and hydrophobic macromonomer has been investigated. A water+glycol co-solvent is used in this study and the steady and dynamic rheological behavior is observed using different polymer concentration (c) in these solvents. The solvent solubility parameter is found to have a direct impact on both the steady and dynamic behavior for the polymer solutions. In particular, scaling of the relative viscosity (η_{rel}) and the plateau modulus (G'_p) with the solvent solubility parameter (δ) reveal a power-law dependence, i.e., η_{rel} (or G'_p)$\sim\delta^n$. In addition, two distinct regions are observed with different power law exponents. However, the power-law exponents are different in the relative viscosity and plateau modulus scaling. The critical solubility parameter (δ_c), defined as the point

where the two regions intersect, is found to increase with temperature but decrease with the polymer concentration. The concentration dependence of the relative viscosity has been measured in each of the solubility regions. In solvents with δ higher than δ_c, $\eta_{rel} \sim c^{3.7}$ compared to $\eta_{rel} \sim c$ for solvents with solubility parameter lower than the critical value. These results are interpreted in terms of the extent of the hydrophobic association above and below the critical solubility parameter.

Symposium FD
Non-Newtonian Fluid Dynamics & Flow Stability

Organizers: Dilip Rajagopalan and Yuriko Renardy

Wednesday   9:45   Elliott   FD14

NUMERICAL SIMULATION OF BRANCHED POLYMER MELTS IN TRANSIENT COMPLEX FLOW USING POM-POM MODELS

Peter Wapperom[1] and Roland Keunings[2]
[1]Chemical Engineering, University of Delaware, Newark, DE 19716; [2]Applied Mechanics, Universite catholique de Louvain, Louvain-la-Neuve B-1348, Belgium

In recent years, a number of constitutive equations have been derived from reptation theory to describe the rheology of both linear and branched polymer melts. While their predictions in rheometrical flows have been discussed in detail, not much is known of their behaviour in complex flows. In the present paper, we study by way of numerical simulation the transient, start-up flow of branched polymers through a planar contraction/expansion geometry. The constitutive equation is the so-called pom-pom model introduced by McLeish and Larson (1998), and later modified by Blackwell et al. (2000). By combining the Backward-tracking Lagrangian Particle (Wappperom et al. 2000) and Deformation Field (Peeters et al. 2000) methods, we obtain results for the original, integral pom-pom model which makes use of the Doi-Edwards orientation tensor. Two simplified versions of the pom-pom model are also considered, namely one based on the Currie approximation for the orientation tensor, and a differential constitutive equation proposed by McLeish and Larson (1998). Finally, the simulation results are compared to those obtained with the so-called MGI model proposed recently by Marrucci et al. (2000) for describing linear polymer melts.

Wednesday   10:10   Elliott   FD15

SEMI-LAGRANGIAN FINITE VOLUME METHODS FOR VISCOELASTIC PLANAR AND AXISYMMETRIC CONTRACTION FLOWS

Timothy N. Phillips[1] and Alison J. Williams[2]
[1]Department of Mathematics, University of Wales Aberystwyth, Aberystwyth SY23 3BZ, United Kingdom; [2]School of Computing and Mathematical Sciences, University of Greenwich, London SE10 9LS, United Kingdom

This paper is concerned with the numerical simulation of viscoelastic contraction flows. In particular, the differences between planar and axisymmetric flows are studied with respect to vortex enhancement. The basis of the numerical simulations is a semi-Lagrangian finite volume method which combines the advantages of fixed grids inherent in Eulerian methods with modifications to treat the convective terms using particle tracking methods. A range of numerical results are presented with particular emphasis given to the convergence and stability of the method and the development of vortex structure with increasing elasticity.

Wednesday   10:35   Elliott   FD16

A SINGULARITY METHOD FOR CALCULATING TIME-DEPENDENT VISCOELASTIC FLOWS WITH INTEGRAL CONSTITUTIVE EQUATIONS

Ronald J. Phillips

Chemical Engineering and Materials Science, University of California at Davis, Davis, CA 95616

The Point-Dipole Method is a singularity method for calculating time-dependent, viscoelastic flows by using integral constitutive equations. The viscoelasticity of the fluid is incorporated by using tens of thousands of point dipoles, which move with the fluid velocity. The dipole strengths are chosen to represent the non-Newtonian portion of the stress, which is found by integrating the Finger strain tensor and a suitable memory function over several relaxation times. Dipole-dipole interactions are accounted for by using the fast-multipole method, which results in the computation time scaling as O(N), where N is the number of dipoles. Here the method is introduced, and results are presented for the flow of fluids represented by convected Maxwell and Papanastasiou-Scriven-Macosko integral models in concentric and eccentric cylinder geometries. These geometries were chosen to permit quantitative comparisons with earlier work. The advantages that integral constitutive equations offer in the description of realistic relaxation time distributions, along with the scarcity of methods for using them in time-dependent calculations, make this approach of general interest. In addition, as a method that requires no mesh, it is well-suited for the time-dependent geometries encountered in simulations of moving drops and particles.

Wednesday   11:00   Elliott   FD17

INFLUENCE OF CLOSURES ON THE EIGEN-SPECTRA OF ELASTIC DUMBBELL BASED MODELS: A MULTISCALE MODELING APPROACH

Madan Somasi and Bamin Khomami

Chemical Engineering, Washington University, St. Louis, MO 63130

Traditionally, stability analysis of viscoelastic flows has been performed by solving generalized eigenvalue problems (GEVP). In complex flow geometries, where GEVP analysis is computationally inefficient, time-integration of the prescribed (or random) disturbances introduced into the system is used to determine the most dominant eigenvalue. However, both the GEVP and time dependent simulations suffer from an inherent need for a closed form constitutive equation for the polymeric stress. Recent studies [Doyle et. al, JNNFM(1998)] have demonstrated that the approximations employed in deriving closed form constitutive equations could result in significant differences in the prediction of polymer stresses. This shortcoming has recently been overcome by the introduction of a new multiscale (i.e., Finite-elements/Brownian dynamics) formulation [Somasi & Khomami, JNNFM(2000)],that allows for probing the stability predictions of the true kinetic models. Although, this approach has been shown to be effective in determining the most dangerous eigenvalue in prototype flows, it is unable to capture the entire spectrum, which is essential in ensuring the accuracy of the simulations in complex kinematics flows. Hence, we have modified this technique by inclusion of an intermediate Arnoldi step. Using this approach, the entire eigen-spectrum can be captured, and the leading values can be obtained in a significantly less CPU time. In fact, we have observed up to 90% reduction in the computational time, which is essential if this CPU intensive multiscale approach is to be used in complex processing geometries. To demonstrate the necessity and versatility of this multiscale technique, the difference in the stability characteristics (i.e., both the discrete and continuous spectrum) obtained for a true kinetic theory based model, such as the FENE model, and a corresponding approximate model, namely, FENE-P, in prototype flows such as the Taylor-Couette flow and the contraction/expansion flows have been investigated.

Wednesday   11:25   Elliott   FD18

LINEAR STABILITY ANALYSIS OF THE FENE-G MODEL FOR VISCOELASTIC FLOW THROUGH A LINEAR ARRAY OF CYLINDERS CONFINED BETWEEN TWO PARALLEL PLATES

Yong Lak Joo, Indranil Ghosh, Robert C. Armstrong, and Robert A. Brown

Dept. of Chemical Engineering, MIT, Cambridge, MA 02139

In recent years, simulation of the viscoelastic flow around submerged objects has received much attention. In particular, Smith, et al. (2000) examined the linear stability of the viscoelastic flow of an Oldroyd-B fluid through a

linear array of cylinders confined in a channel. Although these flows are predicted to be unstable to three-dimensional perturbations, the results lack some key characteristics of the instability that has been observed experimentally (Byars (1996), Liu(1997)). For the linear stability analysis for the Oldroyd-B model the critical De increases with increasing cylinder spacing, and the most unstable mode is always symmetric about the centerline of the channel. However, experiments with a PIB Boger fluid through a widely spaced array of cylinder or an isolated cylinder demonstrate the transition to an anti-symmetric, three-dimensional flow structure at significantly lower De. One possible source of the disagreement is the description of the extensional behavior of the fluid, which is important in the wake of the cylinder.

We examine the linear stability of the viscoelastic flow through a linear array of cylinders in a channel with the new model by Ghosh et al. (2000) that provides a better description of the transient extensional rheology than either the Oldroyd-B or FENE dumbbell models. In the new closed constitutive equation, referred to as the FENE-G model, the polymer molecule is viewed as a set of identical segments that are each small enough to be stretched reversibly. The linear stability analysis is performed by discretizing in space with the finite element method coupled with a fourth-order Runge-Kutta method for time integration.

Our results show that the most unstable mode from the linear stability analysis of the new model is anti-symmetric, as experimentally observed. In addition, the growth rate of the disturbance is higher than that predicted by the Oldroyd-B model. Finally, the mechanism of the instability is investigated through an energy analysis.

Symposium SC
Suspensions and Colloidal Systems

Organizers: Daniel De Kee and Robert Lionberger

Wednesday   9:45   Heyward   SC18

OBTAINING THE COMPRESSIVE YIELD STRESS OF SUSPENSIONS FROM CENTRIFUGE MEASUREMENTS - AN INVERSE PROBLEM

Y L. Yeow
Department of Chemical Engineering, University of Melbourne, Melbourne, Victoria 3052, Australia

Compressive yield stress is the key material property in the processing of concentrated suspensions in industry. Centrifuge measurement is the standard laboratory technique for determining compressive yield stress at different concentrations. Current methods of converting centrifuge data into a compressive yield stress versus concentration curve require extensive data manipulation. This presentation describes a computational procedure based on Tikhonov regularization to perform this task. Since Tikhonov regularization allows for the ill-posed and inverse nature of the problem, it will not only simplify the data conversion but also lead to more reliable results. This new procedure will find immediate application in rheological laboratories.

Wednesday   10:10   Heyward   SC19

A NEW OSCILLATION METHOD ENABLING MEASUREMENTS AT VERY SMALL DEFLECTION ANGLES AND TORQUES

Joerg Laeuger and Siegfried Huck
Physica Messtechnik GmbH, Stuttgart D-70567, Germany

It was shown previously that a rotational rheometer equipped with an electronically commutated motor (EC-motor) allows to conduct real stress and strain experiments with the same rheometer (J. Läuger, S. Huck; Proceedings of the XIIIth International Congress on Rheology, Cambridge, UK (2000), p. 3-10). A new method has now been developed to further improve strain controlled oscillatory measurements by adjusting the strain directly within a single oscillation cycle. Generally, a strain controlled oscillation test in a stress controlled rheometer consists of the following steps: applying one full oscillation cycle with an arbitrary stress amplitude, measuring the strain amplitude, adjusting the stress in the next oscillation cycle, and repeating this routine until the desired strain amplitude is reached. The newly developed direct strain oscillation method uses a different approach. It does not

require a full oscillation cycle but uses a real-time position control and adjusts to the desired strain directly on the sine wave. Therefore, the actual movement of the measuring system follows directly the required change in strain during each individual oscillation cycle. This new oscillation mode has several major advantages including: 1. the possibility of conducting real strain controlled tests in oscillation as well, 2. the exact strain setting right from the first oscillation cycle, i.e. no or only very slight overshoot in strain, 3. faster data acquisition even within an oscillation cycle, 4. it allows the measurement at extremely low angular resolution and low torques. Due to the absence of strain overshoots and the ability of testing at small deflection angles and low torques this new method is especially valuable for measurements on samples with low viscosities and weak structures such as gels, emulsions, suspensions, colloids, and foams.

Wednesday   10:35   Heyward   SC20

PARTICLE SETTLING IN COMPLEX GEOMETRIES: COMPUTATION AND EXPERIMENT

Rekha R. Rao[1], Lisa A. Mondy[1], Stephen A. Altobelli[2], Eric R. Lindgren[1], and Amy C. Sun[3]
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Batch sedimentation of noncolloidal particles is studied with x-ray and Nuclear Magnetic Resonance (NMR) imaging and modeled with a diffusive flux continuum formulation. The x-ray images were produced after the polymerizing system cured, while the NMR images were obtained in near real time. Both experimental techniques give us particle volume fraction as function of position, which is then used to validate our numerical results. The momentum transport, continuity, and diffusive flux equations are solved simultaneously with a finite element formulation that is fully three-dimensional and can be run on a parallel computer platform. Results will be shown for three different flow fields: 1)sedimentation in a cylinder with a contraction, 2) sedimentation around a horizontal rod, and 3) sedimentation around a complex three-dimensional shape. The diffusive flux equation is modified to include a time-dependent viscosity to model the polymerization of the suspending fluid. During the computation the viscosity increases by three orders of magnitude. In addition, the systems modeled are highly concentrated (a volume fraction of about 0.48), which leads to stiff equations and numerical instabilities. Interesting secondary flows appear both in the experiment and model. Overall, good agreement is found between the experiments and the simulations. Results are useful for a manufacturing application, showing areas likely to trap particles leading to inhomogeneities in fill concentration.

Wednesday   11:00   Heyward   SC21

YIELD BEHAVIOR OF STRONGLY AGGREGATED COLLOIDS VIA COMPUTER SIMULATION

Stacy C. Pyett and Robert A. Lionberger
Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136

The transition between liquid-like and solid-like behavior is an important property in the processing of many different suspensions. There are a number of different names for this type of behavior such as the appearance of a yield stress, a gel point, or a glass transition. Rheological measurements can be used to locate these transitions, however the relation between the measurements, inter-particle forces and microscopic events are as yet unclear. The work presented in this talk seeks to improve understanding of yield phenomena by study of the micro-rheology of colloidal suspensions. Specifically, we use Brownian Dynamics simulations to determine the role of temperature and strain rate on the qualitative stress response of aggregated particles interacting through a DLVO potential.

