



THE SOCIETY OF RHEOLOGY

71ST ANNUAL MEETING PROGRAM AND ABSTRACTS

Monona Terrace
Madison, Wisconsin
October 17-21, 1999

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Meeting Schedule

Monday, October 18, 1999

8:30	W. H. Tuminello (PL1)			
9:20	Coffee			
9:45	SG1	IR1	FM1	LC1
10:10	SG2	IR2	FM2	LC2
10:35	SG3	IR3	FM3	LC3
11:00	SG4	IR4	FM4	LC4
11:25	SG5	IR5	FM5	LC5
11:50	Business Luncheon			
1:30	SG6	IR6	FM6	LC6
1:55	SG7	IR7	FM7	LC7
2:20	SG8	IR8	FM8	LC8
2:45	SG9	IR9	FM9	LC9
3:10	Coffee			
3:35	SG10	IR10	FM10	LC10
4:00	SG11	IR11	FM11	LC11
4:25	SG12	IR12	FM12	LC12
4:50	SG13	IR13	FM13	LC13
5:15	End			
7:00	Society Reception			

Tuesday, October 19, 1999

8:30	W. B. Russel (PL2)			
9:20	Coffee			
9:45	SG14	SL1	FM14	PM1
10:10	SG15	SL2	FM15	PM2
10:35	SG16	SL3	FM16	PM3
11:00	SG17	SL4	FM17	PM4
11:25	SG18	SL5	FM18	PM5
11:50	Lunch			
1:30	SG19	SL6	FM19	MS1
1:55	SG20	SL7	FM20	MS2
2:20	SG21	SL8	FM21	MS3
2:45	SG22	SL9	FM22	MS4
3:10	Coffee			
3:35	SG23	SL10	FM23	MS5
4:00	SG24	SL11	FM24	MS6
4:25	SG25	SL12	FM25	MS7
4:50	SG26	SL13	FM26	MS8
5:15	End			
5:30	Business Meeting			
7:00	Awards Reception			
8:00	Awards Banquet			

Wednesday, October 20, 1999

8:30	J. Mewis (PL3)			
9:20	Coffee			
9:45	BC1	HT1	SF1	MS9
10:10	BC2	HT2	SF2	MS10
10:35	BC3	HT3	SF3	MS11
11:00	BC4	HT4	SF4	MS12
11:25	BC5	HT5	SF5	MS13
11:50	Lunch			
1:30	BC6	HT6	SF6	MS14
1:55	BC7	HT7	SF7	MS15
2:20	BC8	HT8	SF8	MS16
2:45	BC9	HT9	SF9	MS17
3:10	Coffee			
3:35	BC10	HT10	GN1	MS18
4:00	BC11	HT11	GN2	MS19
4:25	BC12	HT12	GN3	MS20
4:50	BC13	HT13	GN4	MS21
5:15	End			
5:30	Poster Session & Refreshments			

Thursday, October 21, 1999

8:05	BC14	HT14	GN5	MS22
8:30	BC15	HT15	GN6	MS23
8:55	BC16	HT16	GN7	MS24
9:20	BC17	HT17	GN8	MS25
9:45	Coffee			
10:10	BC18	HT18	GN9	MS26
10:35	BC19	HT19	GN10	MS27
11:00	BC20	HT20	GN11	MS28
11:25	BC21	HT21	GN12	MS29
11:50	BC22	HT22	GN13	MS30
12:15	End			

Session Codes

BC = Blends and Block Copolymers
 FM = Non-Newtonian Fluid Mechanics
 GN = General Session
 HT = Heterogeneous Systems
 IR = Industrial Rheology

LC = Liquid Crystals and Liquid Crystalline
 Polymers
 MS = Rheology of Polymer Melts and Solutions
 PL = Plenary Lectures
 PM = Polymer/Particle Mixtures

SF = Shear-free Flows
 SG = Viscoelasticity of Synthetic and Biological
 Polymer Solutions and Gels
 SL = Rheology of Solids

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Monday Morning

Symposium PL Plenary Lectures

Monday 8:30 Lecture Hall PL1

DETERMINING MOLECULAR WEIGHT DISTRIBUTIONS FROM THE RHEOLOGICAL PROPERTIES OF POLYMER MELTS

William H. Tuminello

Central Research & Development, The DuPont Company, Wilmington, DE 19980-0356

Melt rheology is very sensitive to high MW tails and long chain branching, but these structural features affect melt rheology differently than dilute solution properties (such as from SEC, size exclusion chromatography). For this reason, both melt rheology and SEC can be used to complement each other for better molecular characterization. A brief synopsis will be given of the different approaches used to determine the MWD from rheological properties and we will compare their effectiveness. Special emphasis will be placed on the recent commercial software available from Rheometric Scientific Corporation based on the work of D. Mead. Examples will be given for model polymer systems. Using the Mead approach can lead to a reasonable approximation to MW averages, particularly the weight and z-averages which depend most heavily on the high MW components. However, the shapes of the distributions are still not quantitative and some new mixing rules show promise of getting more quantitative results.

Symposium SG

Viscoelasticity of Synthetic and Biological Polymer Solutions and Gels

Organizers: Ralph H. Colby, Donald J. Plazek and Guy C. Berry

Monday 9:45 Hall of Ideas G SG1

VISCOELASTIC PROPERTIES OF GELATINS FROM ALTERNATIVE SOURCES

Paula M. Gilsean and Simon Ross-Murphy

Biopolymers Group, Division of Life Sciences, King's College London, London W8 7AH, United Kingdom

Gelatin-water systems represent the paradigm of a thermoreversible gelling (bio)polymer system. Furthermore, gelatin gels have found widespread use in the food and photographic industries over the years. As far as the scientific literature is concerned, almost all published work has concentrated on gelatins derived from traditional mammalian collagen sources. Consequently, less attention has been given to gelatin from alternative sources. The present work investigates the properties of gelatin derived from fish, and compares the results obtained with those found for "traditional" samples.

It has been known for many years that the melting and gelling temperature of gelatin has been found to correlate with the proportion of imino acid residues in the original collagen. This is typically ~24% for mammals and 16 - 18% for most fish species. The aim of this work is to examine single component fish gelatins as well as some blends and to investigate how the properties of the single systems are altered in the blends. Rheological measurements have been used to characterise the gelling and melting temperatures and the gel modulus. Such measurements have benefited greatly by improvements in instrumentation following the excellent early work by te Nijenhuis. Fish samples studied were tilapia, tuna, megrim and cod, ranging in order from tropical to cold water.

Monday Morning

Concurrent with this work, we have started to analyse the concentration vs. modulus behaviour and concentration vs. melting temperature of the single systems, using previously published models. Our longer term aim is to relate the melting enthalpy ΔH , and the equilibrium constant for the helical crosslinking reaction and thus to define a master curve relating the critical gelling concentration to the melting temperature. In this presentation, both experimental and future theoretical developments will be discussed.

Monday 10:10 Hall of Ideas G SG2

RHEOLOGICAL BEHAVIOR OF CROSS-LINKED ELASTOMERIC POLYPEPTIDE GELS

Frederic Prochazka, Jonghwi Lee, Christopher W. Macosko, and Dan W. Urry

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

Elastic protein-based polymers are designed analogues of repeating sequences found in the mammalian protein, elastin. They have been successfully synthesized using recombinant DNA technology and expression in transformed *E. coli*. These polymers are commonly composed mainly of hydrophobic amino acids, such as valine (V), isoleucine (I) and phenylalanine (F) in combination with neutral amino acids without functional side chains, such as glycine (G) and proline (P). Thus, hydrophobic hydration has been considered the major interaction with which to understand their transitional behavior in water. All polymers with the correct balance of apolar and polar moieties, including water soluble proteins and protein-based polymers, increase order by a hydrophobic folding and assembly transition as the temperature is raised above a critical onset temperature, designated here as T_t . This interesting capability can provide a unique opportunity for a new class of devices [J. Phys. Chem. B, 101, 11007, 1997]. Here we report initial characterizations for the purpose of facilitating the materials development of this class of biopolymers. To address mechanical strength, a series of protein-based polymers have been cross-linked using different doses of gamma irradiation. Small strain dynamic mechanical analysis was used to investigate the relationship between structure and properties in these gels. First of all, the cross-linked polymers clearly show the same transition temperature as concentrations of 40 mg/ml and higher before cross-linking. The elastic modulus noticeably increases with an increase in the radiation dose. Below T_t , the polymers have the normal behavior of hydrogels with a plateau modulus and a weak G'' . Analyzing this data by means of rubber elasticity theory, the cross-link density has been estimated. Above T_t , the behavior is strongly modified and both G' and G'' exhibit a significant frequency dependence.

Monday 10:35 Hall of Ideas G SG3

DIFFUSING WAVE SPECTROSCOPY OF CYTOSKELETAL POLYMER GELS

Denis Wirtz¹, Andre F. Palmer¹, and Jingyuan Xu²

¹Chemical Engineering Department, Johns Hopkins University, Baltimore, MD 21218; ²USDA, Peoria, IL

We use diffusing wave spectroscopy (DWS) to monitor the thermal fluctuations of microspheres embedded in filamentous-protein networks extracted from the cytoplasm of cells. From the DWS measurements of the displacements of probes, we extract the frequency-dependent viscoelastic moduli over an extended range of frequencies. We use filamentous actin (F-actin), microtubules and keratin filaments as macroscopic models of semiflexible, rigid, and flexible polymers, respectively. These new measurements allow us to gain new insight into the short-time dynamics of polymers in semidilute solutions.

Monday 11:00 Hall of Ideas G SG4

STRUCTURE VS. RHEOLOGICAL PROPERTIES IN THERMOREVERSIBLE GELS FROM POLYMERS AND BIOPOLYMERS

J. M. Guenet

CNRS UPR 9069, BP2488, Institut de Chimie des Surfaces et Interfaces, F-68057 Mulhouse, France

Among the rheological studies of thermoreversible gel systems, the determination of the relation between the elastic modulus and the concentration is usually easy to perform, and its outcomes can be discussed on the basis of theories derived from molecular models. Besides, electron microscopy and scattering techniques provide information as to the actual molecular structure so that the validity of the theoretical approach can be tested. In this talk we shall

present a series of results obtained on various thermoreversible gels obtained from synthetic polymers (isotactic polystyrene [1,2], PMMAs [3,4]) and from biopolymers (agarose and k-carraghenans [5,6]). The gels under consideration are fibrillar, and it will be shown that the use of Jones and Marques theory derived for rigid systems [7] is quite suitable for casting some light on the structure-property relations. This theory relates the elastic properties to the fractal dimension of the objects connecting at the physical junctions. Discrepancy between models derived from theory and those deduced from scattering experiments will be also presented and tentatively accounted for.

- 1) Guenet, J.M. ; McKenna, G.B. J. Polym. Sci. Polym. Phys. Ed. 24, 2499, 1986.
- 2) McKenna, G.B.; Guenet, J.M. J. Polym. Sci. Polym. Phys. Ed. 26, 267, 1988.
- 3) Fazel, N.; Fazel, Z.; Guenet, J.M. J. Phys. II 2 1745 1992 Fazel, N.; Brûlet, A.; Guenet, J.M. Macromolecules 27, 3836, 1994.
- 4) Saiani, A. Thesis Université Louis Pasteur, Strasbourg, 1997.
- 5) Ramzi, M.; Rochas, C.; Guenet J.-M. Macromolecules, 1998, 31, 6106.
- 6) Rochas, C. and Lahaye M.; 1989 Carbohydr. Polym. 10, 289.
- 7) Jones, J.L. and Marquès, C.M. 1990 J. Phys. (les Ulis) 51, 1113.

Monday 11:25 Hall of Ideas G

SG5

SCALING BEHAVIOR: EFFECT OF PRECURSOR CONCENTRATION AND PRECURSOR MOLECULAR WEIGHT ON THE MODULUS AND SWELLING OF ENDLINKED NETWORKS

Kavitha Sivasailam and Claude Cohen

School of Chemical Engineering, Cornell University, Ithaca, NY 14850

Endlinked poly(dimethylsiloxane) (PDMS) networks prepared under optimal conditions and containing a minimal number of pendent defects were prepared in the presence of a theta solvent. Unreactive tri-methyl terminated PDMS of the same molecular weight distribution as the PDMS precursors was chosen as the theta solvent. Four precursor molecular weights ranging from 9900 to 101700 g/mole were studied. The dependences of the initial modulus after cure, the dry modulus after solvent extraction and the degree of equilibrium swelling on precursor preparation concentration were compared to recent scaling law predictions. The scaling exponents were found to be strong functions of the molecular weight of the precursor chains and were found to approach the theoretical predictions as the molecular weight of the precursors increased.

**Symposium IR
Industrial Rheology**

Organizers: Chris E. Scott, Roger A. Ross and William H. Tuminello

Monday 9:45 Hall of Ideas H

IR1

MODELING OF FLOW-INDUCED CRYSTALLIZATION (FIC) IN HIGH-SPEED MELT SPINNING

Antonios K. Doufas and Anthony J. McHugh

Chemical Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801

High-speed melt spinning is an industrial process of great commercial importance, since it leads to the production of as-spun fibers with improved -by many orders of magnitude- mechanical properties. The dramatic change in mechanical properties is attributed to structure formation associated with FIC occurring along the spinline. The discussion of a model that self-consistently couples the stress, velocity and temperature fields of the fiber with crystallization is the focus of this presentation. The model includes the effects of viscoelasticity, non-isothermal conditions, air drag, inertia, surface tension and gravity. A two-phase constitutive/molecular model is used based on

Monday Morning

the FIC formulation developed by Doufas et al. [1]. The amorphous phase is simulated as a modified Giesekus fluid and the semi-crystalline phase is approximated as a suspension of rigid rods that grow and orient in flow. The two phases are coupled with crystallinity through the stress and the momentum balance.