From non-equilibrium simulations with an applied strain the stress-strain curve displays evidence of an apparent yield stress through a departure from linear behavior. Non-equilibrium simulations at constant stress indicate the yield stress directly through the observation of the onset of flow. In equilibrium simulations, systems display a yield stress through a finite, non-zero leveling off of the long-time stress auto-correlation function. We compare the three approaches by locating the temperature and volume fractions at which each method indicates the existence of an apparent yield stress for a given potential.

Wednesday   11:25   Heyward   SC22

THE RHEOLOGY OF HIGHLY-FILLED AND REACTIVE SUSPENSIONS USING SQUEEZE FLOW

Anthony J. McHugh and **Andrew Walberer**

Chemical Engineering, University of Illinois, Urbana, IL 61801

In a recent paper (J.A. Walberer and A.J. McHugh, *J. Rheol.*, **44**, 743 (2000)), we showed that lubricated squeezing flow is a useful technique for evaluating the rheology of highly-filled and reactive suspensions. This talk will present comparisons of results on highly-filled PDMS-glass bead suspensions obtained using rotational, oscillatory compressional, and lubricated squeeze flow rheometry. Results will be presented showing the effect of polymer molecular weight on the relative behavior of the loss and storage moduli in the linear viscoelastic regime as a function of filler content. Data for the extensional viscosity and linear viscoelastic relaxation of several model, highly-filled reactive systems that stiffen due to cross-linking, polymerization, or flocculation, as well as two technologically relevant highly-filled calcium aluminate - polymer systems will also be presented. The model cross-linking and polymerizing systems exhibit viscosity-stress behavior that appears to be less yield-like as stiffening progresses. By contrast, the reactive calcium aluminate-polymer systems become more yield-like as stiffening progresses, indicating that the reactive mechanism in these systems causes changes in the particulate phase structure.

Wednesday Afternoon

Symposium FB
Food and Biopolymers

Organizers: Jeff Byars, Peter Fischer and Jozef Kokini

Wednesday   1:30   Lady Davis   FB6
CONSTITUTIVE ANALYSIS OF B-GLUCAN/AMYLODEXTRIN BLENDS

Jeffrey A. Byars and Craig J. Carriere
Biomaterials Processing Research Unit, USDA ARS NCAUR, Peoria, IL 61604

The solution rheological behavior of β-glucan/amylodextrin blends was investigated. The effects of the blend composition and concentration were studied in small-amplitude oscillatory shear, steady-state shear, transient shear and stress relaxation experiments. The applicability of constitutive equations derived for synthetic polymers to biopolymer systems was also investigated. The K-BKZ, Giesekus, Phan-Thien-Tanner and Bird-Carreau models could all fit the steady shear flow data, but only the K-BKZ and Giesekus models yielded accurate results in transient flows.

Wednesday   1:55   Lady Davis   FB7
MOLECULAR ASSOCIATIONS AND HYDROGEN BONDING IN GUAR SOLUTIONS

Robert K. Prud'homme[1] and Yu Cheng[2]
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Guar galactomannan solutions have unusual rheological properties that derive from their unique ability to form hydrogen bonds. The solutions display viscosities ten times higher than that of non-hydrogen bonding solutions at the same dimensionless concentration. Through derivatization of hydroxyl groups on the polymer it is possible to block this hydrogen bonding and also block enzymatic attack on the backbone. The Osmotic Stress Technique of Parsegian is used to probe interchain hydrogen bonding. Crystalline and liquid crystalline order is shown for these systems at high osmotic stress. The implications of these interactions for enzymatic degradation of guar will be discussed.

Wednesday   2:20   Lady Davis   FB8
MODELLING MIXING FLOWS IN CYLINDRICAL-SHAPED VESSELS

Mike F. Webster[1], Deping Ding[2], and K. Sujatha[3]
[1]Institute of Non-Newtonian Fluid Mechanics, University of Wales Swansea, Swansea, West Glamorgan SA2 8PP, United Kingdom; [2]University of Wales Swansea, Swansea, United Kingdom; [3]University of Wales Swansea, Swansea, United Kingdom

This article is concerned with the finite element simulation of industrial dough mixing.The material is driven by one or two stirrers, fixed to a lid that is placed upon a cylindrical vessel. The stirrers may be positioned in concentric or eccentric arrangement with respect to the axis of the vessel. Problems are considered with or without free surfaces, that correspond to fully-filled and partially-filled cases. Here, we focus on the work involved in fully-filled cases. Normally, the stirrers rotate about the centre of the vessel. Here the motion is assumed to be driven by the rotation of the vessel, as an alternative to the conventional mixer. The motivation for this work is to develop and advance technology to model the mixing of dough. The ultimate target is to predict and adjust the design of dough mixers, so

that optimal dough processing may be achieved. The numerical simulation starts from a two dimensional setting and extends into a three-dimensional analysis. The flow domain setting starts from concentric and extends to eccentric. The two-dimensional study shows the flow details, that occur at the mid-plane of the cylindrical vessel, whilst the three-dimensional investigation shows the flow details at various depths of the vessel. A number of key field variables are analysed. This includes the velocities, the pressure, the stream function, the shear rates, the extension rates, rate of work done, torque and power. For low Reynolds numbers, a reversed motion with stirrer rotation is considered. Various types of fluid models are incorporated of either Newtonian or inelastic models, with shear rate dependent viscosity. Various mixing speeds are considered, ranging from 12.5 rpm equivalent to a Reynolds number of 2, up to 100 rpm equivalent to a Reynolds number of 16. The numerical results are compared against experimental results and demonstrate good agreement.

Wednesday   2:45   Lady Davis   FB9
VISCOELASTIC EFFECTS OBSERVED DURING 2-D NUMERICAL SIMULATION OF FLOW AND MIXING IN A MODEL FOOD MIXER
Jozef L. Kokini and Robin K. Connelly
Department of Food Science, Rutgers, The State University of New Jersey, New Brunswick, NJ 08901-8520

Viscoelastic effects on mixing flows obtained with kneading paddles in a single-screw mixer are explored using 2-D finite element method (FEM) numerical simulations. Models compared include the Newtonian model, the Bird-Carreau generalized Newtonian model, the Oldroyd-B model and a single-mode Phan-Thien Tanner non-linear, viscoelastic fluid model with parameters for a dough-like material. All of the models have the same zero shear viscosity. The steady shear profile of the Bird-Carreau and Phan-Thien Tanner models are closely matched. The limit of the relaxation times that can be achieved in this geometry for the viscoelastic models are found using the streamline upwind (SU) method of Marchal & Crochet (1988) with 4x4 bilinear subelements for the stresses. The single-screw mixer is modeled by taking the kneading paddle as the point of reference, fixing the mesh in time and exposing the secondary flow profile. Rigid rotation and no slip boundary conditions at the walls are used with inertia taken into account.

The most notable viscoelastic effect found is the development of asymetry in the flow and pressure profiles that is not evident with the viscous models. This has a demonstrable effect on the effiency of the mixing. Also of note is the development of significant stress concentrations at the corner singularities with the viscoelastic models, which is a cause of the instability during simulation for the viscoelastic models. The first normal stress difference is zero for the viscous models, but varies greatly with increased viscoelasticity in the viscoelastic models. The oscillations that lead to the early breakdown of the simulation of the Oldroyd-B model are evident in the stress profiles.

Wednesday   3:35   Lady Davis   FB10
MODELING OF MELT CONVEYING IN A DEEP-CHANNEL SINGLE SCREW CHEESE STRETCHER
Chenxu Yu and Sundaram Gunasekaran
Department of Biological Systems Engineering, University of Wisconsin-Madison, Madison, WI 53706

Stretching is an important unit operation in Mozzarella cheese manufacturing. It is performed in a single or twin-screw extruder type stretcher-cooker. During this, thermal and mechanical treatments impart Mozzarella cheese its characteristic fiber-like structure. Accurate description of cheese flow in the stretcher channel is fundamental in understanding the stretching process. For the single-screw unit, common approach to this problem is to use a flat-plate model with modified boundary conditions, neglecting curvature and flight effects. Since the stretcher channel depth-to-width ratio is large, the simple flat-plate model is an oversimplification and significantly overpredicts the volumetric flow rate. Our objectives were to: 1. develop a mathematical model to describe the flow behavior in a deep-channel single-screw stretcher and 2. validate model predictions using experimental results. The finite difference method was used to obtain numerical solutions to the flow equations. Both isothermal and non-isothermal conditions were considered. The mathematical models were first tested for the Newtonian flow. For non-Newtonian fluid, power-law and Bird-Carreau models were considered. The model predicted velocity distribution and screw characteristics were tested using the experimental data published in the literature (Choo et al., 1980; Griffith, 1962).

For Newtonian fluids at screw speeds above 150 rpm, our model predicted volumetric flow rate was within 0.5% of the experimental data compared to the typical 50% overprediction by existing models. In case of the non-Newtonian fluid, our model performed much better than the previously published models. (Tadmor & Gogos, 1979; Rauwendaal, 1986; Chiruvella et al, 1995; Li et al, 1997).

Wednesday   4:00   Lady Davis   FB11

EXPERIMENTAL INVESTIGATION OF LAMINAR-TURBULENT TRANSITION IN PIPE FLOW FOR FRUIT PUREES

Paolo Perona and **Sebastiano T. Sordo**
Dipartimento di Idraulica, Trasporti e Infrastrutture Civili, Politecnico di Torino, Torino 10129, Italy

Rheological characterization of liquid foods is the first fundamental condition to study their fluid dynamics behavior and heat transfer processes in pipe flow. In this work, in particular, the laminar-turbulent transition in pipe flow for several kinds of fruit purees at different temperature and pulp concentrations is experimentally investigated by means of the rectilinear pipe viscometer. Some of those products, even when they are diluted, have an internal structure that is quite sensitive to mechanical stresses. This analysis is useful to predict an upper limit for the flow rate in order to avoid an increasing of the breakdown processes due to the higher mechanical stresses of the turbulent flow. The measurement of the rheological properties has been done limiting as more as possible the duration, so that fruit purees could be reliably considered as purely-viscous time-independent fluids. Moreover, particular attention has been payed to include only the data pertaining to laminar flow and to distinguish transition to turbulence from ultimate Newtonian behavior. As the fresh product generally has an high value of apparent viscosity and consistency, the experimental detection of turbulence transition was possible only below a certain degree of concentration or above a given temperature level. By increasing the temperature or by decreasing the pulp concentration, the flow curve changes and, at the same time, the transition to turbulence on the $\{\tau_w, 8U/D\}$ plane moves back along a curve, toward the corresponding limit value generally valid for water. The Fanning friction factor plotted versus the generalized Reynolds number shows that the transition point is at a generalized Reynolds number of about 2100.

Wednesday   4:25   Lady Davis   FB12

EFFECTS OF POST-MORTEM STORAGE AND FREEZING ON THE VISCOELASTIC PROPERTIES OF VOCAL FOLD TISSUES

Roger W. Chan
Audiology and Speech Sciences, Purdue University, West Lafayette, IN 47907

The viscoelastic shear properties of human vocal fold mucosa (superficial layer of the lamina propria) were recently measured [Chan and Titze, J. Acoust. Soc. Am., **106**, 2008-2021 (1999)]. Since the tissues were harvested post-mortem and some of them were frozen samples, those previous data were valid only if the tissues were not subject to significant structural changes induced by post-mortem storage and freezing. This study attempted to quantify the effects of post-mortem storage and freezing on the viscoelastic shear properties of canine vocal fold tissues. Eleven larynges were excised from adult Mongrel dogs immediately post-mortem. For each larynx, the mucosa of one vocal fold was dissected and its complex shear modulus was measured by a controlled stress rheometer (Bohlin CS-50) twice: once within 30 minutes post-mortem and once after 24 hours of storage in saline solution at room temperature. The rest of the larynx was either frozen slowly (for six larynges) or quick-frozen by liquid nitrogen (for the other five) and stored at -20°C. The larynges were thawed after one month and the complex shear modulus of the other vocal fold mucosa was also measured. Results showed that the stiffness and viscosity of canine vocal fold mucosa did not change significantly following 24 hours of post-mortem changes at room temperature, nor after a month of storage following quick-freezing. These findings supported the validity of the viscoelastic data reported previously and the feasibility of using quick-freezing to preserve vocal fold tissues for biomechanical testing.

Wednesday   4:50   Lady Davis   FB13
A NON-INVASIVE IN-LINE VISCOSITY MEASUREMENT OF CONCENTRATED OPAQUE FLUIDS

Nihan Dogan[1], Young J. Choi[1], David Sheen[2], Richard Pappas[2], David Pfund[2], Michael McCarthy[1], and <u>Robert L. Powell</u>[1]
[1]University of California, Davis, CA; [2]Battelle Pacific Northwest National Lab., Richland, WA

This study focuses on developing a non-invasive, in-line rheological measurement device using ultrasonics. The technique exploits the dynamics of a rheologically complex material undergoing steady pressure driven flow in a circular tube. It combines a measurement of the velocity profile and the pressure drop to determine the shear rate and the shear stress distributions in the pipe, respectively. This method has the potential of obtaining many shear viscosity-shear rate data points under actual pipeline conditions from a single measurement. The velocity profiles were measured using ultrasonic Doppler velocimetry. This technique was applied to obtain shear viscosity versus shear rate data, yield stress and wall slip values for tomato paste with varying percentages of total solids (9%-17 %) and diced tomato samples (all shear thinning fluids) with varying concentrations and at flow rates ranging from 4 l/min. to 30 l/min. The flow loop consisted of a 52.4 mm internal diameter acrylic tube and a progressing cavity pump with variable speed plus two pressure transducers. The ultrasound probe was a 6.35 mm diameter piezoelectric transducer. The yield stress and flow behavior results show reasonable agreement with conventional rotational rheometry.

Symposium AS
Associating Polymers and Surfactant Systems

Organizers: Ralph H. Colby and Andrew M. Howe

Wednesday   1:30   Drayton   AS10
SUPRAMOLECULAR AGGREGATION IN POLYSACCHARIDE GUM SOLUTIONS
<u>Simon B. Ross-Murphy</u> and David R. Picout
Biopolymers Group, Division of Life Sciences, King's College London, London SE1 9NN, United Kingdom

The problem of the characterisation of the solution properties of water soluble polymers is long-standing, and stems from their prevalence for forming aggregated supramolecular structures, which are resistant to molecular dispersion. For phenomenological measurements this is not a serious limitation, because the presence of a small number of very high molecular weight particles tends not to effect the rheology of semi-dilute solutions. However measurement of, for example, Mw by this technique is extremely difficult, and produces many of the anomalous results that appear in the literature. For those interested in molecular rheology this severely limits progress. We have considered a new material, detarium gum, structurally similar to that extracted from the more common tamarind gum. Physico-chemical characterisation of detarium, includes measurements of viscosity at finite concentrations, both above and below C*, the coil overlap concentration, together with detailed studies of the molecular weight and chain properties obtained from (angular dependent) intensity light scattering measurements. These results employed the pressure-heating regime introduced by Vorwerg (1) to establish true solubilisation of starch polymers. Here this was applied for the first time to non-starch polysaccharides. Light-scattering strongly suggests a small element of long chain branching. The longer-term implications for such a branched chain model are intriguing. The assumption is made for a number of polysaccharides that these are linear macromolecules, although the positive evidence for this is nearly always absent. We have now extended the pressure cell technique to other polysaccharides, including the more common guar and locust bean gum. For some of these there is evidence of a reduction in Mw caused by chain scission.

1. Aberle, T., Burchard, W., Vorwerg, W. and Radosta, S. Starch 46 329 (1994).

2. Wang, Q., Ellis, P.R., Ross-Murphy, S.B. and Burchard, W. Carbohydr. Polym. 33 115 (1997).

Wednesday   1:55   Drayton   AS11
**LINEAR AND NON-LINEAR RHEOLOGICAL PROPERTIES OF NANOFIBRILAR
SKELETON STRUCTURES IMBEDDED IN VARIOUS POLYMER MELTS**
Christian Friedrich, Michael Fahrlaender, and Wenke Fraessdorf
Albert-Ludwigs-University Freiburg, Freiburg i. Brsg., Germany

Dibenzylidene sorbitol (DBS) is known to gel polymers by forming a thermoreversible physical network structure. We have investigated the formation, destruction and equilibrium properties of DBS gels in polypropyleneoxide, polypropylene, polystyrene and polymethylmethacrylate by performing dynamic rheological measurements in dependence on temperature, frequency and deformation. The gels under investigation crucially depend on their thermal and mechanical history and the range of linear viscoelastic behavior is restricted to a few percent deformation. Even for very small concentrations of DBS, a reinforcement of the matrices due to the DBS skeleton structure is found, however an equilibrium modulus Ge typical for permanent networks is not observed in the frequency dependent dynamic measurements. Instead a power law behavior occurred for gels with DBS concentrations above 0.3 wt.%. The same power law exponent is found for gels with different matrix molecular weights and samples with the varying derivatives of DBS. Additionally, measurements in the nonlinear deformation regime (amplitude sweeps and start up flow under microscopical control) provide information about the underlying structural changes associated with the observed rheological phenomena. We compare our experimental results to calculations based on the "soft glassy rheology" model and a model for "aggregated colloidal dispersions".

Wednesday   2:20   Drayton   AS12
**RHEO-NMR INVESTIGATION OF SHEAR BANDING AND MOLECULAR ORDERING IN
WORMLIKE MICELLE SOLUTIONS**
P. T. Callaghan and E. Fischer
Institute of Fundamental Sciences - Physics, Massey University, Palmerston North, New Zealand

Rheo-NMR concerns the use of magnetic resonance methods to study molecular organisation and dynamics during deformational flow. Through terms in the spin Hamiltonian which are sensitive to order, NMR spectroscopy gives us access to the molecular order parameters. Through the use of magnetic field gradients, NMR microscopy and velocimetry gives us access to the local shear rate. We present here a study of the wormlike micelle systems CTAB/water and CTAB/KBr/water, in the vicinity of the isotropic/nematic transition, but positioned in the equilibrium isotropic phase. In particular we use deuterium NMR methods in both cone-and-plate and cylindrical Couette cell geometry to compare molecular ordering and shear banding effects. The formation of a shear-induced nematic phase is clearly evident and we draw a comparison between this phase and the appearance of optical birefringence. We present clear evidence however that ordering and shear banding are not simply connected and may indeed be independent of each other. We conclude that the simple notion that a high shear-rate band is associated with a nematic phase in such systems is simplistic.

Wednesday   2:45   Drayton   AS13
SHEAR-INDUCED STRUCTURE IN RHEOTHICKENING SURFACTANT SOLUTIONS
Vincent Weber[1], Reiko Oda[2], Eduardo Mendes[1], and François Schosseler[1]
[1]Institut de Physique, Laboratoire de Dynamique des Fluides Complexes, Strasbourg 67084, France; [2]Institut Européen de Chimie et Biologie, Talence 33402, France

Shear effects on the structure of dilute micellar solutions have been studied by small angle (neutron/light) scattering techniques in the rheothickening regime. The use of both scattering techniques allows one to study the structural changes on two very different length scale ranges : 1 - 200 nm and 0.25 - 1 µm. In both of these ranges, significant effects of the flow are observed in the transient as well as in the stationery regime. Characteristic time scales for the decay of the shear induced structure (SIS) after the cessation of flow span several decades from a few tens of seconds to several hours, significantly larger than those measured previously for the decay of the stress and the flow birefringence (1-10 s) in the same conditions. These findings support the picture of an heterogeneous structure for the SIS in these systems. A tentative picture for the SIS and for the mechanism of its formation will be proposed.

References

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Oda, R.; Weber, V.; Lindner, P.; Pine, D.J.; Mendes, E.; Schosseler, F. Langmuir, 2000, 16, 4859.

Wednesday   3:35   Drayton   AS14
BROWNIAN MOTION IN VISCOELASTIC MEDIA

Samiul Amin[1], Ryan M. van Zanten[2], Karl P. Rufener[3], Thomas W. Kermis[4], Stephen J. Dees[1], and <u>John H. van Zanten</u>[1]
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There is growing interest in using the Brownian or thermal motion of spherical colloidal particles to probe the dynamics of soft materials which exhibit viscoelasticity. In principle, the motion of these colloidal spheres is related to the structure and dynamics of the suspending media. Most current investigations have focused solely on establishing the relationship between the measured Brownian motion and viscoelastic moduli. The approach described here is enhanced in that it utilizes not only measurements of the particle mean square displacement and viscoelastic moduli, but also thorough dynamic and static light scattering characterization of the viscoelastic media of interest. The dynamic and static light scattering measurements provide a measure of the concentration flucutation relaxation spectrum and the osmotic compressibility. This multiple experimental probe approach allows one to account for both transverse and longitudinal contributions to to the suspending medium's response. The approach is illustrated with a whole host of surfactant systems including CTAB/KBr and CTAB/NaSal wormlike micelle solutions as well as aqueous Pluronic solutions.

Wednesday   4:00   Drayton   AS15
INFLUENCE OF ADDITIVES ON THE RHEOLOGY AND STRUCTURE OF WORMLIKE AND RODLIKE MICELLES

Lynn M. Walker and <u>My Hang T. Truong</u>
Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

We are quantifying the rheology and flow-induced structure of systems of wormlike micelles with additives ranging from electrolyte to nonionic, aqueous polymer. Characterization of the flow-microstructure coupling is achieved through a combination of rheometric techniques and small-angle scattering. In this work, we utilize nonionic aqueous polymer, counterions and electrolytes to control the rheological behaviors of micellar systems both in the dilute and semi-dilute concentration regimes. We have found significant differences in the rheology of cetyltrimethyl-ammonium tosylate (CTAT) with small amounts of additives. The observed flow-induced transitions of dilute CTAT solutions can be shifted to higher or lower values of critical stress. At higher concentrations of surfactant, we find that the rheological parameters (relaxation time and modulus) of the system can be varied with additives. These drastic changes indicate the subtle coupling between the sensitive structure of wormlike micelles and macroscopic rheology. SANS and SALS performed on the quiescent system of polymer and CTAT micelles provides structural details. This structural information is being related to the observed rheological phenomena.

Wednesday   4:25   Drayton   AS16
MICELLAR STRUCTURE CHANGES IN AQUEOUS MIXTURES OF NONIONIC SURFACTANTS

<u>Liang Guo</u>[1], Ralph H. Colby[1], Min Lin[2], and Gregory P. Dado[3]
[1]Materials Science and Engineering, Penn State University, University Park, PA 16802; [2]National Institute for Standards and Technology, Gaithersburg, MD 20899; [3]Air Products and Chemicals, Inc., Allentown, PA 18195

Rheology and small-angle neutron scattering are used to probe the structure of nonionic surfactant mixtures in water. Small amounts of a fourteen-carbon diol cause enormous structural and rheological changes when added to aqueous solutions of an ethylene oxide - propylene oxide - ethylene oxide triblock copolymer. The hydrophobic diol is only soluble up to 0.1 wt% in pure water but can be added in large quantities to solutions of the triblock copolymer. The hydrophobic diol incorporates into the propylene oxide core of the existing micelles of the triblock copolymer

solution. This incorporation causes a cascade of changes in micelle structure, with resultant changes in rheology. Particularly striking is the spherical to wormlike micelle transition, where the viscosity changes by more than a factor of 10000.

Wednesday   4:50   Drayton   AS17
SYNERGISTIC ENHANCEMENT OF RHEOLOGY IN SURFACTANT MIXTURES
Srinivasa R. Raghavan and Eric W. Kaler
Department of Chemical Engineering, University of Delaware, Newark, DE 19711

Synergistic interactions between surfactants can lead to structured fluids with interesting rheological properties. This concept is explored for various classes of surfactant mixtures. A combination of rheological and microstructural (small-angle scattering) tools are used in this investigation.

In one case, a long-chain (C18) anionic surfactant (sodium oleate, NaOA) is mixed with a shorter-chain (C8) cationic surfactant (octyl trimethylammonium bromide, OTAB). While each surfactant by itself forms globular micelles, their mixtures at intermediate compositions (~ 70/30 NaOA/OTAB, by weight) form long wormlike or threadlike micelles, leading to highly viscoelastic solutions. Thus, attractive interactions between oppositely charged amphiphiles promote self-assembly.

A second case involves mixtures of long-chain ionics (such as NaOA) with nonionic surfactants from the CiEj (ethoxylated alchohol) family. Here again, adding the uncharged amphiphile to solutions of the charged amphiphile transforms the sample from a low viscosity fluid to a viscoelastic material. For certain compositions, gel-like materials having a yield stress are produced in this system.

Symposium MS
Polymer Melts and Solutions

Organizers: Michael Solomon and H. Henning Winter

Wednesday   1:30   Elliott   MS1
NON-LINEAR RELAXATION DYNAMICS OF HIGHLY ENTANGLED POLYMER LIQUIDS
Mohammad T. Islam[1] and Lynden A. Archer[2]
[1]Texas A&M University, College Station, TX; [2]Cornell University, Ithaca, NY

We investigate step strain relaxation dynamics and steady shear orientation angle response in concentrated solutions of ultrahigh molecular weight polystyrene (Mw = 20.6 x 10^6 g/mol) and polybutadiene (Mw = 1.1 x 10^6 g/mol), using mechanical rheometry and phase modulated birefringence polarimetry measurements in a plane-Couette geometry. Both procedures allow transient shear stress S, first normal stress differences N1, and orientation angle ki to be measured in well entangled polymer liquids subject to flow. In step shear, we find that the strain imposition time has a profound effect on the shear damping function. For imposition times below the longest Rouse relaxation time TRouse, the instantaneous shear damping function varies smoothly from type B to type A and finally to type C damping with increasing time, following imposition of the step. For strain imposition times well in excess of TRouse time-strain factorability is observed at all times and the damping is essentially type A. These results provide direct insight into the role of contour length stretch in stress relaxation dynamics of entangled polymer liquids. In steady shear flow, a shear rate region gdot < 1/TRouse is found where both the shear stress and the first normal stress difference are virtually independent of shear rate. This unusual flow behavior is consistent with premature orientation saturation in entangled polymers, first reported by Mhetar and Archer (J. Polym. Sci.: Polym. Phys. Ed., 28, 222, (2000)). These observations are discussed in terms of entanglement loss caused by convective constraint release and partial extension of polymer strands in steady shear flows.