Our model is robust over a wide range of realistic processing conditions and model parameters. All of its predictions are in excellent agreement with experimental observations both qualitatively and quantitatively. Model predictions such as the neck-like deformation and strain-softening behavior will be demonstrated. The effects of processing conditions, such as the take-up speed and mass throughput, on the process dynamics will be discussed. Air drag is shown to play a critical role and cannot be neglected. Comparisons of our model with conventional melt spinning models will be made. It will be shown that non-linear viscoelasticity coupled with FIC are the main mechanisms for the formation of a stable neck and that the freeze point arises naturally in our model as a result of crystallization. Necking can be predicted, if and only if the rheological response of the semi-crystalline phase is considered appropriately, as done in our formulation.

[1] A.K. Doufas, I.S. Dairanieh, A.J. McHugh, *J. Rheol.* 43, 85-109 (1999).

Monday 10:10 Hall of Ideas H

IR2

ANALYSIS OF NONISOTHERMAL MELT SPINNING WITH ONGOING CRYSTALLIZATION

Junsuo Sun¹, S. Subbiah¹, and Jean-Marie Marchal²

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In industrial melt spinning processes, there is a leading-order radial temperature variation. For viscoelastic flow, the radially nonuniform temperature causes, through thermal history, the radially nonuniform stress, which results in nonuniform crystallinity and fiber microstructure and is of practical importance. Therefore, we use a 2-D approach to study the nonisothermal melt spinning with ongoing crystallization.

In the mathematical formulation, the phase transition (from amorphous phase to crystallized phase) is described by Nakamura's model. The crystallization rate, which is a function of both temperature and molecular orientation factor, is evaluated with the equation proposed by Ziabicki [A. Ziabicki, *Fundamentals of Fiber Formation* (Wiley, New York 1976)]. The constitutive equation used is the nonisothermal PTT model, which is converted from its isothermal form with time-temperature superposition.

The above formulation is implemented in POLYFLOW. The melt spinning of Nylon 6 [J.H. Bheda and J.E. Spruiell, *J. Appl. Polym. Sci.* 39, 447-463 (1990)] is used as a benchmark to verify the simulation. Then, the spinning dynamics and crystallization are investigated. Numerical results show that crystallinity, which depends on both crystallization rate and residence time, may not increase with increasing take-up speed, and the radially nonuniform stress and crystallinity may have a strong influence on spun fiber properties (such as birefringence) under high cooling rate conditions.

Monday 10:35 Hall of Ideas H

IR3

EDGE EFFECTS IN FILM CASTING OF POLYMER MELTS

Kathleen Canning and Albert Co

Department of Chemical Engineering, University of Maine, Orono, ME 04469-5737

In most analyses of the film casting process, edge effects such as necking in and edge beading are usually neglected. In this work, we investigated the significance of these effects and their dependence on the processing conditions and the rheological properties of the melts. Two linear low-density polyethylene (LLDPE) melts and a low-density polyethylene (LDPE) melt were considered. The rheological behaviors of these melts were characterized under shear and elongational flows. Film casting experiments were conducted for these melts at various extrusion rates and draw ratios.

Streamlines from the die exit to the chill roll and velocity profiles along the length and across the width of the molten film were obtained from video images of tracers at different positions between the film edge and the centerline. The streamlines were found to be straight in the central region of the film but curved inward near the film edge. As draw ratio was increased, some curved streamlines straightened and the extent of the central region

expanded. Molten film tension was also measured with a non-contacting air nozzle system at various locations across the width. The variations of the measured tension across the width were related to the behaviors of the streamlines. The neck-in profiles obtained from video images showed considerable differences between the LLDPE and LDPE melts. The thickness profile of the solidified film and the edge bead thickness profile were also examined.

Monday 11:00 Hall of Ideas H IR4

ANALYSIS OF BOWING PHENOMENA AT TENTER PROCESS OF BIAXIALLY ORIENTED POLYPROPYLENE FILM

Soo Wan Kim¹, Moo Hyun Kwon², Byoung Kyu Song¹, Seung Man Yang², and O Ok Park²

¹Daeduk R&D Center, Daelim Industrial Co., Ltd., Taejon 305-405, Republic of Korea; ²Center for Advanced Functional Polymers & Dept.Chem.Eng., Korea Advanced Institute of Science and Technology, Taejon 305-701, Republic of Korea

In order to understand the bowing phenomena in tentering process of biaxially oriented Polypropylene film, the mathematical model has been developed by considering overall continuity equation and relevant momentum equations. Model has been solved analytically by employing lubrication approximation for isothermal, newtonian fluid with variant density with external deformation. Both velocity profiles in the tenter process and stress profiles can be calculated. Geometrical bowing is strongly depending upon the degree of volume change during extensional deformation. Theoretical prediction is compared with experimental birefringence data obtained from Daelim Chonju BOPP plant with two types of PP resins and two different operation conditions to give us an excellent agreement. It can be said that this model is applicable to other oriented film process.

Monday 11:25 Hall of Ideas H IR5

ON SLIP EFFECTS IN FREE COATING OF NON-NEWTONIAN FLUIDS

Kayvan Sadeghy and Mohammad Ghasemian-Amiri

Mechanical Engineering, University of Tehran, Tehran, Iran

Liquid entrainment onto a belt withdrawn vertically from a liquid bath is a phenomenon of many industrial applications. Examples are: the application of coating onto conveyor belts, wall papers, adhesives tapes, etc. Of interest in such applications is the final film thickness which is known to be a function of withdrawal speed and fluid's properties. Film thickness predictions based on Newtonian analysis often fail severely because virtually all coating formulations are non-Newtonian. The use of more realistic rheological models such as Bingham plastic, power-law and Ellis has also proven to be of little use. The discrepancy between theoretical predictions and experimental observations has recently been attributed to wall slip by Dutta and Mashelkar (1982). By ignoring inertia terms in the governing equations, they showed that slip may indeed correct the theoretical predictions for film thickness. Their analysis, however, shows that very high slip velocities are required before any significant improvement in theory could be achieved. In this work we show that by keeping inertia terms in the governing equations, it is possible to significantly improve film thickness prediction for a power-law fluid (both quantitatively and qualitatively) at much smaller more realistic slip velocities. This is done by reducing the governing equations to a single third-order nonlinear ordinary differential with slip velocity ratio as an adjusting parameter. It is shown that under similar conditions, slip ratios as small as 0.2 (in contrast to 0.9 in Dutta and Mashelkar analysis) are sufficient to make theory consistent with experiment.

Symposium FM Non-Newtonian Fluid Mechanics

Organizers: Michael D. Graham, Radhakrishna Sureshkumar and Lars Genieser

Monday 9:45 Hall of Ideas I FM1
RHEOLOGICAL AND STRUCTURAL STUDIES OF ALKANES CONFINED BETWEEN METAL AND METAL OXIDE SURFACES

Rajesh Khare and David Rigby

Materials Science, Molecular Simulations Inc., San Diego, CA 92121

Rheological and structural properties of polymers near surfaces play an important role in many industrial applications such as polymer processing and lubrication. The most commonly employed boundary condition in continuum mechanics treatment of these processes - that of stick or no slip at the interface between fluid and confining surface - has been called into question by recent experimental evidence. These slip effects are believed to give rise to problems such as surface roughness of finished product in polymer processing operations. With this motivation, we have used molecular dynamics simulation to investigate rheological and structural properties of alkanes confined to thin films. Simulations provide us the unique ability to systematically investigate the cause-effect relationship between polymer chain architecture (e.g. branching) as well as the fluid-surface interactions and the observed rheological behavior.

Most of the previous work on simulation of shear flow of confined fluids was carried out using idealized systems such as bead spring chains confined between lattice walls. In this work, we use atomistically detailed models for both the fluid and the surface. The confined fluid consists of linear and branched alkanes and the surfaces consist of realistic metal (e.g. iron) and metal oxide (e.g. iron oxide) surfaces. We investigate fluid behavior under conditions of both equilibrium (no flow) and shear flow. The alkanes are shown to form layers next to the confining metal surfaces under all conditions investigated. It is shown that even when confined to molecularly thin films, rheological behavior (velocity and temperature profiles) of alkanes is consistent with continuum mechanics predictions. In contrast with previous simulations on idealized systems, confined alkane fluids do not exhibit any wall slip effects at the alkane-metal interface.

Monday 10:10 Hall of Ideas I FM2
FLOW-INDUCED ORIENTATION OF A FLEXIBLE-CHAIN POLYMER MONOLAYER

David J. Olson¹, Gerald G. Fuller¹, Joke Hagting², and Arend Jan Schouten²

¹Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025;

²Laboratory of Polymer Chemistry, University of Groningen, Groningen 9747, The Netherlands

Langmuir monolayers of flexible-chain polymers have been shown to exhibit nonlinear rheological behavior ranging from non-Newtonian viscosities to the presence of large vortices in contraction flow. The diminished vortex size in expansion flow suggests that a positive normal stress difference, caused by the orientation of the polymer chains in the flow direction, is present in these monolayers¹. In recent work, Hagting *et al.* observed in-plane orientation of a flexible-chain polymer monolayer transferred to a solid substrate via Langmuir-Blodgett deposition, suggesting that the dipping flow orients the polymer chains during deposition². This is the first observation of flow-induced orientation in a non-rodlike polymer monolayer. In this work, we monitor the anisotropy of the flexible-chain polymer monolayer subject to Couette flow employing standard polarimetry techniques. By quantitatively measuring the degree of orientation in the flexible-chain system, we are able to confirm the presence of a normal stress difference in the polymer monolayer, the first measurement of its kind.

¹D.J. Olson and G.G. Fuller, *J. Non-Newtonian Fluid Mech.*, in press.

²J.G. Hagting, *et al.*, *Thin Solid Films*, 329 (1998) 65-68.

Monday 10:35 Hall of Ideas I

FM3

AN EXPERIMENTAL AND SIMULATION STUDY OF THE BEHAVIOR OF SINGLE POLYMER CHAINS IN EXPONENTIAL AND LINEARLY-RAMPED SHEAR FLOWS**Thomas Kwan and Eric Shaqfeh**

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

We investigate the behavior of single chain polymers in fast transient shear flows as a way of studying polymer extensional characteristics. In particular, we focus on two flows, the exponential shear and the linearly-ramped shear, and we perform both large-scale Brownian dynamics simulations, flow birefringence and mechanical rheometry experiments. In the simulations, we use freely-draining, flexible bead-rod chains as the model for our polymer. The prescribed flow field is applied and then subsequently "turned off" while the stress and birefringence of the chain are calculated throughout the simulation. We find that for finite strains the chain unravels significantly, similar to uniaxial extensional flow, and furthermore, it undergoes an initial stress and index of refraction relaxation that is much faster than a single exponential decay upon cessation of flow. In addition, when the first normal stress difference is plotted against the corresponding component of the index of refraction tensor ($n_{11} - n_{22}$) over a full startup-relaxation cycle, we observe a hysteresis effect that was also previously found in uniaxial extensional flow. The shear component also exhibits hysteresis but in the opposite direction, i.e. when plotted over a full cycle, the branches for the startup and relaxation are opposite to that for the $11-22$ component. To experimentally investigate the effects of transient unsteady shear flows on dilute polymer solutions, we employ both mechanical rheometry and flow birefringence. Polyisobutylene and polystyrene based Boger fluids are prepared and their viscoelastic properties are characterized on a traditional rheometer. Imposing the same kinds of shear flows, we indeed see a very dramatic stress increase during startup and a highly non-linear relaxation. Detailed comparisons between the individual components of the stress and index of refraction are then made and compared to simulation results.

Monday 11:00 Hall of Ideas I

FM4

MODELING FLOWS OF DILUTE POLYMERIC SOLUTIONS IN COMPLEX FLOWS WITH DUMBBELL BASED MOLECULAR MODELS**Madan Somasi and Bamin Khomami**

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

Modeling dilute polymeric solutions in complex flows has attracted considerable attention in recent years. Researchers (Yang and Khomami, JNNFM, in press; Li et al., JNNFM, in press) have used macroscopic constitutive equations based on elastic dumbbell models to perform simulations. Although qualitatively representative, the predictions by these models have not been able to quantitatively describe the experimental measurements. One of the main reasons put forward for this shortcoming is the closure approximation used to derive these constitutive equations. To put this issue to rest, we have performed simulations using models without closures, like the single and multimode FENE models. Since there is no corresponding macroscopic equation for the FENE model, we have used Brownian Dynamics Simulations in conjunction with adaptive Finite Element techniques to investigate the effect of the 'closure' approximation on the predictions. Our technique is based on the concept of 'Brownian Configuration Fields' recently introduced by van den Brule et al. (JNNFM, 70, 79-101). Simulations have been performed for an axisymmetric stagnation flow and for a sphere falling in a tube. On comparison with experiments however, we see that the discrepancies are not solely due to the closure approximation. Incorporating factors like viscous stress and conformation dependent drag into the model also does not seem to bridge the gap between experiments and simulations. It is clear that other factors such as the accuracy of the entropic spring law and intermolecular interactions need to be considered. The next step therefore, is to consider bead-spring chain models, which can capture a better picture of the various conformations of a polymer molecule in a complex flow. We have conducted simulations with various chain models and the predictive capabilities of these models shall be presented in detail.