Wednesday   1:55   Elliott   MS2

CONSTITUTIVE EQUATIONS FOR LINEAR POLYMER MELTS INSPIRED BY REPTATION THEORY AND NON-EQUILIBRIUM THERMODYNAMICS

Adrien Leygue[1], Antony N. Beris[2], and Roland Keunings[1]
[1]Cesame, Universite catholique de Louvain, Louvain-la-Neuve B-1348, Belgium; [2]Chemical Engineering, University of Delaware, Newark, DE

In the context of reptation theory and non-equilibrium thermodynamics, we discuss a number of constitutive equations of the differential type for describing the non-linear rheology of mono-disperse, linear polymer melts. The basic ingredients involved in the models include, in addition to classical reptation, convective constraint release and force balance at entanglements, as proposed recently by Marrucci and his collaborators. On the basis of the general bracket formalism of non-equilibrium thermodynamics, we develop a class of constitutive equations whose dissipative component is linked algebraically to the conformation tensor. Comparison with available experimental data in transient rheometrical shear flows is used to guide the selection of this algebraic expression. As a particular case, we recover the Marrucci-Greco-Ianniruberto model, slightly corrected for thermodynamical consistency. The best results, however, are obtained with a quadratic dissipative term.

Wednesday   2:20   Elliott   MS3

2-DIMENSIONAL RHEOLOGY AND POLYMER DYNAMICS UNDER NON-LINEAR DEFORMATIONS

Dagmar van Dusschoten, Manfred Wilhelm, and Hans W. Spiess
Max-Planck Institute for Polymer Research, Mainz D 55128, Germany

A 2-dimensional rheology experiment is demonstrated that fully separates the relaxation dynamics of linear and non-linear contributions to the stress relaxation. This experiment consists of a combination of large amplitude oscillations and multiple step shear experiments and thereby resembles a discretized sine wave. The stress responses after each of the shear steps are correlated by means of a Fourier transformation for every time t_n between the shear steps. In this manner a series of Fourier spectra are obtained, showing peaks at the fundamental 'frequency' and the odd, higher, harmonics thereof, that decrease with t_n. Since only non-linear processes relevant to the stress relaxation contribute to these overtones, these contributions can be separately fitted from the main linear contributions. When applied to a slightly entangled polydisperse PIB solution the decay of the fundamental harmonic differs from the decay of the higher harmonics, non of which run parallel themselves. On the timescale where Rouse relaxation is relevant the smallest contributions of fast relaxation modes to the higher harmonics are observed. Even for relaxation far exceeding the Rouse time a difference between the decay of the fundamental and higher harmonics is detectable, which is a clear indication for a deviation of the time strain separation. On the other hand, the Time Temperature Separation seems to apply for both the linear and the non-linear contributions to the stress relaxation. When the time window between the shear steps is decremented such that slow relaxation processes still possess memory of the prior steps, an increase in the non-linear contributions of these slow processes is observed. However, the data also show that completely relaxed relaxation modes are significantly affected by this change of non-linearity of the slower relaxation modes. This than points to a significant correlation of relaxation processes in entangled polymer solutions, in contradiction to common constitutive equations.

Wednesday   2:45   Elliott   MS4

RATIO OF DYNAMIC MODULI AND ESTIMATION OF THE RELAXATION TIME DISTRIBUTION

Jianhua Huang and Donald G. Baird
Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061-0211

Three functions as a ratio of the dynamic moduli at different frequencies have been proposed to investigate the relaxation time distribution of a linear viscoelastic system. One of the functions, for example, is the ratio (r) of difference of storage moduli and sum of loss moduli at two angular frequencies (a and b). It is found that the ratio carries the information about the relaxation time distribution of a generalized Maxwell model. That is, the model contains at least one Maxwell element whose relaxation time falls in a region (τ_a, τ_b) which is determined by r, a and b. Accordingly, given dynamic moduli (both G' and G" at a and b), one must select at least one relaxation time in the

region (τ_a, τ_b) for this model to fit the data perfectly. On the same principle, a set of dynamic data can yield a series of regions from which the minimum number and distribution of the relaxation times of the model can be found. The approach has been applied to polystyrene systems using literature data and compared with the nonlinear regression model-fitting method. The result shows that the predicted number and distribution of the relaxation times agree well with that determined by the regression method. The theory is helpful in determining the discrete relaxation time spectrum of polymers when a small number of relaxation modes are used.

Wednesday   3:35   Elliott   MS5
CONSTRAINT RELEASE EFFECTS IN MONODISPERSE AND BIDISPERSE POLYSTYRENES IN FAST TRANSIENT SHEARING FLOWS

Cattaleeya Pattamaprom and **Ronald G. Larson**
Chemical Engineering, University of Michigan, Ann Arbor, MI 48109

ABSTRACT: Predictions of the Mead-Larson-Doi (MLD)[1,2], and the Doi-Edwards-Marrucci-Grizzuti (DEMG) models [3] are compared with the rheological data in start up of steady shearing of concentrated bidisperse polystyrene solutions. Both the MLD and DEMG models are "tube" theories of flow with reptation, but the MLD theory includes both reptative and convective constraint-release effects, which are neglected in the DEMG theory. The only adjustable parameters for the models are the reptation times of each molecular weight component $\tau_{d,i}$ and the plateau modulus. The convective constraint release included in the MLD model remedies the extreme shear thinning predicted by the DEMG model and the reptative constraint release extends the good predictions found for monodisperse polymers to bidisperse systems, especially at steady state. In the transient start-up of shear for monodisperse polymers, both models provide good predictions in both the viscosities and the first normal stress differences at low shear rates. At high shear rates, the MLD model, as well as the DEMG model, can predict the strain at the peak in stress accurately; however, the magnitude of the overshoots predicted by the MLD model are not as high as those of the DEMG model, the latter predicting overshoots that are closer to the observed results.

References:

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[2] Mead DW; Larson RG; Doi M. 2000 in preparation.

[3] Pearson, D.S.; Kiss, A.D.; Fetters, L.J.; Doi M. J. Rheol. 1989,33,517

Wednesday   4:00   Elliott   MS6
USE CUMULATIVE DISTRIBUTION FUNCTIONS IN THE FITTING OF DISCRETE SPECTRA

Bruce Caswell
Division of Engineering, Brown University, Providence, RI 02912

The description of linear viscoelasticity starts with the representation of the relaxation modulus, G(t), or its convolution reciprocal, the compliance, J(t) as time integrals on [0, infinity] whose kernels are H(t) and L(t), the relaxation-time and the retardation-time distributions respectively. An equivalent formulation is obtained from by-parts integration such that the kernels are changed from H(t) and L(t) to their respective integrals over log t, namely the cumulative distributions g(t) and j(t). The representation of the linear viscoelasticity has long been sought as a finite sum of Maxwell elements or modes (Prony series) over a finite time interval [tmin, tmax]. Least-squares fitting of the weights is limited by its tendency to yield unacceptable, negative values when the density of modes exceeds one per decade of time. Recent work has emphasized modification of least squares to enforce positivity, and the filtering of data errors by regularization. While the latter allows for arbitrary refinement, it is not known whether the higher density of modes yields a truer solution or merely portrays, in ever greater detail, a combination of experimental error and distortion due to regularization. In this paper the fitting problem is derived from the governing integral equations in terms of the cumulative distributions. An optimal spacing of times, which improves accuracy without excessive refinement, yields the fitting problem in the familiar form, but with an important distinction. The new formulation requires an accounting of the 'tails' of the integrals below tmin and beyond tmax.

Wednesday   4:25   Elliott   MS7
INTERRUPTED SHEAR FLOW OF UNENTANGLED POLYSTYRENE MELTS
Patrick G. Santangelo and C. Michael Roland
Chemistry, US Naval Research Laboratory, Washington, D.C. 20375

Time-dependent overshoot phenomena in both the shear and first normal stress growth functions were observed in low molecular weight polystyrene melts subjected to interrupted shear flow. Weak maxima were exhibited in both the viscosity and normal stress growth coefficient upon startup of the flow, notwithstanding the absence of entanglements. The strain associated with the viscosity maxima was independent of shear rate, and consistent with the overshoot strains for entangled polymers. The stress overshoots disappeared or were of weaker intensity when the flow was resumed after brief interruption. For sufficiently long rest periods between flow, the original behavior was reproduced. The time scale for recovery of the maxima was about the same as the time scale associated with relaxation of the stress after cessation of steady state flow. This differs from the behavior of entangled polymers.

Wednesday   4:50   Elliott   MS8
TIME-STRAIN NON-SEPARABILITY IN POLYMER VISCOELASTICITY
Kwang soo Cho[1] and **Youngdon Kwon**[2]
[1]R & D Dept., Youngchang Chemical Co. Ltd., Yosu, Jeonnam Province, Republic of Korea;
[2]Dept. of Textile Engineering, Sungkyunkwan University, Suwon, Kyunggi-do 440-746, Republic of Korea

In this work, the mathematical invalidity of the hypothesis "time-strain separability" is shown especially in short time region. Based on the stability theorems formulated previously, it is proven that the viscoelastic constitutive equations with this factorability cannot satisify all the constraints at the same time. Afterwards, the physical meaning of the violation of this stability criterion is illustrated for the step strain experiment. As a result, the mathematical instability exhibited by the separable integral models such as the Lodge, Wagner, Luo-Tanner and K-BKZ equations results from this hypothetical factorability. For the Doi-Edwards constitutive equation, since the configuration tensor is associated with the Finger strain tensor at least implicitly, its ill-posed behavior is also due to the separability hypothesis. At the end, the case of differential constitutive equations are also analyzed for the separable type models.

Symposium SC
Suspensions and Colloidal Systems

Organizers: Daniel De Kee and Robert Lionberger

Wednesday   1:30   Heyward   SC23
NORMAL-STRESS TRANSITIONS IN A CONCENTRATED SUSPENSION OF SPHERES
Venkata G. Kolli, Emily J. Pollauf, and Francis A. Gadala-Maria
Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208

The transient normal force response in a concentrated suspension of spheres upon startup of flow, following a period of rest, was found to depend upon the direction in which the shear was restarted. When shear was restarted in the same direction, the normal force signal rapidly grew to its previous positive steady-state value. However, when shear was restarted in the opposite direction, the normal force signal was initially negative, reached a minimum, and gradually increased from this negative minimum to its positive steady-state value. This is believed to be the first report of this phenomenon in suspensions.

Wednesday   1:55   Heyward   SC24

SIMULTANEOUS FLOTATION AND SEDIMENTATION IN THREE COMPONENT MIXTURES

Stephen A. Altobelli[1] and Lisa A. Mondy[2]
[1]New Mexico Resonance, Albuquerque, NM 87106; [2]Sandia National Laboratories, Albuquerque, NM

We used Nuclear Magnetic Resonance (NMR) imaging to study three component suspensions of 1 mm oil-filled pharmacuetical pills and 40 μm glass-encapsulated micro-bubbles in 100 cS silicon oil. The pills sink in the silicon oil with a Stokes velocity of $5 \ 10^{-2}$ cm/s and the micro-bubbles float, albeit much more slowly. The pills are 850 - 1180 μm in diameter, but the micro-bubbles are polydisperse.

Batch sedimentation / flotation experiments were performed in vertical right circular cylinders. One dimensional images were made in the vertical direction. The NMR signal can be scaled directly to volume fraction in this case. The glass micro-bubbles produce no NMR signal, and the concentration of this phase was calculated by subtracting the sum of the oil plus pill volume fractions from unity.

The NMR imaging sequence exploited the difference in the NMR relaxation properties of the silicon oil and pills to alternately null the signal from one of these two species. Simple interpolation was used to align the timing of the samples. Vertical profiles of the volume fractions of the three phases were produced at intervals of 9.4s with this method.

Vertical velocity profiles were calculated from the evolution of the volume fraction profiles. By combining the volume fraction and velocity data, hindered settling functions for the pills were calculated.

The experiments were evaluated in terms of an effective fluid theory that combines the silicon oil and micro-bubbles. In our experiments, using Krieger's viscosity correlation, the effective fluid picture seems to be inadequate.

Wednesday   2:20   Heyward   SC25

UNIFORM MIGRATION OF CONCENTRATION BANDS IN VARIABLE-DEPTH FREE-SURFACE COUETTE FLOW OF A NONCOLLOIDAL SUSPENSION

Brian D. Timberlake and Jeffrey F. Morris
Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332

New findings in the banding phenomenon in free-surface Couette flow of a suspension (Tirumkudulu, et al., 1999. Phys. Fluids v. 11, p.507-9) have been observed. A concentric cylinder device with solid inner cylinder of radius 1/4" and outer cylinder radius 7/8" was partially filled with a viscous, neutrally buoyant, and nearly monodisperse suspension of spheres (mean radius 275 micron) at bulk particle volume fractions of 0.05-0.3; the focus here is upon a filling level of 45-50%. The device was placed with axis in a range of orientations, from perpendicular to gravity to an angle of roughly 6.5 degrees, and the inner cylinder was rotated. The gap-scale Reynolds number was in all cases discussed less than 0.55. The observation made by time-lapsed visualization is that particle-rich bands are spontaneously formed in the end of the cylinder at elevation (the end with shallower bulk fluid), and these bands move steadily down the axis of the cylinder toward the opposite (lower) end of the cylinder, where they are observed to vanish into the bulk mixture. A fraction of a packet of tracer particle introduced to a concentrated band immediately after its formation are observed to remain in the packet along the entire axis. The band formation phenomenon apparently ceases to occur at a sufficiently large angle, with this angle dependent upon the particle fraction and cylinder rotation rate. Under large angles, global secondary flows are driven by the elevation difference between the portions of the free surface "fore" and "aft" of the rotating cylinder, with a flow toward the shallow end on the side with the higher elevation. An extreme variation in concentration (local ϕ = 0-0.35 at a bulk fraction of ϕ_{bulk}= 0.2) along the axis with higher concentration in the deep end is observed at under larger angles, and is related to this global circulation in a manner not completely understood.