Monday 11:25 Hall of Ideas I

FM5

LAGRANGIAN PARTICLE METHODS FOR COMPUTING TRANSIENT VISCOELASTIC FLOWS**Peter Wapperom, Xavier Gallez, Pierre Halin, Roland Keunings, and Vincent Legat**

CESAME, Universite catholique de Louvain, Louvain-la-Neuve B-1348, Belgium

We discuss the development of Lagrangian particle methods for the simulation of transient viscoelastic flows in 2d geometries, using either a constitutive equation or a kinetic theory model. The starting point is the Lagrangian Particle Method (LPM) proposed in [1]. In LPM, the velocity and pressure fields are calculated at each time step by solving the conservation equations with a classical finite element method. The polymer contribution to the stress is computed at a discrete number of Lagrangian particles that are convected along the fluid trajectories. Obviously, if a highly-graded mesh is used, LPM needs a rather large total number of Lagrangian particles in order to ensure that enough particles are located at all time steps in the smallest elements of the mesh. LPM has been improved along two distinct lines, yielding the Adaptive Lagrangian Particle Method (ALPM, [2]), and the Backward Lagrangian Particle Method (BLPM). The main idea behind ALPM is to smoothly and continuously adapt the number and distribution of Lagrangian particles during the simulation. On the other hand, BLPM uses in each element an a priori specified distribution of a small amount of particles. In the present communication, we briefly describe the main features of ALPM and BLPM, and compare their numerical performance in the context of transient flows of dilute polymer solutions described by the kinetic theory of FENE dumbbells [3]. The flow geometries are a large-eccentricity journal bearing, and a 4:1 abrupt contraction.

[1] P. Halin, G. Lielens, R. Keunings, V. Legat, *J. Non-Newtonian Fluid Mech.* 79 (1998) 387-403. [2] X. Gallez, P. Halin, G. Lielens, R. Keunings, V. Legat, *The Adaptive Lagrangian Particle Method for Macroscopic and Micro-Macro Viscoelastic Flow Computations*, *Comp. Meth. in Appl. Mech. and Eng.*, in press (1999). [3] G. Lielens, R. Keunings, V. Legat, *The FENE-L and FENE-LS Closure Approximations to the Kinetic Theory of Finitely Extensible Dumbbells*, submitted to *J. Non-Newt. Fluid Mech.* (1999)

Symposium LC**Liquid Crystals and Liquid Crystalline Polymers**

Organizers: Julie Kornfield, Jan W. van Egmond and Jimmy Jingtao Feng

Monday 9:45 Hall of Ideas J

LC1

IN-SITU X-RAY SCATTERING INVESTIGATION OF THE EVOLUTION OF MOLECULAR ORIENTATION DURING TRANSIENT FLOWS OF MODEL THERMOTROPIC LIQUID CRYSTALLINE POLYMERS**Victor M. Ugaz¹, Wesley R. Burghardt¹, Julia A. Kornfield², and Weijun Zhou²**¹Department of Chemical Engineering, Northwestern University, Evanston, IL 60208; ²Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

Liquid crystalline polymers (LCPs) are the object of considerable commercial interest because they can potentially be used to produce lightweight materials with exceptional mechanical properties. These properties are primarily due to the highly anisotropic molecular structure characteristic of LCPs, and the resulting complex interplay between molecular orientation and applied flow fields. Unfortunately, experimental difficulties have limited the amount of available data probing the evolution of fluid structure under flow in melt processable thermotropic LCPs, and as a result their behavior remains rather poorly understood. In this study, we use in-situ x-ray scattering techniques to probe the evolution of molecular orientation during transient shear flows in two different model thermotropic LCPs. These materials, a thermotropic polyester and polyether respectively, incorporate molecular architectures specifically designed to provide a stable nematic phase over a wide temperature range. We present a detailed investigation of structural evolution during shear flow in the nematic phase, focusing on measurements of molecular orientation in the transient periods during shear flow inception and reversal. When compared with corresponding rheological data, we find that the shear stress response to these transient flows generally correlates well with the x-

ray data, while the first normal stress difference evolves somewhat differently. The absence of large scale oscillatory behavior in the transient evolution of molecular orientation and stress suggests that these materials exhibit flow aligning behavior. This hypothesis is supported by comparison with an adaptation of the Ericksen transversely isotropic fluid model and the Larson-Doi model, both of which account for the polydomain texture characteristic of LCP materials. Finally, the transient flow predictions of these two models are compared, and the discrepancies between them are explored.

Monday 10:10 Hall of Ideas J

LC2

SHEAR ORIENTATION AND RHEOLOGY OF A MAIN-CHAIN THERMOTROPIC LCP: FLOW-ALIGNMENT AND ORIENTATIONAL FLIPPING IN STEADY AND OSCILLATORY SHEAR

Weijun Zhou¹, Julia A. Kornfield¹, Victor M. Ugaz², Nitin Vaish², and Wesley R. Burghardt²

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Steady and oscillatory shear behavior of a model thermotropic main-chain liquid crystalline polymer (DHMS-7,9) has been studied using *in situ* X-ray scattering and rheology. DHMS-7,9 shows a wide liquid crystalline temperature range (100°C): a nematic phase over most of this range; and an intermediate mesophase ("x-phase") at the low temperature end (between nematic and crystalline phase). In the nematic phase, both steady and oscillatory shear produce strong alignment in the flow direction ("parallel") with little dependence on shear rate or applied frequency, consistent with flow-aligning character directly confirmed by flow-conoscopy studies on a homogeneous monodomain sample. In the x-phase, a predominantly parallel orientation is induced at high shear rate or oscillatory frequency, while alignment along the vorticity direction ("perpendicular") was observed at low shear rate or frequency. This orientation flips between perpendicular and parallel in response to either a step change of temperature between the nematic and x-phase or a step change of shear rate or frequency between two orientation regimes in the x-phase. The relationship between rheology and shear orientation will be discussed as well as a comparison of orientation development in steady shear and oscillatory shear.

Monday 10:35 Hall of Ideas J

LC3

DYNAMICS OF SHEAR ALIGNING OF NEMATIC LIQUID CRYSTAL MONODOMAINS

Brett L. Van Horn¹, David Boudreau², and H. Henning Winter¹

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²Chemistry, University of Massachusetts - Amherst, Amherst, MA

The equations of linear and angular momentum for nematic liquid crystals have been described with Ericksen's transversely isotropic fluid (TIF) model and solved for start-up of shear flow at constant rate and varying initial alignment conditions. An analytical solution for the rotation provides predictions of the nematic director which closely agree with experimental results, supporting the validity of Ericksen's TIF model. The solution is limited to flows where the effects of director gradients are negligible. Experiments with polymeric systems are in progress.

Monday 11:00 Hall of Ideas J

LC4

FLOW-INDUCED ISOTROPIC-NEMATIC TRANSITION IN THERMOTROPIC POLYMERS OF VARYING SPACER LENGTH

Patrick T. Mather¹, Hong G. Jeon², Dong-Ok Kim³, and C. D. Han³

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Polymer Engineering, University of Akron, Akron, OH 44325

Advances in the understanding of thermotropic polymer rheology can be achieved through the study of well defined polymers using both mechanical and morphological examinations. In this presentation we report the dependence of the flow-induced isotropic-to-nematic phase transition phenomenon on the spacer length of the model thermotropic polymers, PSHQ_n, where n represents the spacer length. Using optical microrheology methods and mechanical

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rheological methods, we have measured the critical shear rate required for the onset of nematic formation for temperatures above the quiescent isotropic-nematic transition temperature. In particular, flow-induced birefringence is measured for materials of varying spacer length as functions of both temperature and shear rate. As shear rate increases for a fixed temperature higher than the quiescent isotropic-nematic transition temperature, a clear transition from low-level birefringence (0.0 - 0.005) to nematic-level birefringence (> 0.01) is observed for most PSHQn materials. Interestingly, the critical shear rates for nematic-phase formation are significantly larger for even-n materials compared to odd-n materials. We will discuss the origin of this rheological odd-even effect and present a comparison of a range of PSHQn response in the form of a dimensionless nonequilibrium phase diagram.

Monday 11:25 Hall of Ideas J

LC5

STUDY OF RHEOLOGICAL TRANSITION BY PHOTO-INDUCED ISOMERIZATION ON LANGMUIR MONOLAYERS OF AZOBENZENE DERIVATIVES

Kang Sub Yim, Gerald G. Fuller, and Curtis W. Frank

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Azobenzene-containing materials are receiving increasing attention because of their special properties and their potential applications. They can be liquid crystalline, have nonlinear optical properties, and show light-induced reversible transitions from the trans form to cis form upon irradiation with UV or visible light. This transition is observed with very well ordered phase structure on two-dimensional system. The purpose of this paper is to study rheological transition induced by the conformational change on Langmuir monolayers. UV absorption spectroscopy is used to determine molecular orientation on 4-Octyl-4'-(3-carboxytrimethyleneoxy)-azobenzene (8A3) monolayer. Interfacial stress rheometer is used to measure the rheological properties. A well-defined extensional flow is imposed in the monolayer to study the dynamics of flow-induced anisotropy. In trans form, the first order phase transition between L2 and L2' is observed by isotherm study, which is also found on aliphatic fatty acid monolayers. The trans phase (L2') at the high surface pressure shows non-Newtonian behavior such as shear-thinning and liquid crystalline anisotropy. On the other hand, cis form shows Newtonian interface and no anisotropy. These thermodynamical and rheological transitions are explained by molecular structural model.

Monday Afternoon

Symposium SG

Viscoelasticity of Synthetic and Biological Polymer Solutions and Gels

Organizers: Ralph H. Colby, Donald J. Plazek and Guy C. Berry

Monday 1:30 Hall of Ideas G

SG6

NETWORK STRUCTURE DEPENDENCE OF FREE VOLUME ON CHAIN ENDS

Jeffry J. Fedderly¹, Gilbert F. Lee¹, John D. Lee¹, Bruce Hartmann¹, Karel Dusek², and Miroslava Smrckova²

¹Naval Surface Warfare Center, West Bethesda, MD 20817-5700; ²Institute of Macromolecular Chemistry, Prague, Czech Republic

It was pointed out by Ferry (1) that the free volume fraction is linearly dependent on the number of chain ends in a polymer as a result of the increase in free volume associated with chain ends. This observation was based on data as a function of reciprocal molecular weight, which is proportional to the number of chain ends. In this paper, the variation in number of chain ends is achieved differently. We synthesized a series of polyurethanes using blends of monofunctional, difunctional, and trifunctional poly(propylene oxides) reacted with 4,4'-diphenylmethane diisocyanate (2). Each functional component had the same nominal equivalent weight. Thus, regardless of blend ratio, the polymers all had the same urethane content, aromatic content, and propylene oxide content. They differed only in their network structures. Polymers with trifunctional and monofunctional polyols have significantly more chain ends than do linear polymers formed from purely difunctional polyols. The dynamic mechanical properties of these polymers were measured and the WLF constants determined. From these values, the free volume fraction at the glass transition was obtained and correlated with the number of chain ends, calculated both from computer simulations using the theory of branching processes and from the method of additive properties. A comparison was also made with the results obtained from variations with molecular weight.

1. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York, 1980.

2. J. J. Fedderly, G. F. Lee, J. D. Lee, B. Hartmann, K. Dusek, J. Somvarsky, and M. Smrckova, *Polym. Sym.*, submitted for publication.

Supported by NATO Collaborative Research Grant CRG 970041, the CDNSWC In-house Laboratory Independent Research Program sponsored by the Office of Naval Research, and by Grant Agency of the Academy of Sciences of the Czech Republic, Grant No. A4050808.

Monday 1:55 Hall of Ideas G

SG7

POLYMER SOLUTIONS AND GELS IN NEMATIC SOLVENTS

Julia A. Kornfield¹, Michael D. Kempe¹, Shin-Tson Wu², and Christopher K. Ober³

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Liquid crystalline (LC) materials are commonly used in electro-optic devices that depend on controlling their orientation and optical uniformity. The alignment and mechanical stability of a LC could be improved through the use of polymers that are homogeneously dissolved throughout the volume of the device creating a nematic gel. Addition of even a small amount polymer greatly increases the viscosity coefficients of a nematic solution. Since the ability of a liquid crystal to switch is adversely affected by a high viscosity, a dilute gel must be made requiring a

Monday Afternoon

very large molecular weight polymer. Therefore we are interested in synthetic strategies to produce well-defined SGLCPs that are long relative to their entanglement molecular weight (Me approx. 300,000 g/mol). Extending polymer analogous chemistries to produce SGLCPs of a few million g/mol, we can prepare polymers with narrow distributions of chain length starting from anionically synthesized prepolymers (e.g. 1,2-polybutadiene). The rheology and thermodynamics of these materials in the melt and when solvated by small-molecule liquid crystals are studied to determine their effects on phase transitions and switching speed.