Wednesday 2:45 Heyward SC26

THE INFLUENCE OF WALLS ON PARTICLE MIGRATION IN SUSPENSIONS

Shihai Feng[1], Allen E. Kaiser[1], Alan L. Graham[1], James R. Abbott[1], and Marc S. Ingber[2]
[1]Chemical Engineering, Texas Tech University, Lubbock, TX 79409; [2]Mechanical Engineering, University of New Mexico, Albuquerque, NM

The trajectories of particles subjected to inhomogeneous shear flows are affected by the presence of containing walls. In this coupled experimental and numerical effort, particles subjected to a number of different inhomogeneous shear flows are observed to migrate away from the containing walls. Experiments on suspensions of neutrally buoyant spheres in Newtonian fluids reveal that clusters of particles placed near the containing walls of a wide-gap Couette migrate towards the center portion of the gap, but the migration rates that are dependent on the local shear rate gradients. Falling ball experiments in suspensions of similarly sized neutrally buoyant spheres in which a dense ball is allowed to settle near a containing wall show that the falling ball experiences a lateral migration away from the containing walls. The extent of this migration increases as the distance to the wall decreases and the particle concentration increases. Fully three-dimensional boundary element simulations confirm these experimental observations and show the effect on suspensions subjected to identical shear rate gradients in the proximity of walls and in flow fields without bounding surfaces.

Wednesday 3:35 Heyward SC27

CONSOLIDATION OF AGGREGATED SUSPENSIONS IN DRYING

Lloyd A. Brown and Charles F. Zukoski
Department of Chemical Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801

The compressive rheology of suspensions of aggregated alumina particles is used to characterize their consolidation behavior during drying. A two-phase consolidation model that predicts the rate of drying, volume fraction profiles and the end of consolidation is used during saturated drying. Drying behavior when the bed begins to desaturate is predicted using a model that considers liquid remaining in the bed at this stage as being in one of two zones. The first zone is one in which moisture remains only on the surface of particles in a thin film and in the spaces between particles and, the second, a zone where the bed is still saturated. Liquid evaporates from these two zones and the vapor is carried through the bed to the surface by diffusion. Our description yields a diffusion equation with a source term to account for the evaporation of liquid from the spaces between particles and the particle surfaces and the subsequent diffusion of the vapor. These two models incorporate the role of particle interaction forces during drying and present a complete picture of consolidation and subsequent bed drainage. We present comparative experimental data to verify the accuracy of our simulations.

Wednesday 4:00 Heyward SC28

THE RHEOLOGICAL BEHAVIOR OF "STRUCTURED" FIBRID SUSPENSIONS

Ruifeng Liang, Long Han, Deepak Doraiswamy, and Rakesh K. Gupta
Department of Chemical Engineering, West Virginia University, Morgantown, WV 26506

Aramid fibrid (platelet) suspensions have unusual "space-filling" structures with power law indices as low as 0.2 and viscosity enhancement factors of ~ 5000 at loadings of less than 1 %; this behavior makes them good candidates for use as thickening agents in sealants, caulks and adhesives. The flow responses of aramid fibrids dispersed in mixtures of corn syrup and water were determined in oscillatory, steady shear, transient step rate, low shear capillary, and extensional stretching flows. The effects of fibrid type, concentration, medium viscosity and dispersion intensity were studied. Instruments used included a Rheometrics RMS 800 rheometer, a glass capillary viscometer and a fiber-spinning-type extensional viscometer. Yield stress, strong shear thinning, thixotropy, elasticity after step shear, and strong dispersion effects were observed, which were consistent with equilibrium structures defined by the degree of space-filling and the total imposed strain. Intrinsic viscosity measurements on dilute fibrids suspensions revealed Einstein coefficients about 200 times larger than the corresponding value for spheres, which helped demonstrate their remarkable viscosity enhancement as well as the strong effect of dispersion. The viscosity data over 6 decades of shear rate were described very well by traditional models such as the Ellis, Cross or Carreau equations.

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Wednesday   4:25   Heyward   SC29
RHEOLOGY AND FILTRATE PROPERTIES OF MONTMORILLONITE SUSPENSIONS WITH THE TERPOLYMER OF ITACONIC ACID-ACRYLAMIDE-2-ACRYLAMIDO-2-METHY-L-PROPANESULFONIC ACID AT HIGH TEMPERATURE

Yumin Wu, Baoqing Zhang, <u>Dejun Sun</u>, and Chunguang Zhang
Key Lab of Colloid and Interface Chemistry, Shandong University, Jinan, Shandong 250100, China

The terpolymer of itaconic acid (IA), acrylamide (AM) and 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS) is synthesized through the free-radical polymerization. An experimental investigation is undertaken into the rheology and filtrate properties of the terpolymer-montmorillonite suspension. The fliltrate volume reduces with the increase of the terpolymer concentration before or after aging test at 220°C, meaning that the clay maintains its gel strength and structure at high temperature. The particle size data demonstrates that only a little change of the clay particle size occurrs before and after aging test, this further confirms the thermal stability of the terpolymer-clay dispersion from another point of view. The rheology properties of the terpolymer-clay dispersion are improved by IA-AM-AMPS terpolymer. Apparent viscosity, plastic viscosity and yield point of the clay suspension increase with the increase of terpolymer concentration in fresh water, while these viscosities give minimum values with the increase of terpolymer concentration in salt water. Clay particles in water are attracted to each other to build up a gel structure with viscosity and strength through attraction and repulsion of the electric double layer, and the electrostatic forces are usually effected by the screening effect of electrolytes in salt water according to DLVO theory.

Wednesday   4:50   Heyward   SC30
RHEOLOGICAL PROPERTIES AND STABILIZATION OF MAGNETORHEOLOGICAL FLUIDS IN A WATER IN OIL EMULSION

Jong hyeok Park and <u>O Ok Park</u>
Korea Advanced Institute of Science and Technology, Taejon, Republic of Korea

In the present article, the rheological properties and dispersion stability of magnetorheological (MR) fluids consisting of hydrophilic treated carbonyl iron particles dispersed in a water in oil emulsion were studied for the first time by the use of a stress-controlled rheometer and sedimentation test. In order to improve the stability of MR fluid, carbonyl iron was chemisorbed by Tween80 and a water in oil emulsion was employed as a MR fluids. Attraction between hydrophilicity of treated carbonyl iron and water emulsion play a critical role in improving stability tremendously against sedimentation of dense carbonyl iron particles and the rheological properties are not restricted. On application of magnetic fields, the suspensions show a striking increase in viscosity. Since the constant stress is generated within the limit of zero shear rate, the plateau in the flow curve corresponds to the Bingham yield stress. Under a low external field, the yield stress varied as T3/2, indicating that local magnetization saturation occurs between the neighboring magnetized particles. The yield tress has an approximately linear relation with the particle volume fraction.

Thursday Morning

Symposium LC
Liquid Crystalline Systems

Organizers: Jeff Byars and Mohan Srinivasarao

Thursday   8:05   Lady Davis   LC1
RHEOLOGICAL THEORY FOR CHIRAL LIQUID CRYSTALS

Alejandro D. Rey

Chemical Engineering, McGill University, Montreal, Quebec/ Canada H3A2B2, Canada

A macroscopic model for chiral cholesteric liquid crystals is used to predict the rheological materials functions for small amplitude oscillatory shear flow. The sensitivity of the rheological material functions to the helix orientation is established. It is found that the strongest viscoelastic response arises when the helix is oriented along the velocity gradient. The contributions of the Frank elasticity and the short range elasticity are identified and characterized in terms of resonant frequencies.

Thursday   8:30   Lady Davis   LC2
A UNIFIED HYDRODYNAMICS THEORY FOR NONHOMOGENEOUS LIQUID CRYSTAL POLYMERS

Qi Wang

Mathematical Sciences, Indiana U-Purdue U Indianapolis, Indianapolis, IN 46202

I will present a hydrodynamical theory for nonhomogeneous liquid crystal polymers (LCPs). The new theory provides a unified approach for both rodlike and disklike molecules accounting for the molecular aspect ratios. In the weak flow limit, the new theory predicts the three elastic moduli obeying the ordering $K_1 < K_3 < K_2$ in the neighborhood of the phase transition concentration and $K_3 < K_1 < K_2$ at high concentration for discotic LCPs. The ordering is reversed for rodlike LCPs. It also exhibits enhanced shape effects in the viscous stress and yields a positive Leslie viscosity α_2 (α_3) in the flow-aligning (tumbling) regime for disklike (rodlike) LCPs. Finally, we derive a moment averaged, approximate, mesoscopic theory for complex flow simulations via simple closure approximations and demonstrate the rheological behavior of the model.

Thursday   8:55   Lady Davis   LC3
MESOSTRUCTURE EVOLUTION IN TUMBLING NEMATIC LCPS BETWEEN SHEARING PLATES

Greg Forest

Mathematics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250

Mesoscale structures are routinely observed in shear and extensional flows of nematic liquid crystalline polymers. Light scattering images reveal banded and more complex patterns, both steady and transient. Unstable or unsteady phenomena such as flow-induced phase transitions or director tumbling play some role in the emergence of mesoscopic structures. This presentation reports our progress on the modeling and simulations of mesostructures that emerge between shearing plates, motivated by experiments of Burghardt, Mather and others, and the recent numerical/modeling work of Tsuji and Rey and of Kupfermann, Kawaguchi, and Denn. We apply current mesoscopic models for flow-orientation coupling due to Doi, Marrucci, and Greco, with recent modifications. This work is joint with Qi Wang, IUPUI, and Hong Zhou, UC-Santa Cruz.

Thursday   9:20   Lady Davis   LC4
SIMULATING DISCLINATIONS IN SHEARED NEMATIC POLYMERS

Jimmy J. Feng[1], Jianjun Tao[1], and L. Gary Leal[2]
[1]Levich Institute, City College of CUNY, New York, NY 10031; [2]Chemical Engineering,
University of California, Santa Barbara, CA 93106

We use the Leslie-Ericksen theory to simulate the shear flow of tumbling nematic polymers. The objectives are to explore the onset and evolution of the roll-cell instability and to uncover the flow scenario leading to the nucleation of disclinations. With increasing shear rate, four flow regimes are observed: stable simple shear, steady roll cells, oscillating roll cells and irregular patterns with disclinations. In the last regime, roll cells break up into an irregular and fluctuating pattern of eddies. The director is swept into the flow direction in formations called ``ridges'', which under favorable flow conditions split to form pairs of +1 and -1 disclinations with nonsingular cores. The four regimes are generally consistent with experimental observations, but the mechanism for defect nucleation remains to be verified by more detailed measurements.

Thursday   10:10   Lady Davis   LC5
PREDICTION AND OBSERVATION OF CHAOTIC DYNAMICS IN SHEARED LIQUID CRYSTALLINE POLYMERS

Massimiliano Grosso[1], Jan Vermant[2], Paula Moldenaers[2], and Pier Luca Maffettone[3]
[1]Dipartimento di Ingegneria Chimica, Universita' Federico II Napoli, Napoli I-80125, Italy;
[2]Department of Chemical Engineering, K.U. Leuven, Leuven 3001, Belgium; [3]Dipartimento di
Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Torino 10129, Italy

Time resolved measurements of the linear conservative dichroism of 12% liquid crystalline polybenzylglutamate solutions in m-cresol show an irregular response at intermediate shear rates in experiments were the shear rate is decreased from the flow-aligning regime. The rigid rod model for rodlike polymers in the nematic liquid crystalline phase is analyzed to characterize that irregular dynamical response. The model is studied with a continuation approach, and a period doubling scenario is detected at intermediate shear rates. Both experimental and simulated time series are studied with nonlinear-analysis tools. The Poincare' section, the largest Lyapunov exponent and the correlation dimensions of the reconstructed attractors are calculated. The results suggest the existence of chaotic regimes.

Thursday   10:35   Lady Davis   LC6
TRANSIENT MEASUREMENTS OF LYOTROPIC LCP ORIENTATION WITHIN THE 1-2 PLANE

Wesley R. Burghardt and Franklin E. Caputo
Chemical Engineering Department, Northwestern University, Evanston, IL 60208

We report studies of molecular orientation in lyotropic solutions of poly(benzyl glutamate) (PBG) and hydroxypropylcellulose (HPC). Synchrotron x-ray scattering was used to obtain time-resolved measurements of molecular orientation in transient flows such as flow reversals and step increase/decrease in shear rate, and during relaxation upon flow cessation. A new annular cone and plate x-ray shear cell was used to allow measurements of both molecular orientation and average orientation direction in the 1-2 plane, by sending the incident x-ray beam along the vorticity (3) direction of the shear flow. In steady shear flow, the orientation angle changes sign from positive to negative in both PBG and HPC solutions, in agreement with the Doi molecular theory. At low shear rates, both materials exhibit a biaxial average orientation state; comparisons between 1-3 and 1-2 plane measurements of anisotropy in HPC show large differences in the degree of anisotropy measured in these two projections of the orientation state. In transient flow reversals, transient 'orientation trajectories' in PBG agree qualitatively with the Larson-Doi model, but only after an initial period of around 5 strain units. In step change flows, the evolution of molecular orientation in PBG is qualitatively consistent with Larson-Doi model predictions but the behavior of orientation angle is are almost exactly the opposite of the model prediction.