Monday 2:20 Hall of Ideas G SG8

SOLVENT AND ION EFFECTS ON THE GELATION OF KAPPA-CARRAGEENAN

Srividya Ramakrishnan and Robert K. Prud'homme

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Carrageenans are negatively charged biopolymers that undergo coil to helix transitions upon cooling and form gels through specific interactions of the helices with metal ions. The rheology and conformational helix transition of carrageenan in aqueous solutions of glycerol at low water activity is studied. Gelation occurs through helix aggregation in water, but in glycerol, the lower solubility of carrageenan results in a more random network. The binding of ions to the carrageenan helix is studied through NMR and dialysis experiments. The effect of both specific and non-specific ions on the gelation is also investigated.

Monday 2:45 Hall of Ideas G SG9

RHEOLOGY OF F-ACTIN SOLUTIONS DETERMINED FROM TRACER MOTION

Thomas G. Mason¹, Thomas Gisler², and David A. Weitz³

¹Corporate Research, Exxon Research and Eng. Co., Annandale, NJ 08801; ²Physics Dept., University of Konstanz, Konstanz 78457, Germany; ³Department of Physics, University of Pennsylvania, Philadelphia, PA 19104

We report measurements of the frequency-dependent complex shear modulus of semidilute F-actin solutions based on optical observations of the thermally-excited motion of monodisperse tracer microspheres. Because the tracer spheres cause incident laser light to be strongly scattered, we can determine the average tracer motion using the formalism of diffusing wave spectroscopy (DWS). For actin concentrations near 1 mg/ml and for a range of microsphere sizes around one micron, we find that the complex modulus exhibits a dominant low frequency plateau modulus and a high frequency rise with the loss modulus dominating above a crossover frequency. Over a limited range of frequencies well above the crossover frequency, the magnitude of the complex modulus appears to scale as a power law with an average exponent of 3/4. By rescaling the complex modulus with the plateau storage modulus and the frequency by the crossover frequency, we are able to obtain a master curve describing the characteristic rheological behavior of F-actin solutions.

Monday 3:35 Hall of Ideas G SG10

DYNAMIC LIGHT SCATTERING AND DYNAMIC VISCOELASTICITY OF POLY(VINYL ALCOHOL) IN AQUEOUS SOLUTIONS: TEMPERATURE EFFECT

Norio Nemoto

Molecular and Material Sciences, Kyushu University, Fukuoka, Fukuoka 812-8581, Japan

Steady viscosity, dynamic viscoelasticity(DVE), and static(SLS) and dynamic(DLS) light scattering measurements were made to study effects of temperature, T, on association behaviors of poly(vinyl alcohol) (PVA) with weight-average degree of polymerization DPW = 350 in aqueous borax solution at a constant weight ratio of PVA/SB=2/1. Intrinsic viscosity, $[\eta]$, monotonically decreased by 23% with raising T from 10 to 65°C. At low T, enhancement in viscosity was observed with increasing polymer concentration, C, due to formation of viscoelastic network with the didiol complex as temporal cross-links, and the time-temperature superposition principle was found to be applicable for construction of the composite curve at respective C. The system tended to lose its viscoelastic nature with raising the temperature toward to viscous solution owing to a decrease in the number of the didiol complexes as well as the shrinkage of the PVA chains. We found from a analysis of DVE and DLS data that a clear boundary between viscoelastic behaviors and viscous behaviors could be drawn in the T-C plane using the temperature T_N defined as the inflection point in the η vs. C plot for respective C.

Scattering intensity $I(q)$ was almost independent of the scattering vector q as long as the samples formed the viscoelastic network. At sufficiently high T where the samples became viscous fluid, however, a steady increase in $I(q)$ as time elapsed was observed. This anomalous time evolution of $I(q)$ was analyzed as the growth process of spherical particles in solution with a diameter $R(t)$ caused by complicated interactions between borax and PVA chains with 12% hydrophobic acetate residues. Time dependence of $R(t)$ was closely represented by the power law with an exponent $a = 0.25\text{--}0.28$.

Monday 4:00 Hall of Ideas G SG11

MOLECULAR WEIGHT EXPONENTS FOR DIFFUSION AND VISCOSITY IN ENTANGLED POLYMER SOLUTIONS AND MELTS

Timothy P. Lodge

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The current general consensus is that the zero-shear-rate viscosity of entangled polymer liquids scales with the 3.4 (± 0.2) power of molecular weight, whereas the self-diffusion coefficient exhibits exponents close to -2.0 in melts but closer to -2.4 or -2.5 in solutions. This situation presents two significant challenges to theory (whether or not the theory is based on reptation). First, it implies a fundamental difference between entangled solutions and melts, yet this difference is somehow apparent in diffusion but not in the viscosity. Second, longest chain relaxation times may be defined on the basis of either diffusion or viscosity, and the melt results imply that these longest relaxation times have different molecular weight dependences, which is physically hard to interpret. A thorough re-examination of the published self-diffusion data for seven different polymers suggests a possible resolution to both of these dilemmas. Some implications for theory will also be summarized.

Monday 4:25 Hall of Ideas G SG12

ROLE OF THE FORCE BALANCE ON THE NODES OF AN ENTANGLED NETWORK

G. Marrucci, F. Greco, and G. Ianniruberto

Dipartimento di Ingegneria Chimica, Università di Napoli, Napoli, Italy

There is a general consensus that the chains of an entangled network are subjected to an average tension of entropic origin of the order of kT/a , where a is the entanglement mesh size or 'tube' diameter. Little attention has been given so far to the fact that, at each entanglement node, these tensions must somehow fulfill a force balance. Since over the time scale of reptation the tension is a constant, it appears that the force balance couples the local orientation of the primitive chain segments participating to the entanglement. Consequences of this concept will be discussed.

Monday 4:50 Hall of Ideas G SG13

THE PACKING LENGTH INFLUENCE IN LINEAR POLYMER MELTS ON THE ENTANGLEMENT, CRITICAL AND REPTATION MOLECULAR WEIGHTS

Lewis J. Fetters

Exxon Research and Engineering Company, Annandale, NJ 08801

A primary goal of polymer physics has been to relate macromolecular structure to macroscopic properties. The development of the packing length (p) concept by Witten, Milner and Wang has proven to be of prime importance in achieving this goal. Previously we have shown that p is critical in relating polymer coil size to the entanglement molecular weight, M_e . Two other molecular weight parameters are of rheological importance; the melt viscosity, M_c marking the onset of entanglement effects and M_r the crossover to the reptation form. M_e and M_r scale with p but the exponents differ from one another and that found for M_e . Hence, the finding that M_r/M_e depends upon p demonstrates that the long-held ansatz of $2M_e \sim M_c$ for flexible chain species in the melt is incorrect. We show that, whereas $M_e \sim p^3$, $M_c \sim p^{2.34}$ and $M_r \sim p^{-1}$. Further, the observed and predicted values of M_r for two species, 1,4 polybutadiene and polyisobutylene, have been found to agree, within the uncertainties, with the projected values. Intriguingly, these relations further imply that at p of 9 to 10 Å we have a convergence of M_e , M_c and M_r . As yet, no species with such a large packing length has been completely studied rheologically. But the range is not outlandish and is clearly reachable by appropriate synthetic methods. If all of this continues to hold true, we have indeed a powerful method to predict many rheological properties of polymers from knowledge of their density and unperturbed chain dimensions.

Symposium IR Industrial Rheology

Organizers: Chris E. Scott, Roger A. Ross and William H. Tuminello

Monday 1:30 Hall of Ideas H IR6

WIRE COATING BY DRAWDOWN OF AN EXTRUDED ANNULAR MELT

Fan Ding¹, Alan J. Giacomin¹, John C. Slattery², and Aaron J. Hade¹

¹Mechanical Engineering, University of Wisconsin-Madison, Madison, WI 53706; ²Texas A&M University, College Station, TX 77843

An analytic solution for parallel tube coating wire with a highly viscous Newtonian fluid is developed. The melt flow is assumed extensional. We obtain expressions for the melt cone shape, coating thickness, contact length, contact pressure, drawing force, apparent contact angle and contact convexity. The extension to power-law and Noll simple fluids is also briefly considered. A numerical solution, which is developed independently from force balance on the melt cone, is compared with the analytic result. Angular tube coating, where the die annulus is at an acute extrusion angle to the wire is solved similarly as in the parallel case. Effects of extrusion angles are discussed.

Monday 1:55 Hall of Ideas H IR7

TIME DEPENDENT RHEOLOGY OF PAPER COATINGS

Rajan R. Iyer

Technology Center, ECC International, Sandersville, GA 31082

Coating colors are high solids mixtures of pigments, binders and additives. High solids suspensions have been shown to have shear and time dependent-shear behavior. End use sheet properties and coater runnability are critical issues in high speed coating applications. The development of suspension structure, break down under shear and the recovery of the structure in time after the shear is removed, are of interest in this paper. This paper describes the determination of the magnitude of time dependent behavior of suspensions using a Haake RS-75 controlled stress rheometer at two temperatures and the analyses of the area under the Shear Stress-Shear Rate hysteresis curves. The coating suspensions had Kaolin, ground calcium carbonate, and or precipitated calcium carbonate as well as natural and synthetic binders. Controlled stress is applied to break down structure in the coating. After the structure break down, the recovery is monitored at low deformation. Results indicate that the hysteresis loop in a up and down shear ramp is not eliminated. The recovery of the storage and the loss moduli show complex behavior. The non-precipitated calcium carbonate containing coating does not show structure break down after the 2nd or 3rd cycle of shear ramps. There seems to be a correlation between an end sheet property like opacity and the recovered storage modulus.

Monday 2:20 Hall of Ideas H IR8

RHEOLOGICAL CHARACTERIZATION AND PROCESSING OF RECYCLED POLYMERS

Ruifeng Liang and Rakesh K. Gupta

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Recycling of polymers is becoming increasingly important in order to protect the environment and minimize the use of virgin non-renewable resources. Although polymers can be recycled in many ways, material recycling back into the original application is the preferred technique. In this paper, we present our work on the rheological characterization of Polycarbonate (PC) and Acrylonitrile-Butadiene-Styrene (ABS) recovered from computer housings and other electronic applications. The rheological properties of both the recycled and virgin polymers are measured in simple shear using a Rheometrics RMS 800 Rheometer at a number of temperatures. Different compositions are also prepared using a twin screw extruder by blending recycled polymer with virgin pellets. Constitutive modelling of the rheological properties of these blends is carried out by using the Wagner integral constitutive equation. The differences in the rheological behavior of these polymers with changing composition and the applicability of the Wagner model will be reported. Their mechanical properties and processing behavior are also discussed.

Monday 2:45 Hall of Ideas H

IR9

MULTILAYER COEXTRUSION REVEALS INTERFACIAL SLIP**Rui Zhao and Christopher W. Macosko**

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

Using layer multiplication dies in coextrusion, two or more polymers can be alternatively combined into hundreds or even thousands of continuous layers(1). One of the unique features in the layer multiplication process is the large amount of well-defined interfacial area generated in such a way that the effect of rheology and interfacial properties is eliminated up to the point of layer breakup. This provides a model system to study interfacial phenomena in blending of immiscible polymers.

Some researchers have reported an anomalous lowering of viscosity in immiscible polymer blends(2). Interfacial slip has been proposed to explain these observations. De Gennes (3) and Goveas Fredrickson (4) have given theoretical predictions of interfacial slip viscosity. By measuring pressure drop in the flow of multilayers, we were able to test the interfacial slip hypothesis. Coextruded multilayers of PE/PS and PP/PS with a number of layers ranging from tens to hundreds were used. The pressure drop of the multilayers through a slit die was measured, and compared with the theoretical prediction assuming no interfacial slip. The measured value was 2 to 3 times lower than the theoretical prediction. The interfacial slip viscosity was estimated, and the value showed a reduction of 30 times, even greater than that of de Gennes' and Goveas' predictions. The apparent viscosity of multilayers were also measured on a parallel plate rheometer. Significant viscosity reduction was also observed. The effect of premade or in situ polymerized block copolymers on the rheological behavior of the multilayers will be examined.

References: 1. Schrenk, W. J. and T. Alfrey, in *Polymer Blends*, edited by D. R. Paul and S. Newman, 2,129, 1978. 2. Utracki, L. A. and M. R. Kamal, *Polymer Engineering and Science*, 22, 96, 1982. 3. de Gennes, P. G., *Physics of Polymer Surfaces and Interfaces*, Butterworth-Heinemann, Massachusetts, 55,1992. 4. Goveas, J. L. and G. H. Fredrickson, *European Physical Journal B*, 1998.