Thursday   11:00   Lady Davis   LC7
SHEAR-INDUCED TEXTURE AND ITS EFFECT ON THE VISCOELASTIC RESPONSES OF A MAIN CHAIN THERMOTROPIC COPOLYESTER HBA/HQ/SA
Chi-Kwong Chan and <u>Ping Gao</u>

Department of Chemical Engineering, Hong Kong University of Science and Technology, Hong Kong

Experimental investigations on the shear-induced textures of a model main chain thermotropic copolyester of hydroxybenzoic acid, hydroquinone and sabacic acid (HBA/HQ/SA), denoted by TLCP3, has been performed using an optical shearing apparatus in conjunction with a polarized microscope. It is observed that the viscoelastic properties of the material correlate closely with the texture of the material. TLCP3 exhibits a very wide range of linear viscoelastic responses within the fully nematic phase with strain amplitude up to 200%. Within the linear viscoelastic regime, the texture of the material is fully reversible. In the non-linear viscoelastic region, the material undergoes significant textural changes during and after cessation of shear. Banded textures develop during the start up of shear with the bands directions are controlled by a combination of the local director field as well as the external shear. Multiple loop textures develop at steady state and these loops rapidly annihilate out on cessation of shear (within 1 minute). We believe the formation of banded textures is responsible for the stress overshoot observed during the start-up process of the step shear rate stress relaxation experiments. The material also exhibits very similar responses to that of lyotropic systems with the first normal stress differences being negative at low shear rates and become positive at high shear rates.

Thursday   11:25   Lady Davis   LC8
CURE CHARACTERIZATION OF NEMATIC BISMALEIMIDE THERMOSETS
Haihu Qin and <u>Patrick T. Mather</u>

Polymer Program, University of Connecticut, Storrs, CT 06269

We are pursuing the development of thermosetting resins that combine heat resistance and fracture toughness. Our challenge is that most approaches toward increasing toughness have resulted in concomitant lowering of the glass transition temperature and/or increased shear viscosity, detrimental to processing. The use of nematic thermosets with controlled disclination microstructures offers one alternative. As such, we have designed and prepared a series of triaryl bismaleimide thermosets, with variation in pendant group, that melt to a nematic phase and subsequently cure through chain growth polymerization of the maleimide groups. We will report our recent findings on the cure kinetics, chemorheology, and rheological microscopy of these novel resins, giving particular attention to the evolving disclination texture that depends strongly on thermomechanical history.

Thursday   11:50   Lady Davis   LC9
RECOVERABLE COMPLIANCE AND VISCOSITY OF ALIGNED BLOCK COPOLYMER LAMELLAE
<u>Nitash P. Balsara</u>[1], H Hahn[1], and Hiroshi Watanabe[2]

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The viscous and elastic forces that resist the flow of aligned, weakly ordered block copolymer lamellae are quantified by dynamic viscoelastic measurements. The viscosity and the recoverable shear compliance of the aligned ordered phase are significantly lower than that of the disordered state. The measured value of the compliance of the ordered state in zero shear rate limit is in agreement with predictions based on the Rouse model.

Symposium AS
Associating Polymers and Surfactant Systems

Organizers: Ralph H. Colby and Andrew M. Howe

Thursday   8:05   Drayton   AS18

THE RHEOLOGY OF CHARGED, WORM-LIKE MICELLES

Beth A. Schubert, Norman J. Wagner, and Eric W. Kaler
Department of Chemical Engineering, University of Delaware, Newark, DE 19716

Mixtures of cationic and anionic surfactants can self-assemble into worm-like micelles. The length scales of the resulting worm-like micellar network, including the contour and persistence lengths, can be independently controlled through the variation of surfactant concentration, surfactant mixing ratio, and ionic strength. Here we study mixtures of cetyl trimethylammonium tosylate (CTAT) and sodium dodecyl benzyl sulfonate (SDBS) in aqueous solutions of various salts. Some organic salts with small hydrophobic groups (so called "penetrating" salts, such as tosylate) can enter the outer region of the micelle, changing the charge density.

The rheology, flow-birefringence, and flow-small angle neutron scattering of CTAT/SDBS worm-like micellar solutions are studied as functions of solution composition. This combination of experimental methods enables independent determination of the various length scales (persistence, entanglement, interaction, and contour) that govern the rheological properties. Comparison and contrast of the effect of "penetrating" salts with those of merely screening electrolytes (e.g. NaCl) demonstrates the importance of micellar charge on the rheological and microstructural properties.

Thursday   8:30   Drayton   AS19

DETERMINATION OF THE END CAP ENERGY OF WORM-LIKE MICELLES

Martin In
Universite Montpellier 2, Groupe de Dynamique des Phases Condensees, Montpellier cedex 05 34095, France

Worm-like micelles are living polymers whose equilibrium size is determined by the concentration, the temperature, and the end-cap energy. The experimental determination of the end cap energy will be the topic of this presentation.

In the semi-dilute regime, the concentration dependence of the rheological properties of various surfactant systems, suggests the existence of a non-entangled regime. The cross-over to a fully entangled regime occurs when the size of the micelles is of the order of the mesh size of the entanglement network. The temperature dependence of the cross-over concentration reflects the temperature dependence of the micelles size and provides with a good estimate of the end cap energy. Several systems of gemini surfactants and surfactant oligomers are presented to validate this approach.

Thursday   8:55   Drayton   AS20

UNSTEADY MOTION OF BUBBLES AND SPHERES IN WORMLIKE MICELLAR SOLUTIONS

Andrew L. Belmonte and Anandhan Jayaraman
Department of Mathematics, W. G. Pritchard Laboratories, Penn State University, University Park, PA 16802

Experimental results are presented of falling spheres and rising bubbles in aqueous solutions of CTAB/NaSal, a surfactant system which forms wormlike micellar structures. Spheres (bubbles) larger than certain radius undergo oscillations as they fall (rise) through the fluid. In the case of the bubble a cusp-like tail also periodically forms and retracts. The oscillations are believed to be caused by the breaking of the micelles under shear. A simple model which captures the physics of the oscillations is proposed.

Thursday 9:20 Drayton AS21

DILUTE SOLUTIONS OF POLYMER-SURFACTANT COMPLEXES: EXTENSIONAL PROPERTIES AND DROP IMPACT BEHAVIOUR

Justin J. Cooper-White, Regan C. Crooks, Karuppiah Chockalingham, and David V. Boger
Chemical Engineering, University of Melbourne, Melbourne, Victoria 3010, Australia

Flows that involve a significant extensional component are encountered in many industrial practices, for example spraying, roller coating and inkjet printing. Polymers are often added to mixtures used in these applications to improve processibility, due to the associated enhancement of elasticity and extensional viscosity.[1] Surfactants are also added to enhance wetting in some of these applications, for example, agricultural spraying.

Many solutions used in such applications contain both polymers and surfactants of various types and concentrations. When a charged surfactant is added to a solution containing non-ionic polymer, hydrophobic associations result in considerable changes in the bulk properties of the solution.[2,3] While much work has been carried out on the shear properties of polymer-surfactant solutions, in particular non-ionic polymer-charged surfactant solutions [4] and oppositely charged polymers (polyelectrolytes) and surfactants,[5] there has been little work carried out on the extensional properties of such systems, especially in dilute regimes.

In this paper, the outcomes of a recent drop impact study using a polymer-surfactant system are described. The observed extensional and dynamic surface tension properties of these solutions are discussed in terms of the already understood structural phenomena of the complex, showing that these techniques are very sensitive to the changes in the adsorption of the surfactant to the polymer chain. The outcomes of this investigation provide insight into previous unseen advantages associated with the use of polymer-surfactant complexes when tuning fluid properties of solutions.

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Thursday 10:10 Drayton AS22

MICRORHEOLOGICAL INVESTIGATION OF THE DYNAMICS OF COLLOIDAL PARTICLES DISPERSED IN SOLUTIONS OF ASSOCIATIVE POLYMERS

Qiang Lu and Michael J. Solomon
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Telechelic associative polymers (AP) are linear polymers with chain ends of different chemical functionality than the remainder of the molecule. The association of chain ends leads to unusual rheological properties such as single mode Maxwell linear viscoelasticity, strong shear thinning and, sometimes, shear thickening. These properties have been exploited for applications in paints, drilling fluids, and potentially, genomic sequencing. We have studied the interactions of these polymers with colloidal particles by means of diffusing wave spectroscopy (DWS) and epifluorescence microscopy. The mean square displacement,$<\Delta r^2(t)>$,of dilute (1-3 vol%) probe particles dispersed in AP solutions of varying chemistry and molecular weight has been extracted from DWS measurements according to the methods of Weitz, Pine and coworkers. The diameter of the probe particles was varied from 0.6-3.0 microns. The AP used in this research are HEUR polymers with hydrophobic chain length varying from C9-C16. The hydrophilic chain molecular weight was varied between 12,000 g/mole-35,000 g/mole. The studies of the effect of polymer concentration precisely probe the critical concentration required for the formation of the network structure. The effect of particle size on the mean square displacement, $<\Delta r^2(t)>$, did not obey the scaling predicted by recent microrheology theories, particularly at short times. The deviations from the predicted scaling are examined in light of the special chemistry of AP solutions, as well as the local interactions between probe particles and the surrounding material. The temporal range of the studies of probe dynamics was extended by combining results of independent measurements by DWS, photon correlation spectroscopy in the single scattering limit, and particle tracking by means of epifluorescence microscopy. By applying theories of microrheology, the results are compared to those directly obtained from mechanical rheology.

Thursday   10:35   Drayton   AS23
EFFECTS OF SURFACTANT AND SALT ADDITION ON THE RHEOLOGY OF HASE POLYMERS

Carlos Tiu[1], Angie Kit Ming Lau[1], and Michael Kam Chiu Tam[2]
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Steady and dynamic shear properties of two hydrophobically modified alkali soluble emulsions (HASE), NPJ1 and NPJ2, were experimentally investigated. At the same polymer concentration, NPJ1 is much more viscous than NPJ2. The high hydrophobicity of NPJ1 allows hydrophobic associations and more junction sites to be created, leading to the formation of a network structure. Under shear deformation, NPJ1 exhibits shear-thinning behaviour as compared to Newtonian characteristics of NPJ2. Beyond a critical concentration, c*, the zero-shear viscosity increases dramatically for NPJ1 due to inter-molecular association. The relaxation time, as obtained from the crossover of G' and G", increases with increasing concentration for NPJ1. No relaxation time was detectable for NPJ2, where G" is always greater than G' over the frequency range measured.

Three different surfactants - anionic SDS, cationic CTAB, and non-ionic TX-100 - were employed to examine the effects of surfactants on the rheology of HASE. Due to the ionic behaviour of the surfactant, each type of surfactant imposed different electrostatic mechanisms to the two HASE polymers. In general, at low surfactant concentration, an increase in viscosity is observed until a maximum is reached, beyond which a continuous reduction of viscosity is ensued at high surfactant concentration. Viscosity development is a result of HASE-surfactant interactions, accompanied by constant rearrangement of the hydrophobic associative junctions.

The rheological effect of salt (NaCl) concentration on the HASE polymers was also investigated. Salt added to the polymer solution induces an electrostatic shielding effect on the polymer backbone, and hence reduces the size of the polymer macromolecules. This results in a reduction of both steady shear viscosity and dynamic moduli of NPJ1 and NPJ2 with increasing salt concentration. The degree of shear thinning diminishes in NPJ1 with increasing salt addition.

Thursday   11:00   Drayton   AS24
DIFFUSION-DRIVEN STRESS RELAXATION IN DRY SOAP FOAMS

Andrew M. Kraynik[1], Sascha Hilgenfeldt[2], Douglas A. Reinelt[3], and Frank van Swol[4]
[1]Engineering Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185-0834; [2]Harvard University, Cambridge, MA; [3]Southern Methodist University, Dallas, TX; [4]Materials and Process Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185-1349

Different pressures in neighboring cells of a dry soap foam cause gas diffusion that leads to coarsening, whereby the average cell radius R grows as the square root of time. This mechanism causes stress relaxation since the shear modulus scales as 1/R. In 2D, the growth rate in area of individual cells with n edges is proportional to (n-6). This elegant formula, known as von Neumann's law, is exact. In 3D, the growth rate of individual cells does not depend on number on faces, F, alone, so efforts have focused on finding an average growth law. A mean-field theory, based on a theorem by Minkowski, and Surface Evolver simulations are used to show that the growth rate scales as the square root of F for large F. The role of foam structure and cell topology in 2D and 3D will be compared and contrasted.

Thursday   11:25   Drayton   AS25

ASSOCIATION OF SURFACTANTS AND HYDROPHOBICALLY MODIFIED POLYELECTROLYTES

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When surfactants of the same charge are added to hydrophobically modified polyelectrolytes (HMP) that already have micelles, the surfactant starts to incorporate into the existing micelles at the critical incorporation concentration (CIC). Since this initial incorporation only involves a single surfactant entering a nonionic micelle, no counterion condensation is needed, making the tail length dependence of the CIC similar to the tail length dependence of the critical micelle concentration of nonionic surfactants. We demonstrate this using a series of alkyl sulfate surfactants added to a graft copolymer of poly(acrylic acid) and poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide). Surface tension measurements determine the CIC as a local minimum in surface tension plotted against added surfactant. Rheological consequences of this incorporation will be discussed for both the low temperature liquid phase and the high temperature gel phase of our hydrophobically modified polyelectrolyte. Initially, the added surfactant promotes intermolecular associations of the HMP, but larger amounts of added surfactant break up the inter-polymer associations. At large concentrations of added surfactant, the HMP becomes saturated with surfactant, with a single HMP hydrophobic group inside the mixed micelles that contain mostly surfactant.

Thursday   11:50   Drayton   AS26

THE SOLUTION PROPERTIES OF POLYELECTROLYTES: A CLASSICAL TREATMENT

Lawrence C. Cerny and Elaine R. Cerny

RESEARCH, CERNYLAND OF UTICA, Huber Hts., OH 45424-3467

The present investigation examines the dilute solution properties of two polyelectrolytes: potassium-p-polystyrene sulfonate and polymethacrylic acid. The Donnan approximation is used as a model for these systems. The molecular weights of the fractionated samples were evaluated and used to determine the theta conditions. The intrinsic viscosities were used to measure the expansion coefficients as a function of added electrolytes. The agreement with the theory was satisfactory. The activity coefficients for the gegenions in the polyelectrolytes were determined using a dropping potassium amalgam electrode. The conductivity of the potassium-p-polystyrene sulfonate solution was compared with those of potassium benzene sulfonate.

Symposium MS
Polymer Melts and Solutions

Organizers: Michael Solomon and H. Henning Winter

Thursday   8:05   Elliott   MS9

REPTATION-BASED MODELING OF FLOW-INDUCED POLYMER CRYSTALLIZATION

Pier Luca Maffettone[1], Salvatore Coppola[2], and Nino Grizzuti[2]

[1]Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Torino 10129, Italy; [2]Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli Federico II, Napoli 80125, Italy

It is well known that flow can strongly enhance polymer crystallization. Flow acts on both thermodynamics and kinetics of crystallization. On the one hand, the application of flow may induce crystallization at temperatures above the quiescent melting point, T_{m0}. On the other hand, for $T < T_{m0}$, flow produces an increase in the crystallization rate.

Most literatures studies have proposed empirical relationships where the crystal nucleation rate is a function of some measure of either the velocity gradient or the stress. Only in a few cases the nucleation rate is directly related to the flow-induced conformation of the polymer chain.

In this work, molecular models are used to calculate the free energy change, ΔG_{flow}, generated by the conformational changes of the polymer chains in the melt. The Doi-Edwards (DE) model with the Independent Alignment Approximation (IAA) is used, as it provides a relatively simple expression for ΔG_{flow} in both simple shear and uniaxial elongation. Such a change in free energy is then inserted in classical expressions for the nucleation kinetics, thus allowing for prediction of the flow-enhanced crystallization rate. The same approach is also followed by using simpler molecular models, such as the dumbbell model, both in its linearly elastic and finite extensible (FENE) versions.

Comparisons with experimental results available in the literature show that both linear and FENE dumbbell models largely overpredict the increase in crystallization rate during flow. On the contrary the DE model with IAA, for which flow induces only chain orientation and no chain stretching, is able to predict the correct order of magnitude changes of the crystallization rates.

Thursday   8:30   Elliott   MS10
THE APPEARANCE OF THREADS DURING EARLY STAGES OF SHEAR-INDUCED CRYSTALLIZATION IN ISOTACTIC POLYPROPYLENE

Henning Winter and **Natalia Pogodina**
Chemical Engineering, University of Massachusetts, Amherst, MA 01003

Quiescent and shear-enhanced melt crystallization of high-Mw isotactic polypropylene was studied by time resolved rheometry, optical microscopy, small-angle light scattering (SALS), birefringence, and turbidity. In quiescent crystallization, spherulites grow of uniform size which suggests simultaneous nucleation and uniform growth rate. The gel point is reached before the spherulites impinge. The crystallinity at the gel point is estimated from Hv SALS data as about 17%. Shear flow causes (1) an increase in crystallization rate and (2) highly elongated structures (threads) which are visible in the optical microscope and in anisotropic SALS patterns. The threads thicken until, at later stages, additional spherulites grow. The early growth is attributed to the nucleation of shear induced anisotropic molecular conformations, preferably in the high molecular weight fraction of the iPP sample, while the later growth of spherulites is assumed to occur from the less oriented short chains in the sample.

Thursday   8:55   Elliott   MS11
RHEOLOGICAL STUDIES OF MESOMORPHIC POLY(DIETHYLSILOXANE)

Himanshu Saxena, Ronald C. Hedden, and <u>**Claude Cohen**</u>
Chemical Engineering, Cornell University, Ithaca, NY 14853

Poly(diethylsiloxane) (PDES) of molar masses above 28,000 daltons exhibit a mesophase that will melt into an amorphous phase at temperatures above ambient. PDES samples with low polydispersity were prepared and the rheological behavior of five different molar masses PDES ranging from 45,000 to 200,000 daltons was studied. At room temperature, these samples have a stable mesomorphic (biphasic) structure consisting of a mesophase ("condis crystal") and an amorphous phase. The effects of molar mass and the mesophase on the rheological properties of PDES were examined.

At ambient temperatures, the high molar mass samples are highly elastic as evident from a weak dependence of G' and G" on frequency and a nearly flat relaxation spectrum. This elastic behavior is attributed to the presence of mesophase domains that act as effective cross-links in the melt. The mesophase melts on heating and the transition from a mesophase to an amorphous phase is characterized by an isotropization temperature that depends on molar mass. The biphasic and amorphous states exhibit large differences in their low frequency rheological responses similar to those observed between ordered and disordered phases of diblock copolymers.

Thursday 9:20 Elliott MS12

ON-LINE CONOSCOPIC MEASUREMENT OF FLOW INDUCED ORIENTATION IN FLEXIBLE POLYMERS

Brett L. Van Horn and H. Henning Winter

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

A method for the on-line inspection and evaluation of optical properties of oriented polymer films has been developed. Flow of flexible polymer melts induces orientation of entangled chains that can yield macroscopic anisotropy in the material. The optical anisotropy of stretched or orientated polymers is easily investigated through conoscopy where the sample is probed with highly convergent, monochromatic light. The resultant conoscopic interference figures can be analyzed to provide optical orientation, refractive indices, birefringence, and sample uniformity. The method can be incorporated on-line and provide a continuous and simple means for visual inspection of the processed polymer film. Liquid-crystalline polymers are model systems to study with this method, and much work has been done in this field, though the method is particularly well suited for the investigation of orientated films of flexible polymers.

Thursday 10:10 Elliott MS13

STRESS-OPTICAL PROPERTIES OF POLYSTYRENE AND POLYCARBONATE ACROSS THE DYNAMIC GLASS TRANSITION

Hee Hyun Lee[1], Julie A. Kornfield[1], Grant Hay[2], and Kyunghwan Yoon[3]

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Rheo-optical properties of polystyrene and polycarbonate are investigated from the terminal and plateau regions, where the familiar stress-optic-rule holds, up to the high frequency, glassy regime. The intrinsic birefringence of a polymer chain is closely related the molecular structure of the monomer unit. But the induced birefringence by stress, called the stress optical ratio (SOR), also depends on the molecular dynamic modes. In the terminal regime of low frequency and high temperature where polymers have enough time to relax, the SOR is determined by entropic elasticity. On the other hand, in the glassy region of high frequency and low temperature, molecular motion is restricted to short range where enthalpic free energy costs dominate the stress. These two molecular contributions appear to coexist as one passes through glass transition region, as manifested in the rheo-optical properties of both polystyrene and polycarbonate for the whole dynamic region from glassy to melt. The molecular weight dependence of the SOR of these samples gives insight into the molecular length scales associated with the above molecular motions.

Thursday 10:35 Elliott MS14

THE EFFECT OF PRESSURE ON THE RHEOLOGICAL PROPERTIES OF MOLTEN POLYETHYLENES

Hee Eon Park and John M. Dealy

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

A high pressure sliding plate rheometer was used to measure the rheological properties of three polyethylenes having different molecular structures. The rheometer generates simple shear flow between parallel plates under a hydrostatic pressure, and the resulting stress is measured using a shear stress transducer. Since the transducer senses the stress in the center of the sample, no corrections are necessary. Viscosity curves were obtained at four pressures ranging from one atm to 70 MPa. Pressure shift factors were found to be exponential functions of pressure. Long chain branched polyethylene showed more pressure sensitivity than linear polyethylenes, and the combination of short chain branching and polydispersity had little effect on the pressure sensitivity of the viscosity. By use of feedback-control based on the signal from the shear stress transducer, stress control experiments were also carried out, and creep and creep recovery data at high pressures were obtained.

Thursday   11:00   Elliott   MS15

HIGH-PRESSURE RHEOLOGY OF POLYMER MELTS PLASTICIZED WITH CO_2:
EXPERIMENTAL MEASUREMENTS AND PREDICTIVE VISCOELASTIC SCALING
Joseph R. Royer[1], Joseph M. DeSimone[2], and Saad A. Khan[1]
[1]Chemical Engineering, North Carolina State University, Raleigh, NC NC; [2]Department of
Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599

Carbon dioxide has been shown to be highly soluble in many polymer melts, as well as act as an effective plasticizer that can be easily removed. We have developed a high-pressure extrusion slit die rheometer to study the steady shear behavior of various polymer melts with dissolved liquid and supercritical carbon dioxide. A novel gas injection system was devised to accurately meter the flow of CO_2 into the system. The rheometer was tested to ensure that fully developed, one-phase flow was obtained and experiments could be conducted at elevated pressures of up to 35 MPa. Experimental measurements of viscosity as a function of shear rate, pressure, temperature and CO_2 concentration was conducted for various polymer melts. The results reveal reduction in the viscosity by as much as 80%, depending on process conditions and CO2 concentration. Predictive viscoelastic scaling models developed from the combination of traditional free-volume principles and a theoretical prediction of T_g depression resulting from a diluent, were used to quantify the effects of CO_2 concentration, pressure and temperature on viscosity. This unique free-volume approach allows the high-pressure polymer/CO_2 rheology to be predicted based solely on physical parameters of the polymer melt and CO_2. Therefore, only rheological measurements at ambient pressures are required to predict the high-pressure polymer/CO_2 solution behavior over the concentration and temperature ranges for which the models are valid.

Thursday   11:25   Elliott   MS16

NOVEL COUETTE RHEOMETER FOR HIGH PRESSURE, HIGH TEMPERATURE SYSTEMS
Griffin Gappert and H. Henning Winter
Department of Chemical Engineering, Universityof Massachusetts at Amherst, Amherst, MA
01003

A novel Couette rheometer was constructed for the study of high pressure, high temperature polymer solutions, e.g. supercritical polyolefin-alkane binary systems.

The rheometer is a closed system with a servo motor and magnetic bracket existing outside a high pressure vessel containing the Couette flow cell. Sample fills the entire sealed vessel allowing high pressure conditions and preventing solvent loss. The flow cell is comprised of a rotating outer cup and inner magnetic cylinder which is suspended on coaxial steel pin-sapphire bearing assemblies and held in place by interactions with outside magnets. The outer cup is driven by a sealed shaft attached to a strain-controlled servo motor outside of the pressure vessel. The inner cylinder of the flow cell is magnetically coupled to a magnetic bracket which is attached on the outside of the pressure vessel by a torsional spring. The deflection of the outer bracket is determined optically to deduce torque acting on the inner cylinder. The torque transducer has a range .01 to 1.6 N m. The interchangable rotating outer cylinders of different sizes and geometries allow for control of gap size and the inclusion of additional mixing functions. Preliminary experiments were conducted with a Ri/Ro = 0.97. The strain-controlled motor is capable of steady and oscillatory motion at various strain levels. LabVIEW software is used for motor control and data acquisition. The sealing functions of the rheometer have been tested at 600 bar.

Steady and oscillatory shear experiments were conducted on PDMS viscosity standards and polymer solutions at a variety of temperature and pressure conditions.

Thursday   11:50   Elliott   MS17
STANDARD REFERENCE MATERIALS: NON-NEWTONIAN FLUIDS FOR RHEOLOGICAL MEASUREMENTS
Carl R. Schultheisz[1] and Gregory B. McKenna[2]
[1]Polymers, National Institute of Standards and Technology, Gaithersburg, MD 20899-8544;
[2]Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121

NIST develops and sells Standard Reference Materials for calibration, quality assurance and for research into improved measurement methods. Two fluid standards are being developed to exhibit shear thinning and normal stresses typical of polymeric fluids. SRM 2490 is a solution of polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane. SRM 2491 will be a poly(dimethylsiloxane) melt, giving less temperature dependence than SRM 2490. NIST will certify the shear-rate dependence of the viscosity and first normal stress difference at 0 °C, 25 °C and 50 °C, and the linear viscoelastic behavior over the same temperature range. A round robin with the fluids is planned to investigate variability in rheological measurements. We report progress on the project.