Monday 3:35 Hall of Ideas H

IR10

CROSS-CHANNEL LAYER REARRANGEMENT IN COEXTRUSION**Douglas A. Devens, Jr.**

Corporate Process Technology Center, 3M, St. Paul, MN 55144-1000

Encapsulation, or cross-channel layer rearrangement, in coextrusion is a significant problem in the industrial practice of coextrusion. In a series of papers twenty five years ago Southern and Ballman first described this problem as the tendency of a less viscous fluid to surround a more viscous fluid, although there appeared to be other important factors, possibly including elasticity. Since then several authors have used energy minimization arguments, stability arguments and explicit interfacial force balances to study this problem, though we believe previous uses of the last technique to have been flawed. In this study we generate an interfacial elastic force balance using a nonsingular perturbation technique inspired by Wineman and Pipkin's 1966 examination of free surface deformation of a weakly elastic fluid flowing down a trough. Our technique, like theirs, is applicable to creeping viscoelastic flows where inertia and capillary forces are negligible. We also require the fluids' elastic responses to be roughly similar. We then limit ourselves to study small perturbations of the interface from its original, flat character. We find that the interface shape can deform monotonically from plane, as often observed and predicted by numerical flow simulations and energy minimization theories. However, we also predict the interface can form curtate cycloids like those observed by Southern and Ballman for certain combinations of elasticity and viscosity, although we consider only second order fluids. Moreover, in a prediction similar to that proposed by Chen for interfacial stability analysis, we predict the existence of interface deformation caused solely by a difference in the elasticities of the fluids.

Monday 4:00 Hall of Ideas H IR11
SUSPENSIONS IN ELONGATIONAL FLOWS: CHARACTERIZATION OF THE FLOW BEHAVIOR AND ITS CORRELATION TO APPLICATION PROPERTIES

Norbert Willenbacher

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Elongational (converging) flows play an important role in processing and application of multi-phase systems like dispersions or emulsions and corresponding formulations like coatings or inks. The flow behavior especially of strongly interacting colloidal systems in complex flow fields can not simply be described by shear viscosity data alone. Pressure drop measurements using appropriately chosen capillary geometries and the opposing jet rheometer are well suited means to characterize the elongational flow behavior of such fluids under technically relevant conditions and can for example be correlated to the runnability of paper coating colors, the atomization and sprayability of automotive coatings, or the flow induced aggregation of suspensions during filtration or pumping. Examples are presented showing, that the opposing jet rheometer is more sensitive to changes in the elongational viscosity than entrance pressure loss measurements. On the other hand higher shear / elongation rates can be reached in capillary flow as compared to the opposing jet technique.

Monday 4:25 Hall of Ideas H IR12
IN LINE STUDY OF DROPLET DEFORMATION DURING BLENDS EXTRUSION: DROPLETS, STRINGS AND VORTICITY ALIGNMENT

Kalman B. Migler, Erik K. Hobbie, and Fang Qiao

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We present in situ measurements of a dilute polymer blend in channel flow using an optical flow cell placed at the exit of a twin screw extruder. At weak shear stress, we find mildly deformed ellipsoidal droplets whereas at moderate shear rates we find coexistence between large aspect ratio strings and ellipsoidal droplets. In the regime of low to moderate stress, depth resolved optical microscopy reveals that the deformation is a function of local shear stress. At large shear stress, the droplet breakup is suppressed; mildly deformed droplets at high capillary number are observed, in contrast to the Taylor model. Near the wall, at the highest shear stress, the droplets align in the vorticity direction. Optical light scattering provides complementary morphological information that is averaged over the channel depth and confirms the optical microscopy. We discuss these results in terms of Taylor theory and normal forces.

Monday 4:50 Hall of Ideas H IR13
RHEOLOGICAL CHARACTERIZATION OF ONE-COMPONENT EPOXY ADHESIVES FOR AUTOMOTIVE APPLICATIONS

Suzanne I. Dakin, Joseph M. Smolinski, and Charles W. Manke

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The rheological properties of several one-component epoxy adhesives have been investigated, to help understand how these properties may influence the performance of robotic dispensing processes used in automotive manufacturing. One-component epoxy adhesives are typically used to join body panels together and provide structural support. These materials consist of low molecular weight liquid epoxy resins, solid cure chemicals, fillers, plasticizers, pigments, rubber modifiers, and other additives. Their compositions typically contain at least 30 wt.% solids and their rheological behavior can be quite complicated. Linear viscoelastic properties, and viscosity and first normal stress coefficients in steady shear flow have been measured at different temperatures for several one-part epoxy adhesive formulations. To a good approximation, time-temperature superposition is successful in producing master curves over a broad range of shear rates and frequencies for all of the measured rheological properties. The viscosity curves for the different adhesives are found to be similar, reflecting the fact that these products have been formulated to meet the same nominal set of manufacturer's specifications. However the first normal stress coefficients of these materials show significant differences; some materials exhibit significant first normal stress differences, while others show no measurable response. These differences in normal stress behavior, which may have important consequences for dispensing performance, can be attributed to differences in the molecular weight

distributions of the base epoxies. Significant variations are also observed in the storage modulus (G') of different adhesive formulations. These variations are attributed to differences in the filler materials.

Symposium FM Non-Newtonian Fluid Mechanics

Organizers: Michael D. Graham, Radhakrishna Sureshkumar and Lars Genieser

Monday 1:30 Hall of Ideas I FM6

ON THE USE OF OPEN BOUNDARY CONDITION METHOD IN THE NUMERICAL SIMULATION OF NONISOTHERMAL VISCOELASTIC FLOW

Seung Joon Park and Seung Jong Lee

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Numerical simulation of nonisothermal viscoelastic flow through a 4:1 contraction die is carried out using the open boundary condition method along the outflow boundary. Upper convected Maxwell (UCM) model is used as a constitutive equation for the viscoelastic fluid and elastic viscous stress splitting (EVSS) formulation with streamline upwinding (SU) method is used to treat the convergence problem at high Weissenberg number. The validity of the open boundary condition method is tested on two meshes having different downstream lengths. In isothermal flow, the results obtained on the mesh having long downstream length using fully developed velocity boundary condition are in good agreement with those obtained on the mesh having short downstream length using the open boundary condition method. In the case of nonisothermal flow, the results obtained on both meshes using the open boundary condition method show almost the same profiles. In nonisothermal contraction flow, the velocity profile along the symmetry line shows more pronounced overshoot than in isothermal case due to the viscous heating. The shape of velocity profile at the outflow boundary is more flattened than parabolic profile in isothermal case with increasing flow rate. The level of normal and shear stresses along the downstream wall decreases in the flow direction due to the high viscous heating unlike the stresses in the isothermal flow.

Monday 1:55 Hall of Ideas I FM7

VISCO-ELASTIC ANALYSIS OF POLYMER MELTS IN COMPLEX FLOWS

Wilco Verbeeten, Arjen Bogaerds, Gerrit Peters, and Frank Baaijens

Materials Technology, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands

Numerical simulation of visco-elastic flows remains a subject of extensive investigations. For example, in regard to polymeric melt flows in industrial applications. Eventually, the objective is to perform simulations of visco-elastic flows in characteristic geometries under industrial processing conditions. This means, flows with a realistically rheological behaviour at high elasticity rates in three dimensional geometries.

A mixed low-order finite element technique, based on the *Discrete Elastic Viscous Stress Splitting / Discontinuous Galerkin* (DEVSS/DG) method, has been developed to analyse visco-elastic flows. The DEVSS/DG technique allows for efficient handling of multiple relaxation times using an implicit/explicit implementation. Especially for three dimensional calculations, this necessity becomes clear in regard to CPU time and memory requirement.

In order to evaluate the predictive capabilities of constitutive equations, results of two and three dimensional numerical simulations are compared with experimental results. In general, visco-elastic fluids are characterised in shear, and, in a lesser extent, also in elongation. The characterisation of polymer melts in complex flows, where combined shear/elongational regions occur, is investigated.

For higher Weissenberg numbers, *i.e.* higher elasticity rates, the established constitutive equations, like the Giesekus and Phan-Thien Tanner models, are unable to describe the stress related experimental observations satisfactorily. These models mostly underpredict elongation. Alteration of the parameter sets of the models does not give any improvement.

Monday Afternoon

Therefore, a new constitutive equation has been developed. This *Feta* model is based on the PTT model, where the shear viscosity is fixed to experimental data, while still allowing for flexibility in describing extensional properties. Performances of the *Feta* model in complex flows is investigated.

Monday 2:20 Hall of Ideas I

FM8

THE INFLUENCE OF THE TRANSIENT EXTENSIONAL VISCOSITY ON THE COUETTE PRESSURE CORRECTION AND THE VORTEX GROWTH DYNAMICS IN AN AXISYMMETRIC CONTRACTION-EXPANSION

Jonathan P. Rothstein and Gareth H. McKinley

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

Recent measurements and Brownian dynamics simulations of the tensile stress growth and birefringence in transient uniaxial elongation of dilute polymer solutions have revealed the existence of a 'stress-conformation' hysteresis [Doyle et al. JNNFM 1998]. In a strong stretching flow, the average configuration and resulting stress in a polymer chain are found to evolve along very different paths during stretching and relaxation. This hysteresis arises from non-equilibrium coupling between the macroscopic flow field and the fluid microstructure, providing an additional mechanism for dissipation of mechanical energy. In a complex, spatially-nonhomogeneous flow such effects may be expected to result in enhanced values of dynamical quantities such as the total pressure drop. We investigate this hysteresis in a prototypical complex flow: the motion of a viscoelastic fluid through an abrupt axisymmetric contraction-expansion. The test fluid is a well-characterized dilute polymer solution of monodisperse polystyrene dissolved in oligomeric styrene. Measurements of the total pressure drop across the orifice plate show a monotonic increase with Deborah number that can be decomposed into three distinct pressure growth regimes independent of the contraction ratio and the local curvature of the re-entrant lip. Flow visualization, LDV and DPIV measurements are employed to further characterize the flow; specifically the upstream vortex growth dynamics. Increasing the contraction ratio beyond a fluid dependent critical value results in a transition from a shear dominated regime characterized by the appearance of an elastic lip vortex near the re-entrant corner at moderate Deborah numbers to an extension dominated regime characterized by a large elastic corner vortex which fingers out towards the re-entrant corner. We show that these drastic differences in vortex growth dynamics for different contraction ratios and fluids can be related to the degree of strain hardening the fluid experiences in transient uniaxial extension.

Monday 2:45 Hall of Ideas I

FM9

EFFECTS OF LONG CHAIN BRANCHING ON THE FLOW STABILITY OF LLDPE'S

Phillip J. Doerpinghaus, Sujan E. Bin Wadud, and Donald G. Baird

Chemical Engineering, Virginia Tech, Blacksburg, VA 24061

There is still considerable debate as to the effect of a few long chain branches (i.e. less than one branch per chain) on the rheology and flow behavior of LLDPE. Here we investigate the flow stability of three LLDPE's of similar MW and MWD but with different degrees of long chain branching. Whereas there are not always distinct differences in their shear properties, there are noticeable differences in their transient extensional rheology. The melt fracture behavior of the three LLDPE's is distinctly different in that sharkskin and slip-stick fracture are evident in the unbranched polymer followed by a regime of shear rates where there is no evidence of melt fracture. On the other hand, the LLDPE's with a few long chain branches exhibit sharkskin and slip-stick fracture, but at higher shear rates it appears that fracture associated with flow in the die entry occurs. Flow birefringence is used to investigate the flow behavior of the three LLDPE's in a planar contraction. Even for samples with similar flow curves the stress fields are noticeably different. Incipient flow instability is observed in certain regions as the fringes begin to oscillate slowly with time. Initial attempts to model the flow of these materials with subtly different rheological properties in the contraction are reported.

Monday 3:35 Hall of Ideas I FM10
STUDYING EXTRUDATE SWELL OF POLYMER MELTS USING FLOW BIREFRINGENCE AND LINEAR VISCOELASTICITY

Justin R. Barone and Shi-Qing Wang

Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106

In this work we examine the effects of viscoelasticity and die stress distribution on extrudate swell behavior of linear polyethylene and polybutadiene during capillary and slit die extrusion. The stress field inside the die is elucidated using a flow birefringence technique. It is found that the stress is largest near the die exit and this contributes to the overall die swell ratio. The exit stress is reduced by using a localized fluoroelastomer coating on the die exit wall. This allows us to examine extrudate swell in terms of viscoelastic parameters. To do this, we obtain first normal stress (N_1) measurements using flow birefringence and storage and loss moduli (G' , G'') from oscillatory shear experiments. These data are used to predict extrudate swell and to include the effects of the boundary discontinuity introduced at the die exit.

Monday 4:00 Hall of Ideas I FM11
FURTHER STUDIES ON THE DEFORMATION OF A VISCOELASTIC DROP IN A POTENTIAL VORTEX

Kausik Sarkar and William R. Schowalter

Dept. of Chemical Engineering, Univ. of Illinois at Urbana-Champaign, Urbana, IL 61801

In earlier work we have shown that the kinematics of a potential vortex offers insights not available from the usual studies of viscoelastic responses in shear or elongational flows. We have been able to extend our earlier work to drops characterized by a nonlinear constitutive model, and have obtained an unanticipated resonance.

The field due to a vortex is modeled by a time-periodic linear straining flow, and simulations are performed at small non-zero Reynolds numbers using a front-tracking/finite difference model with ADI time-stepping. A discretization scheme with analytic integration was used, allowing a natural elastic/viscous stress splitting. We investigate the effects of relaxation time, surface tension, forcing frequency due to the vortex, and Reynolds number for both viscous and viscoelastic drops. The drop is found to execute a time-periodic shape oscillation with a steady value for deformation in the long-time limit. The value of the deformation displays a non-monotonic resonance behavior with variation in the frequency, the surface tension, and the relaxation time. A perturbation analysis of the unsteady Stokes problem indicates that the results are explained by analogy to a damped, forced oscillator.

Monday 4:25 Hall of Ideas I FM12
SHEAR-INDUCED RUPTURING OF A VISCOUS DROP

Yuriko Renardy, Jie Li, and Michael Renardy

Mathematics, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0123

Deformation and breakup of a viscous drop, sheared between parallel plates, are investigated numerically with a volume-of-fluid method. The scheme incorporates a semi-implicit Stokes solver to enable computations for flows at low Reynolds number and Stokes flows. When the outer fluid is also Newtonian, our simulations compare well with previous theoretical, numerical and experimental results for capillary numbers less than the critical value. In this range, the drop deforms to a steady shape. Beyond this regime, for capillary numbers larger than the critical value, the dynamic process during drop breakup is explored. When the outer fluid is a Bingham liquid, the drop also evolves to a steady state for low capillary numbers, and beyond a critical capillary number, we show the breakup process.

Monday 4:50 Hall of Ideas I FM13
MODELING VISCOELASTIC DROP DEFORMATION VIA FEM

Russell W. Hooper, Christopher W. Macosko, and Jeffrey J. Derby

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

We explore both 2D and 3D drop deformations in extensional and simple shear flows, respectively. 2D modeling consists of examining the effects of viscoelasticity on dispersed phase morphology during start-up uniaxial

extensional flow (an axisymmetric 3D flow). Specifically, the deformation of an isolated Oldroyd-B drop suspended in another Oldroyd-B fluid is tracked using a robust finite element method (FEM). Viscoelasticity is seen to affect both deformation rates and steady shapes as well as the rate and mode of retraction once the flow is removed and the drop is allowed to relax back to a spherical shape. In an effort to extend the 2D FEM to fully 3D, simple shear of Newtonian drops in another Newtonian fluid is modeled. This allows for validation by comparing with results of others employing other methods and provides a starting point for incorporating viscoelasticity into both fluid phases. The magnitude of the problem requires use of parallel supercomputers and efficient solution techniques. Progress made to date in these areas will be discussed along with preliminary results. **This work was supported in part by the U.S. Army, Army Research Laboratory, Army HPC Research Center. No official endorsement should be inferred. Additional computational support was provided by the Minnesota Supercomputer Institute.

Symposium LC **Liquid Crystals and Liquid Crystalline Polymers**

Organizers: Julie Kornfield, Jan W. van Egmond and Jimmy Jingtao Feng

Monday 1:30 Hall of Ideas J LC6

BROWNIAN DYNAMICS SIMULATIONS OF THE DOI THEORY FOR LIQUID CRYSTALLINE POLYMERS

Todd W. Bell¹, Jay D. Schieber², Juan J. de Pablo¹, and Michael D. Graham¹

¹Gore, -, MD; ²Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616

The three-dimensional Doi theory for the dynamics of rigid-rod-like polymers is solved using a novel and highly efficient Brownian dynamics simulation algorithm. A simplifying assumption employed in previous work which averages away the orientational dependence of the rotational diffusivity is avoided. Important differences from previous approximate calculations are observed in shear flows, including an apparent manifestation of chaos.

Monday 1:55 Hall of Ideas J LC7

A WAVELET-GALERKIN METHOD FOR SIMULATING THE DOI MODEL WITH ORIENTATIONAL DEPENDENT DIFFUSIVITY

Jason K. Suen, Robert A. Brown, and Robert C. Armstrong

Chemical Engineering, M.I.T., Cambridge, MA 02139

In this talk, we present simulation results for the dynamic behavior of the Doi model with orientational dependent diffusivity obtained by using a wavelet-Galerkin method. Wavelets are a class of basis functions which are defined based on translation and dilation. The specific class of Daubechies wavelets further possesses properties such as compact support and orthonormality, and they can represent exactly polynomials up to a specific order n . These properties make the Daubechies wavelets an attractive candidate for approximating the sharply peaked distribution function and the highly nonlinear integro-differential operator in the Doi model.

By using the wavelet basis function together with a novel time integration scheme and an effective iterative solver, we demonstrate h - p refinement convergence with a wavelet-Galerkin method for simulating the Doi model. Furthermore, we present, for the first time, a bifurcation diagram which captures all the dynamics of the original Doi model.

Next, we investigate the kinetic theory of a more realistic model for representing LCPs, namely, a suspension of hard ellipsoids. The new model overcomes several unrealistic assumptions in the Doi model. For example, the Doi model assumes LCPs are hard ellipsoids with infinite aspect ratio. As a result, the potential parameter, U , is essentially meaningless. In the field of molecular simulation (molecular dynamics and Monte Carlo simulations), hard ellipsoids with finite ratio, a rigid version of Gay-Berne molecules, are the standard molecular model for simulating LCP systems. Therefore, a kinetic theory for hard ellipsoid allows us to compare directly the simulation results between molecular dynamics and kinetic theory. Furthermore, it allows us to verify or to improve approximations made in the phase space kinetic theory when one derives the diffusion equation from the Liouville equation.

Monday 2:20 Hall of Ideas J LC8
**SIMULATION OF THE FLOW OF A NEMATIC POLYMER IN AN ECCENTRIC CYLINDER
 GEOMETRY USING THE DOI THEORY**

**Massimiliano Grosso¹, Pierre Halin¹, Roland Keunings¹, Vincent Legat¹, Nino Grizzuti²,
 and Pier Luca Maffettone³**

¹CESAME, Université Catholique de Louvain, Louvain-la-Neuve B-1348, Belgium; ²Dept. of
 Chemical Engineering, University of Naples, Naples, Italy; ³Material Science and Chemical
 Engineering, Politecnico di Torino, Torino 10129, Italy

The start-up flow in an eccentric cylinder geometry (journal bearing problem [1]) of a nematic rodlike polymer is studied using the Doi theory. The simulations are performed by integrating the equations of motion for the fluid flow using the Lagrangian Particle Method (LPM) [2], which combines the solution of the conservation laws with a Lagrangian computation of the liquid crystalline polymer configuration at a discrete number of flowing particles. The polymer configuration is obtained by integrating the continuity equation for the orientational distribution function with a Galerkin approach. The predictions obtained with the exact Doi theory are compared with those obtained by introducing closure approximations. Such a comparison shows that available closure approximations do have an important qualitative impact on the results.

[1]Feng J, L.G. Leal, J RHEOL 41: (6) 1317-1335 (1997)

[2] P. Halin, G. Lielens, R. Keunings, V. Legat, J. Non-Newt. Fluid Mech., Vol. 79, 387-403 (1998)

Monday 2:45 Hall of Ideas J LC9
PHASE COEXISTENCE AND PHASE SEPARATION OF THE DOI MODEL IN SHEAR FLOW
Peter D. Olmsted¹ and C-Y D. Lu²

¹Department of Physics and Astronomy, University of Leeds, Leeds LS29JT, United Kingdom;
²Department of Physics, National Central University, Chung-li, Taiwan

We analyze the behavior of a suspension of rigid rod-like particles in shear flow using a modified version of the Doi model, and construct diagrams for phase coexistence under conditions of constant imposed stress and constant imposed strain rate, among paranematic, flow-aligning nematic, and log-rolling nematic states. We calculate the effective constitutive relations that would be measured through the regime of phase separation into shear bands. We calculate phase coexistence by examining the stability of interfacial steady states and find a wide range of possible "phase" behaviors.

Monday 3:35 Hall of Ideas J LC10
A THEORY FOR FLOWING NEMATIC POLYMERS WITH ORIENTATIONAL DISTORTION
Jimmy Feng¹, Giorgia Sgalari², and Gary Leal²

¹Levich Institute, City College of New York, New York, NY 10031; ²Chemical Engineering,
 UCSB, Santa Barbara, CA 93106

Using the nonlocal nematic potential of Marrucci and Greco, we generalize the Doi theory for nematic polymers to include distortional elasticity. A nonlocal stress tensor is derived, which is consistent with the long-range order in nematic polymers. The anti-symmetric part of the stress arises from the mean-field torque on molecules as they are forced away from the preferred orientation by flow. At the weak flow limit, the theory does not reduce exactly to the Leslie-Ericksen theory because of the cumulative effect of small biaxiality inevitable in the polymer distribution function. The theory offers a platform for exploring complex flows of nematic polymers, especially the dynamics of disclinations.

Monday 4:00 Hall of Ideas J LC11

EXACT AND MODULATED LCP PATTERNS

Greg Forest¹, Qi Wang², and Hong Zhou¹

¹Mathematics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250;

²Mathematical Sciences, IUPUI, Indianapolis, IN 46202

We survey a variety of homogeneous and non-homogeneous patterns of LCPs using the flow-orientation, moment-averaged, equations of Doi-Edwards. We are interested in steady patterns that exist in pure nematics dominated by short-range (Maier-Saupe) and intermediate-range (Marrucci-Greco) potentials, their stability, and phase transitions. We then study how these phenomena persist in simple flows, and what new phenomena arise due to flow interactions. While these questions are now traditional, our full tensor analysis of orientation leads to exact patterns whose modulation are viable candidates for experimentally observed textures.

Monday 4:25 Hall of Ideas J LC12

ON PATTERNS IN FLOWS OF NONHOMOGENEOUS LCPS

Qi Wang¹, Greg Forest², and Hong Zhou²

¹Mathematical Sciences, IUPUI, Indianapolis, IN 46202; ²Mathematics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250

We present our latest results on orientational patterns in flows of nonhomogeneous liquid crystal polymers. In particular, we focus on periodic, quasi-periodic, spatially fluctuating patterns emerge in idealized, steady state flows.

Monday 4:50 Hall of Ideas J LC13

LINEAR VISCOELASTICITY OF NEMATIC LIQUID CRYSTALLINE POLYMER MELTS

Didier R. Long¹ and David C. Morse²

¹Laboratoire de Physico-Chimie Theorique, ESPCI, Paris 75231, France; ²Chemical Engineering and Materials Sciences, University of Minnesota, Minneapolis, MN 55455

We describe the linear viscoelastic response of monodomains of unentangled nematic liquid crystalline polymers, using a generalized Rouse model to calculate the dynamic relaxation functions analogous to the Leslie viscosities. Coupling of the macroscopic director orientation n to the relaxation of the chain conformations is manifest in the predicted transient response of n following a small step strain, and in a phenomena of "magnetic compliance", which is the evolution of n as a function of the duration of the application of a strong magnetic field. We predict continuous tumbling of extended chains (with no hairpins) in shear flow and steady alignment of anisotropic Gaussian chains.

Tuesday Morning

Symposium PL Plenary Lectures

Bingham Lecture

Tuesday 8:30 Lecture Hall

PL2

INTERPRETING THE RHEOLOGY OF DISPERSIONS IN TERMS OF TIME SCALES AND FORCES

William B. Russel

Department of Chemical Engineering, Princeton University, Princeton, NJ 08544

The rheology of colloidal dispersions is nonlinear and time-dependent to an extent that depends critically on the particle size and the interactions between particles. The underlying thermodynamic state varies from the equilibrium fluid phase, through a metastable fluid, into non-equilibrium or equilibrium solid phases with increasing strength of colloidal interactions. The rheology inevitably follows, becoming more complex in the process. In general, though, the behavior is pseudo plastic and reasonably isotropic, as opposed to the nonlinear elasticity and large anisotropy common in polymeric fluids.

This talk will begin with the underlying thermodynamics and dynamics to illustrate the connections with the interparticle potential and Brownian motion. Then the focus will turn to the role of non-equilibrium structure in generating the deviatoric stresses controlling the rheology for weak and strong flows. With that information we address the body of data available on model dispersions to illustrate the characteristic features of the rheology over the full range of concentrations. This will relate the low and high shear viscosities, the high frequency modulus, and various transition shear rates or stresses and frequencies to the particle size and interparticle potential/force for hard and adhesive hard spheres and dispersions containing nonadsorbing or associative polymer.

Symposium SG

Viscoelasticity of Synthetic and Biological Polymer Solutions and Gels

Organizers: Ralph H. Colby, Donald J. Plazek and Guy C. Berry

Tuesday 9:45 Hall of Ideas G

SG14

BROWNIAN DYNAMICS SIMULATIONS OF EXTENSIONAL FLOWS OF DNA AND POLYSTYRENE SOLUTIONS

Lei Li and Ronald G. Larson

Dept. of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109

Brownian dynamics simulations of a bead-spring chain are used to predict the shear and extensional flow properties of dilute polystyrene "Boger fluids" in the filament-stretching device and also dilute DNA solutions in extensional flow in a crossed-slot device. In deformation histories of dilute polystyrene solutions in which there is a sudden step up in extension rate or a re-start of extensional flow after a pause, the stress rises very rapidly in a viscous-like manner. The simulations show that this behavior occurs because the conformations of the sub-population of molecules that contributes most to the stress contains long, fully-extended, portions. We also introduce hydrodynamic interaction (HI) into the Brownian dynamic simulation for both DNA molecules and also dilute polystyrene solutions. HI is introduced but in a simplified one dimensional form, and in a fully three dimensional

Tuesday Morning

form using the Rotne-Prager tensor. The simulation results with HI will be compared with simulation results without HI and with experimental results.