Symposium MR
Microscopic Rheology & Single Chain Dynamics: Experiments & Analysis

Organizers: Matteo Pasquali and Eric S. G. Shaqfeh

Thursday   8:05   Heyward   MR1
THE PHYSICS OF THE ACTIN CYTOSKELETON: FROM NONEQUILIBRIUM POLYMER PHYSICS TO NERVE REGENERATION AND CANCER DIAGNOSIS
Joseph A. Kas
Physics Department, University of Texas at Austin, Austin, TX

All eukaryotic cells (any cell more advanced in evolution than a bacterium) depend in their internal structure and organization on the cytoskeleton, a polymer network within the cell interior. These cells reversibly assemble protein filaments (actin filaments, intermediate filaments, microtubles) and accessory proteins into extensive, three-dimensional networks. Among these proteins, actin forms semi flexible polymers, which create a homogeneous network underlying the plasma membrane and stress fibers which span the entire cell interior, with unique physical properties, distinguishing actin filaments from other polymer chains described by established polymer physics. The polymer dynamics of conventional polymer systems and the consequential viscoelastic properties are a result of the Brownian motions of the polymer chains. In the case of the actin cytoskeleton, actin binding proteins behave as energy consuming nanomachines (e.g.. the molecular motor myosin), which control its polymer dynamics and its resulting viscoelastic behavior. The proteins impact on polymer dynamics, and thus on viscoelasticity, cannot be described by existing polymer theories. To unravel the physics underlying the complex and highly dynamic features of actin networks, we synergistically apply soft condensed matter physics, nonlinear dynamics, mesoscopic physics, laser physics, single molecule microscopy, and molecular biology to study, in vivo, the actin cytoskeleton of cells as well as, in vitro, reconstituted elements of this cytoskeleton. Our research explains how single actin chain dynamics generates the viscoelasticity of actin networks by analyzing the motion of individual filaments in a network with nanometer resolution. Due to the central role of the actin cytoskeleton for cell function our newly gained knowledge in polymer physics directly results in novel strategies for the early detection of cancer cells and for quick nerve regeneration.

Thursday   8:30   Heyward   MR2
VISCOELASTICITY OF DILUTE SOLUTIONS OF SEMIFLEXIBLE POLYMERS
Matteo Pasquali[1], V. Shankar[2], and David C. Morse[2]
[1]Chemical Engineering, Rice University, Houston, TX 77005; [2]Chemical Engineering, University of Minnesota, Minneapolis, MN 55455

The linear viscoelasticity of dilute solutions of semiflexible polymers is studied by Brownian dynamics simulation and theoretically. The shear relaxation modulus $G(t)$ for chains that are shorter than their persistence length exhibits

three time regimes: At very early times, when longitudinal deformation is affine, G(t) and the tension both decay with time with a -3/4 power law. Over a broad intermediate regime, during which the chain length relaxes, G(t)decays with a -5/4 power law. At long times, G(t) is similar to that of rigid rods. A model of the polymer as an effectively extensible rod with a frequency dependent modulus accurately describes G(t) throughout the first two regimes.

Thursday   8:55   Heyward   MR3

STRESS AND CONFORMATIONAL RELAXATION OF DILUTE SEMIFLEXIBLE POLYMER SOLUTIONS

Panagiotis Dimitrakopoulos, John F. Brady, and Zhen-Gang Wang

Department of Chemical Engineering 210-41, California Institute of Technology, Pasadena, CA 91125

This study considers the conformational and stress relaxation of dilute semiflexible polymer solutions at equilibrium. The main objective of this work is to identify the effects of local stiffness on the properties of semiflexible polymers. In addition, we show how the conformational relaxation affects the stress relaxation and we provide scaling laws based on these relationships. To achieve these goals, Brownian Dynamics simulations based on a discretized version of the wormlike model are employed. The properties of the polymer chain are expressed as a function of the two parameters of the model, the number of segments N and the dimensionless bending energy E (or equivalently, the chain length L and the persistent length L_p). The longest relaxation time for both the conformational and material properties is that associated with the rotation or translation of the chain and is well described in terms of the average length of the chain and the diffusivity of the center of mass. The stress relaxation exhibits a plateau at early times, followed by an algebraic decay towards the rotation regime. This change is caused by the transverse relaxation of the chain ends. An accurate estimation for this time scale (as well as a scaling law) for any bending energy E, may be found from the relaxation of the chain ends. The intermediate decay can be described by a power law, which varies from $t^{-5/4}$ for very stiff chains, to $t^{-1/2}$ for flexible ones.

Thursday   9:20   Heyward   MR4

BROWNIAN DYNAMICS SIMULATIONS OF SINGLE DNA MOLECULES IN STEADY AND TRANSIENT MIXED FLOW

Joe S. Hur and Eric S. G. Shaqfeh

Chemical Engineering, Stanford University, Stanford, CA 94305-5025

We have investigated the dynamics of single DNA chains in both steady and transient mixed flows. By mixed flows we mean flows that combine the characteristics of shear and extensional flows (de Gennes 1974). It is of great interest to examine single chain dynamics in the intermediate regime where the ratio of strain to vorticity (p) is arbitrarily chosen and directly compare to the many fascinating observations that have already been reported in two limiting cases, i.e. in extensional (Perkins et al. 1997, Smith et al. 1998, Larson et al. 2000) and shear flows (Smith et al. 1999, Lyulin et al. 1999, Hur et al. 2000, Li et al. 2000). In our study, we have used the worm-like chain and Kramers' freely jointed bead-rod to model DNA molecules. These models have previously been shown to successfully capture the experimental findings in steady and the start-up of shear flow (Hur et al. 2000, Babcock et al. 2000). When the ratio of strain to vorticity (p) exceeds unity, the steady average molecular extension is found to reach its maximum contour length at high flow strength similar to the observations seen in pure extensional flow(Perkins et al. 1997). Furthermore, when the flow strength is scaled with the eigenvalue of the velocity gradient tensor we see an overlap of steady molecular extension in these flows with that in pure extensional flow. Thus these flows demonstrate coil-stretch transition. For the case where the ratio of strain to vorticity(p) is less than unity a comparison is made to the chain dynamics in steady shear flow (Smith et al. 1999, Hur et al. 2000). In order to gain better insight into chain dynamics in these mixed flows we further examine the probability distribution of the molecular extension at various values of p. Finally, we present simulation results on both macroscopic rheological properties as well as miscroscopic states in transient mixed flows where a flow is suddenly imposed, and compare to reported birefringence measurements (Fuller et al. 1980).

Thursday   10:10   Heyward   MR5
SINGLE-POLYMER DYNAMICS IN STEADY MIXED FLOWS
Hazen Babcock[1], Rodrigo Teixeira[2], Eric S. G. Shaqfeh[2], and Steve Chu[1]
[1]Physics Department, Stanford University, Stanford, CA 94305; [2]Stanford University, Stanford, CA

In 1974 de Gennes proposed that for strong flows, where the elongational component is larger than the rotational component, a polymer coil-stretch transition would be seen at sufficiently large strain rates [1]. It has been difficult to test this theory experimentally because traditional polymer experiments measure the average conformation of the polymers, while individual polymer molecules can take different pathways to the stretched state, smearing out the transition. To overcome this obstacle we built a novel apparatus that enabled us to study the conformational dynamics of individual, flexible polymers in steady mixed flows with a high resolution optical microscope. This apparatus can create mixed flows that are very close to pure shear flow. The flow lambda parameter could be varied from 0.0165 (50.8% elongation, 49.2% vorticity) down to approximately 0.0010 (50.06% elongation, 49.94% vorticity). DNA stained with fluorescent dyes was used as a model polymer to study polymer dynamics in these flows. The conformation of single DNA molecules was directly observed using video fluorescence microscopy. It was found that there was indeed a large heterogeneity in the dynamics of individual polymers similar to that seen in elongational flow [2,3]. Histograms of the extension of molecules that had passed the vicinity of the stagnation point show that many of the molecules have still not come to equilibrium with the flow even upon an accumulated strain greater than 20. At sufficiently large Weissenberg number it was found that the flow completely stretched some of the molecules for all the lambda values studied. Furthermore, the stretched state was stable, unlike in pure shear where even at high Weissenberg number the molecules fluctuate between coiled and stretched conformations [4].

(1) de Gennes, J. Chem Phys 60, 5030 (1974). (2) Perkins,Smith,Chu, Science 276, 2016 (1997). (3) Smith,Chu, Science 281, 1335 (1998). (4) Smith,Babcock,Chu, Science 283, 1724 (1999).

Thursday   10:35   Heyward   MR6
FLUORESCENCE MICROSCOPY EXPERIMENTS AND BROWNIAN DYNAMICS SIMULATIONS OF FLOW BEHAVIOR OF DNA MOLECULES CONFINED TO TWO DIMENSIONS
David J. Olson[1], Prateek D. Patel[1], Eric S. G. Shaqfeh[1], Steven G. Boxer[2], and Gerald G. Fuller[1]
[1]Department of Chemical Engineering, Stanford University, Stanford, CA 94305; [2]Department of Chemistry, Stanford University, Stanford, CA 94305

We present fluorescence microscopy and Brownian dynamics simulation studies of the flow behavior of individual DNA molecules confined to two dimensions. In the experiments, the DNA molecules are electrostatically adsorbed to a cationic-supported lipid bilayer. Previous work in our group has demonstrated the existence of flow obstacles in the lipid bilayer, which cause the DNA molecules to adopt hairpin conformations during electrophoresis. These obstacles have been observed experimentally to affect both the diffusivity and electrophoretic mobility of the chains. The results of Brownian dynamics simulations of chains constrained to two dimensions and flowing through a dilute array of obstacles are compared to the experimental observations. Upon cessation of the electric field, the fully-stretched DNA molecules were observed to relax back to an equilibrium, random-coil conformation. The initial relaxation of the chains is very rapid, followed by a slower exponential decay to the equilibrium state. These experimental observations are compared to Brownian dynamics simulations of a bead-spring polymer, which incorporates the worm-like chain description of the DNA force law.

Thursday   11:00   Heyward   MR7
ENTANGLEMENT RELAXATION AND RELEASE IN MODEL POLYMER MELTS
Julie A. McCormick, Carol K. Hall, and Saad A. Khan
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The nature of entanglements, and thus entanglement release, is treated very distinctly in different theories. Some theories include specific interchain entanglements while others reduce the many-chain problem to that of a single chain in a mean field. Two such distinct theories discussed presently are the tube model and local knot theory. These

two theories give very different descriptions for entanglement release. The tube model suggests that entanglements cause tube confinement which relaxes first from the chain ends and finally at the chain middle. However, local knot theory dictates that entanglements will only be released as a chain end moves through a knot. Therefore, observing the mechanism of entanglement release provides a means for distinguishing between the two theories' ability to describe polymer dynamics.

In this study, discontinuous molecular dynamics simulations were performed to investigate entanglement relaxation and release in model polymer melts. By applying highly efficient simulation techniques to the hard-chain model, we have been able to perform an extensive computer simulation study of entanglement relaxation dynamics. We have explored the properties of long chain fluids (N = 192, and 300) at high packing fractions over time scales that span 6 orders of magnitude. By sampling such long times, we have obtained some interesting insight into the entanglements affecting the dynamics of polymer melts. A detailed analysis of the systems containing 32 chains of 192mers has revealed that a combination of relaxation methods is responsible for the release of entanglements. We have analyzed the mean squared displacements and the end-to-end vector autocorrelation functions of single chains within the systems, as well as the system averages, to obtain information about chain motion and relaxation. A comparison between the properties of individual chains reveals a large variation in the behavior of chains within the same system and suggests the discrete nature of entanglements.

Thursday   11:25   Heyward   MR8
NON-EQUILIBRIUM BROWNIAN DYNAMICS STUDIES OF DENDRIMERS AND HYPERBRANCHED POLYMERS
Anand T. Lee and Anthony J. McHugh
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Nonequlibrium Brownian dynamics (NEBD) simulations are used to model the dynamics of dendrimers and hyperbranched polymers under shear and extensional flow conditions. A bead -spring model for dendritic molecules is proposed and six generations of perfect dendrimers are studied. Rheological and conformational properties such as viscosity, normal stress differences, visco-elastic moduli, flow birefringence and mean-squared radius of gyration are observed under both transient and steady-state conditions. Comparisons are made with the corresponding linear chain analogs of identical molecular weight. The model qualitatively describes many of the experimentally observed effects in these systems, most notably a Newtonian viscosity profile (no shear thinning), Rousean moduli and a maximum in the dependence of the intrinsic viscosity on the molecular weight. Dumbbell-based models are also proposed to investigate the effects of architectural parameters such as the "ratio of linear segments to branch-points" and the "average distance between branch-points" on the rheological properties of hyper-branched molecules.

Thursday   11:50   Heyward   MR9
GRABBING THE CAT BY THE TAIL: MANIPULATING POLYMERS ONE BY ONE
Jed C. Macosko and Carlos J. Bustamante
Departments of Physics and Molecular and Cell Biology, Unversity of California, Berkeley, Berkeley, CA 94720

Mark Twain claimed that he knew a man who grabbed a cat by the tail and learned 40% more about cats than the man who didn't. A host of single molecule manipulation techniques allow polymer chain dynamics to be studied at a new level. Two types of methodology will be discussed: Mechanical transducers and external field manipulators. Mechanical transducers, such as glass microneedles or the cantilevers used in atomic force microscopy(AFM), apply and sense forces through the displacement of a bendable beam directly coupled to the polymer chain. External field manipulators, on the other hand, act on polymers from a distance. Examples include flow fields, magnetic fields, and photon fields--often called "laser tweezers". Though the techniques are quite different, all single molecule experiments must take into consideration novel aspects of signal strength, thermal noise and time resolution in order for results to be properly interpreted. In this overview, the key elements of single molecule measurements will be presented and their usefulness as a tool for microscopic rheology will be highlighted, particularly in the physics of biopolymers.

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