Tuesday 10:10 Hall of Ideas G SG15
LOW VISCOSITY ELASTIC LIQUIDS

David V. Boger

Chemical Engineering, University of Melbourne, Parkville, Victoria 3052, Australia

A series of low, constant and equal viscosity elastic liquids have been constructed using the mixed water-glycerol solvent system, with well characterised water soluble polymers of different molecular weights. The viscosity is of such a low level that normal stresses are not observed using conventional rheometry, nor is it feasible in most instances to obtain dynamic property measurements. However, opposed jet measurements of an apparent elongational viscosity do show significant deviation from the expected Newtonian behaviour for these materials. The Trouton ratio generally increases with elongation rate and as the polymer weight and concentration increases.

The behaviour of these ideal materials is examined in processes where the relaxation time of the fluid is of the same order of process time and thus where influences of fluid elasticity may be expected. These processes include jet breakup, atomisation, splash, and a model swirling flow. Large effects relative to expected Newtonian behaviour are observed as a result of fluid elasticity in all of these flows. Many of the solutions used in the work are in fact dilute and lend themselves to description by dilute solution constitutive equations. A video illustrating some of the phenomena will be shown.

Tuesday 10:35 Hall of Ideas G SG16
**PREDICTION OF THE NONLINEAR SHEAR RHEOLOGY OF BETA-
GLUCAN/AMYLODEXTRIN SOLUTION BLENDS USING A K-BKZ MODEL**

Craig J. Carriere¹ and George E. Inglett²

¹Biomaterials Processing Research Unit, USDA ARS NCAUR, Peoria, IL 61604; ²Biopolymer Research Unit, USDA ARS NCAUR, Peoria, IL 61604

The nonlinear solution rheological behavior of various beta-glucan/amylopectin blends was investigated. The rheological properties of the solutions were investigated using thixotropic loop, small-amplitude oscillatory shear, and steady-state shear experiments. The solutions were found to exhibit an unexpected region of shear-thickening behavior with a critical shear rate of 50 1/s. Startup of steady-state shear experiments, conducted above the critical shear rate for shear thickening, exhibited multiple nonlinear stress-overshoot behavior. The presentation will discuss the findings and compare the experimental results to the predictions of a strain-separable BKZ-type integral constitutive model.

Tuesday 11:00 Hall of Ideas G SG17
**THE DAMPING FUNCTION IN POLYSTYRENE/ORTHO-TERPHENYL SEMIDILUTE
SOLUTIONS**

Vannarong Soulivong and Gregory B. McKenna

Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

Semi-dilute solutions of polystyrene in ortho-terphenyl have been characterized in a parallel plate geometry and over a range of concentrations and molecular weights. Both the torque response and the normal force response as functions of time and deformation magnitude have been measured. The data have been analyzed to examine the effects of the polymer concentration and molecular weight on the damping function and on the time dependent strain energy function derivatives $W1(t)$ and $W2(t)$. Initial results indicate that time-strain separability is valid for our materials and the damping function depends on molecular weight and concentration, contrary to results found by Osaki for semi-dilute solutions using higher molecular weight polymers than those studied here. The combined normal force and torque measurements allow comparison of the $W1(t)$ and $W2(t)$ and we compare how the damping function compares with various models proposed in the literature.

Tuesday 11:25 Hall of Ideas G

SG18

BINARY CONTACTS IN SEMI-DILUTE SOLUTION: GOOD AND THETA SOLVENTS**Mireille M. Adam¹, Bela Farago², Eric Raspaud³, and Didier Lairez⁴**¹University North Carolina, Chapel Hill, NC; ²Institut Laue-Langevin, Grenoble, France;³Laboratoire de Physique des Solides, Université Paris Sud, Orsay, France; ⁴Laboratoire Léon Brillouin CEA Saclay, Gif/Yvette, France

The dynamic properties of semi-dilute solutions are fully described by theory if two lengths, the tube diameter and the correlation length of concentration fluctuation are considered. In both theta and good solvent conditions the tube is defined by binary contacts. In a theta solvent the tube diameter and the correlation length are not proportional, the latter being the mean distance between ternary contacts. This theory provides an understanding of two important experimental features. The plateau elastic modulus is, within experimental accuracy, independent of the solvent quality. Whatever the polymer species and the solvent quality, the ratio of the viscosity to its value in the unentangled regime is, vs the entanglement ratio C/C_e , a universal power law. At the entanglement concentration C_e the tube diameter is equal to the polymer size. The viscosity (the self-diffusion coefficient) decreases (increases) as the temperature is raised from the theta point, while the opposite behavior is predicted. The local viscosity to which monomers are sensitive is responsible for this temperature variation. The concentration dependent local viscosity is deduced from neutron spin echo measurements [1], it is independent of the polymer molecular weights, solvent viscosities and theta temperatures. Measurements were performed on two different polymers (polyisoprene and polystyrene) in semi-dilute theta solutions. In the latter case different solvents ($22C < \theta < 155C$) and different mass ($20.6 \text{ million} < M < 44000$) were studied. The local viscosity reduced by the solvent viscosity varies as $1+BC$ where B depends on the polymer species. B is proportional to the concentration at which persistence length overlap. The role of the macroscopic concentration on a local scale seems to indicate that, in semi-dilute theta solutions, the polymers are transparent to each other.

[1] Adam M., Farago B., Schleger P., Raspaud E., Lairez D. *Macromolecules*, 31, 9213, 1998.

Symposium SL Rheology of Solids

Organizers: Alan Wineman and Roderic S. Lakes

Tuesday 9:45 Hall of Ideas H

SL1

ISOTHERMAL, ISOCHRONAL AND ISOSTRUCTURAL RESPONSES OF AMORPHOUS PEN IN THE GLASSY STATE**Maria L. Cerrada¹ and Gregory B. McKenna²**¹Instituto de Ciencia y Tecnología de Polímeros (CSIC), Madrid 28006, Spain; ²Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

For polymer glasses that have a single relaxation mechanism in the temperature window in which aging experiments are performed it is found that global thermo-rheological simplicity holds. On the other hand, materials such as poly(ethylene naphthalate)(PEN) which have a large beta relaxation in the aging window, it is generally agreed that time-temperature and time-aging time superposition both break down. Here we report experiments performed on PEN in stress relaxation in which appropriate annealing treatments at 100 C were used to create constant fictive temperature T_f glasses at test temperatures of 30, 50, 70 and 90 C. We find that at constant T_f time-temperature superposition is valid. At the same time, the materials having different structures as measured by T_f , time-structure superposition did not hold. We refer to this as simple thermo-rheological simplicity and discuss its implications for the measurement of glassy structure.

Tuesday Morning

Tuesday 10:10 Hall of Ideas H SL2
**SIMULTANEOUS MEASUREMENT OF TORQUE, AXIAL FORCE AND VOLUME CHANGE
IN THE TORSIONAL DILATOMETER: EXPERIMENTS AND ANALYSIS**

Carl R. Schultheisz and Gregory B. McKenna

Polymers Division, National Institute of Standards and Technology (NIST), Gaithersburg, MD
20899

The NIST Torsional Dilatometer measures simultaneously the torque, axial normal force and volume change in response to a torsional deformation. In stress-relaxation experiments with an epoxy cylinder near its glass transition temperature, the torque and normal force decay monotonically, but the volume change associated with the torsion shows a significant non-monotonic decay at lower temperatures. The measurements are investigated with a series solution for torsion of an elastic, compressible material [Murnaghan, F.D. (1951) Finite Deformation of an Elastic Solid. Wiley, New York.]. To a large extent, the behavior can be modeled as thermorheologically simple, with the volume behavior caused by different relaxation times for the higher-order modulus functions from the series solution.

Tuesday 10:35 Hall of Ideas H SL3
**MATERIAL DAMPING VIA RESONANT ULTRASOUND SPECTROSCOPY: A
COMPARISON WITH BROADBAND VISCOELASTIC SPECTROSCOPY**

Taeyong Lee¹, Roderic Lakes², and Amit Lal³

¹Biomedical Engineering, University of Wisconsin - Madison, Madison, WI 53706; ²Engineering Mechanics, University of Wisconsin - Madison, Madison, WI 53706-1687; ³Electrical Engineering, University of Wisconsin - Madison, Madison, WI 53706

Resonant ultrasound spectroscopy (RUS) involves scanning the resonance structure of a compact specimen such as a cube, parallelepiped, or short cylinder. In a typical embodiment of the method, a rectangular parallelepiped or cubic sample is supported by transducers at opposite corners. Corners are used since they always move during vibration (they are never nodes) and they provide elastically weak coupling to the transducers. It is not necessary to cement or to align the specimen. A piezoelectric polymer film, such as polyvinylidene fluoride (PVDF) is suitable as a transducer. RUS is usually used to determine all the anisotropic elastic moduli of one specimen of material. RUS is also capable of damping measurements but interpretation depends on identification of the vibration mode. The frequency range, from about 100 kHz to more than 10 MHz depending on the specimen size, is complementary to that of broadband viscoelastic spectroscopy (BVS) which covers the range of micro-Hz to about 100 kHz with no appeal to time-temperature superposition.

RUS scans from 50 kHz to 500 kHz were conducted on cubical and circular cylindrical specimens of several materials including alloys of low melting point and PMMA, a glassy polymer. 5000 data points were taken for each scan.

Comparison of damping results over the frequency ranges for broadband viscoelastic spectroscopy (BVS) and resonant ultrasound spectroscopy (RUS) for indium tin alloy in shear modes of deformation discloses a continuation of the tan delta power-law trend for ultrasonic frequencies up to 300 kHz. Tan delta values via RUS were 0.003 to 0.0045. For PMMA, resonant peaks were sufficiently broad that higher modes began to overlap.

Tuesday 11:00 Hall of Ideas H SL4
**VISCOELASTIC BEHAVIOR OF SUPERPLASTIC EUTECTIC PB-SN
OVER ELEVEN DECADES OF FREQUENCY AND TIME**

Roderic Lakes¹, Patrick Buechner¹, and Donald Stone²

¹Engineering Mechanics, University of Wisconsin, Madison, Madison, WI 53706-1687;

²Materials Science, University of Wisconsin, Madison, Madison, WI

The purpose of the present study is to experimentally study the viscoelastic behavior of a superplastic Pb-Sn alloy over eleven decades of time and frequency using broadband viscoelastic spectroscopy. No appeal is made to time temperature superposition; all experiments were done at ambient temperature. Ambient temperature is a high homologous temperature for this material which melts at 183 °C.

Cast ingots of eutectic Pb-Sn were rolled at room temperature in increments of 10% permanent deformation in thickness for each pass for a reduction of almost 90%. Viscoelastic testing was performed using a modified broadband viscoelastic spectroscopy apparatus developed in our laboratory. The instrument is capable of torsion and bending studies in creep, sub-resonant dynamic and resonant dynamic oscillation upon the same specimen. The maximum frequency is about 100 kHz. The maximum time in creep is limited by experimenter patience.

Tan delta in torsion followed a frequency to the $-n$ dependence with $n = 0.199$ over four decades from 0.01 to 100 Hz. This is in contrast to a similar power law dependence over about seven decades of frequency for In-Sn examined earlier. The creep compliance showed no evidence of an asymptotic stiffness. The slope of the creep curve on a log-log scale progressively increased, reaching a value of $m = 0.62$ at the longest times. This is in contrast to a time power law creep behavior over more than four decades with $m = 0.28$ for In-Sn. Since $m < 1$, the strain rate is not constant so the creep is not secondary creep; it is still primary creep even at long times. Torsional tan delta of superplastic eutectic Pb-Sn is considerably higher than that of cast Pb-Sn, and of solder wire. Tan delta in torsion is higher than in bending; the difference is more marked at high frequency. The damping, tan delta, falls into the category of high temperature background of metals. The cause is considered to be dislocation movement.

Tuesday 11:25 Hall of Ideas H SL5
VISCOELASTIC BEHAVIOR OF POLYHEDRAL OLIGOSILSESQUIOXANE REINFORCED POLYMERS

Andre Lee¹, Hai-Ping Geng¹, Shawn Phillips², and Joseph D. Lichtenhan³

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The properties of nanostructured plastics are determined by complex relationships between the type and size of the nanoreinforcement, the interfaces, and the chemical interactions between the reinforcement and the polymeric chain, along with the macroscopic processing and microstructural effects. Recently, families of mono- and multi-functionalized polyhedral oligomeric silsesquioxane (POSS) macromers with different organic groups have been developed. Depending on the organic group and the functionality used, the microstructure of POSS reinforcements is significantly altered when blended with organic polymers such as polystyrene or polyethylene. This paper presents an investigation of mechanical and viscoelastic property of POSS macromer reinforced polystyrene and polyethylene. Small-strain stress relaxation and small-stress creeps under torsional deformation at different temperatures were examined to provide insight on the influence of microstructures to the time-dependent viscoelastic behavior of these reinforced plastics.

Symposium FM Non-Newtonian Fluid Mechanics

Organizers: Michael D. Graham, Radhakrishna Sureshkumar and Lars Genieser

Tuesday 9:45 Hall of Ideas I FM14
STABILITY OF VISCOELASTIC PERIODIC CHANNEL FLOW
Jianxin Liu and R Sureshkumar
 Washington University, St. Louis, MO

Stability of periodically constricted channel (PCC) flow is investigated using qualitative flow visualization, quantitative kinematic characterization using digital particle imaging velocimetry (DPIV) and linear stability analysis. We consider three different types of instabilities: (i). inertial instability in viscous (Newtonian) flows for Reynold number $Re \gg 1$ (ii). influence of flow elasticity E , defined as the ratio of the Weissenberg number We and Re , on the inertial instability, and (iii). purely elastic instability observed for $O(1) We$ under creeping flow conditions. The Newtonian instability is caused by the convection of streamwise gradients of vorticity perturbations by the base flow, and its onset is characterized by quasi-periodic oscillations of the near wall vortex in the diverging portion of the channel. Linear stability analysis for an Upper Convected Maxwell liquid shows that flow elasticity has a non-monotonic influence on critical Re . Flow destabilizes with increasing E until a limiting value E^* is reached. Increasing E beyond E^* stabilizes the flow. The value of E^* depends on the geometric parameters.

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However, the We corresponding to E^* is $O(1)$. The purely elastic instability that occurs for $O(1)$ We , manifests as a quasi-periodic cycle that consists of movement of bulk fluid towards the wall followed by motion of fluid away from the wall to the bulk. From streak photographs obtained from flow visualization experiments, it appears that the sharp gradients of elastic stress near the wall, created by the presence of the weak circulation region, is highly susceptible to velocity perturbations. We will compare the mechanisms and spatio-temporal evolution of this instability with those reported for other periodic geometries, such as periodic array of cylinders in a channel. Acknowledgements: ACS/PRF, NSF, SEAS.

Tuesday 10:10 Hall of Ideas I FM15
END EFFECTS AND INERTIAL-ELASTIC INTERACTIONS IN UNSTABLE VISCOELASTIC TAYLOR-COUPETTE FLOW

James M. White and Susan J. Muller

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

End effects and inertial-elastic interactions were observed using particle visualization of the flow field of a dilute polymer solution in the gap between concentric rotating cylinders (Taylor-Couette flow). The test fluid was formulated so that inertial and elastic effects would have equal strengths in the experimental geometry. The role of centrifugal destabilization in the flow was separated from that of elastic destabilization by independent rotation of either the inner or outer cylinder. The inertial and elastic modes were found to interact and thus produce structures sensitive to choice of inner or outer cylinder rotation. The presence of the horizontal boundaries causes strong, localized secondary flows near the ends of the cylinders. In addition, under certain conditions, the end disturbances propagate far into the gap and result in distortions to the axial wavenumber of the disturbance flow. The Newtonian solvent was also investigated in the apparatus so that weak finite-geometry and inertial effects could be clearly distinguished from the effects of elasticity.

Tuesday 10:35 Hall of Ideas I FM16
TURBULENT FLOW IN AN ELASTIC POLYMER SOLUTION AT LOW REYNOLDS NUMBERS

Alexander Groisman and Victor Steinberg

Department of Physics of Complex Systems, Weizmann Institute of Science, Rehovot 76100, Israel

We present an experimental study of an apparently turbulent flow of a Boger fluid at low Reynolds numbers. Transition to this flow occurs as a result of a purely elastic instability and we call the phenomenon "elastic turbulence". The drag increases by more than an order of magnitude compared to a laminar flow with the same flow rate that is analogous to the turbulent viscosity in Newtonian fluids. The fluid motion is excited in a broad range of scales that is a characteristic feature of turbulence. The time spectra of velocities in the elastic turbulence resemble those of the usual inertial and convective turbulence exhibiting power law scaling in a broad range of frequencies. Velocity profile in the transverse direction is also similar to that of a turbulent flow in a pipe at moderate Reynolds numbers.

Tuesday 11:00 Hall of Ideas I FM17
TURBULENT PIPE FLOW WITH POLYMER ADDITIVES AT MAXIMUM DRAG REDUCTION

P. K. Ptasinski, B. H. van den Brule, M A. Hulsen, and F. T. Nieustadt

J. M. Burgers Centre for Fluid Dynamics, Delft Institute of Technology, Delft 2628 AL, The Netherlands

We consider LDV experiments on drag reduction of a flexible polymer solution in a turbulent pipe flow. In contrast to most experiments in the past, which are performed under small drag reducing conditions, we have focused on relatively high polymer concentrations (100-200 wppm) for which maximum drag reduction of approximately 65% occurs. The Reynolds number in our experiments is equal to approximately 10000. The objective of this research is to discuss the effect of addition of polymers on the turbulence.

In the experiments we have focused on the turbulence statistics (mean velocity and turbulence intensities), the various contributions to the total shear stress and the budgets of the turbulent kinetic energy. The turbulent (Reynolds) stress is decreased by 70% due to the addition of the polymers. This is mainly caused by suppression of the radial velocity fluctuations and by loss of the correlation between axial and radial velocity fluctuations. The loss of turbulent stress is mainly compensated by the build up of a large polymeric stress. The balance of mean flow kinetic energy shows a large transfer of energy directly to the polymers instead of to the turbulent fluctuations. The turbulent kinetic energy balance suggests possibly negative polymeric stress work.

Tuesday 11:25 Hall of Ideas I

FM18

NONLINEAR ANALYSIS OF VISCOELASTIC DEAN VORTEX FLOW

K A. Kumar and Michael D. Graham

Chemical Engineering, University of Wisconsin, Madison, WI 53706

Experiments and theory have shown that hydrodynamic instabilities can arise in the flow of viscoelastic fluids in curved geometries. These instabilities pose fundamental challenges for polymer fluid dynamics as well as posing practical difficulties in the polymer processing industry. We focus here on one prototypical flow instability, that of pressure-driven flow in a curved channel: Dean flow. Linear and weakly nonlinear bifurcation analyses have previously been performed on this flow, but there is little understanding of the flow far from onset. We present results from a pseudo-arclength continuation of the stationary, spatially periodic, axisymmetric bifurcating solutions for a FENE-P fluid. The computation shows that, very near onset, the flow evolves into a pattern with a small region of strong radial inflow accompanied by larger regions of weak radial outflow. In the inflow region, the degree of polymer stretch becomes very large and sharply localized. This solution is qualitatively similar to the stationary "diwhirl" pattern experimentally observed by Groisman and Steiberg [Phys. Fluids 10 (1998)] in viscoelastic circular Couette flow.

Further, we show the existence of a Takens-Bogdanov bifurcation point in the linear stability curve of Dean flow, where the nature of the bifurcation changes from pitchfork to Hopf. This point represents a transition to the instability mechanism of viscoelastic circular Couette flow, thus demonstrating a connection between the two mechanisms.

Symposium PM Polymer/Particle Mixtures

Organizers: Daniel De Kee, Lisa Mondy and Mike Solomon

Tuesday 9:45 Hall of Ideas J

PM1

EFFECT OF FILLERS ON THE CROSSLINKING OF A PHOTOCURABLE POLYMER: GEL POINT RHEOLOGY AND THE WINTER-CHAMBON CRITERION

Bor-sen Chiou¹, Srinivasa R. Raghavan², and Saad A. Khan¹

¹Chemical Engineering, North Carolina State University, Raleigh, NC 67695-7905; ²Chemical Engineering, University of Delaware, Newark, DE 19711

The effects of colloidal silica fillers on the UV cross-linking behavior of a model photopolymer (thiol-ene) were examined using in situ rheology. Validation of the Winter-Chambon criterion for determining the chemical gel point was investigated for two different types of colloidal silica particles, one with tethered octyl chains and the other with methyl surface groups. The Winter-Chambon criterion was satisfied for all concentrations of the methyl-terminated silica systems studied. However, the criterion broke down for formulations containing greater than 2% of the octyl-modified silica, with the loss tangents not converging at a single point. Examination of the pre-cure rheology revealed that the samples which failed the Winter-Chambon criterion existed in a flocculated state. This suggests that the pre-cure agglomerated state of the silica could have possibly affected formation of a critical gel. FTIR data, however, showed that the silica particles did not affect the order of the reaction but retarded the polymerization kinetics. An alternative method is thereby suggested for determining the chemical gel point of filled systems that fail

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to obey the Winter-Chambon criterion. This method consists of monitoring the critical strains at various UV exposure times. As the sample reaches its gel point, a dramatic increase is observed in the critical strain, marking the transition from the dominance of physical cross-links to chemical cross-links. This approach could be successfully applied to all the filled systems studied.

Tuesday 10:10 Hall of Ideas J

PM2

BLOCK COPOLYMERS FOR DISPERSING SILICA IN POLYMER MELTS

Daniel Gurovich, Christopher W. Macosko, and Matthew Tirrell

Department of Chemical Engineering, University of Minnesota, Minneapolis, MN

Successful manufacturing of silica-reinforced polymeric products requires achievement of uniform dispersion of the reinforcing filler. This depends on the proper balance between filler-filler and polymer-filler interactions. The highly active polar surface of silica particles interacts very strongly with like polar surfaces, at the expense of the interactions with the polyisoprene (PI) matrix. As a result, silica is difficult to disperse in polyisoprene, and the resulting dispersions tend to re-agglomerate upon aging. Polydimethyl siloxane (PDMS) chains have been shown to interact strongly with silica surfaces via hydrogen bonds. Therefore, a PDMS-PI diblock copolymer can be expected to anchor to a silica surface via its PDMS block and still interact with the PI matrix. In the present work, precipitated silica, polyisoprene, and PDMS-PI copolymer are mixed in different formulations. The influence of copolymer addition and mixing time on the structure and properties of the resulting dispersions is investigated. The rheological properties are tested in dynamic oscillatory shear of the uncured compound, and the low-frequency plateau in the storage modulus (G') is used to assess filler-filler network formation. Both optical and electron microscopies are used to visualize the state of dispersion. Bound rubber is measured after extraction in a good solvent.

Tuesday 10:35 Hall of Ideas J

PM3

YIELD STRESS AND MICROSTRUCTURE IN FERRITE FILLED POLYVINYL CHLORIDE

Suresh K. Ahuja, Hui Chang, and Tsu-Sen Chow

Materials, Xerox Corporation, Webster, NY 14580

Processing of filled polymers and composites through control of microstructure can lead to materials that are tough and resistant to damage. Material properties such as molecular weight of the polymer, level of network, particle size of filler, concentration of filler and aggregate size of filler affect mixing of filler in the polymer. Under similar temperature and shearing conditions, polyvinyl chloride was melt mixed in a Banbury and a roll mill with ferrite at different concentrations. The fluids were subjected to rotational flow and capillary flow at different shear rates and temperatures producing shear stresses, normal stresses. The yield stresses and normal stresses as function of filler concentration are analyzed as power laws. Domains of microstructure by Electron Microscopy are related to particle-particle interaction and to yield and normal stress response in the filled system.

Tuesday 11:00 Hall of Ideas J

PM4

MIXING AND RHEOLOGICAL BEHAVIOR OF HIGHLY-FILLED POLYMER CERAMIC PASTES

J. A. Walberer and Anthony J. McHugh

Chemical Engineering, University of Illinois, Urbana, IL 61801

Reactive polymer ceramic composites represent an important new class of high strength materials. These systems have the advantage that they can be processed at or near room temperature as extrudable pastes prior to heat treating to produce high strength products. The paste state is generated by chemical and/or physical interactions that take place between the polymer and ceramic phases during high shear mixing leading to rheological properties similar to highly filled polymer melts. Results of our studies of the effect of the paste structuring level on the rheological behavior will be presented. A combination of torque rheometry in banbury mixing and biaxial extensional rheometry (lubricated squeezing flow) was used. The relationship between the mixing behavior, measured as a torque-time profile, and the rheological behavior, as measured by the relaxation modulus and viscosity, was found to depend strongly on the underlying structuring mechanism responsible for the paste stiffening. This relationship has been studied and experimental results will be shown for four different model systems which show stiffening due to the following mechanisms: 1) polymerization of the polymer phase, 2) crosslinking of the polymer phase, 3) flocculation of the ceramic phase particles, and 4) chemical linking of the ceramic phase particles to the polymer

phase molecules. The effect of structural level in the model systems will be compared with the effect of filler volume fraction in a non-reactive highly filled melt.

Tuesday 11:25 Hall of Ideas J

PM5

RHEOLOGY OF POLYMER LAYERED-SILICATE NANOCOMPOSITES

Ramanan Krishnamoorti, Jiaxiang Ren, and Adriana Silva

Chemical Engineering, University of Houston, Houston, TX 77204

The melt-state rheological properties of layered-silicate based nanocomposites containing a disordered block copolymer of polystyrene and polyisoprene have been investigated. The linear dynamic moduli can be superposed well using time temperature superposition utilizing shift factors comparable to those of the pure copolymer. Further, the data indicate that the nanocomposites with silicate fractions exceeding 5 wt. % are solid-like. These dynamic moduli are corroborated by an extensive study of the stress relaxation behavior. Further, these systems can be alligned by the application of large amplitude oscillatory shear, similar to that seen in other intrinsically anisotropic materials such as liquid crystalline polymers. The rheological properties can be reconciled in terms of the percolation of the highly anisotropic fillers and will be discussed in the meeting.

Tuesday Afternoon

Symposium SG

Viscoelasticity of Synthetic and Biological Polymer Solutions and Gels

Organizers: Ralph H. Colby, Donald J. Plazek and Guy C. Berry

Tuesday 1:30 Hall of Ideas G

SG19

ON THE USE OF MOLECULAR MODELS TO DERIVE THE MOLECULAR WEIGHT DISTRIBUTION OF LINEAR POLYMERS FROM VISCOELASTIC MEASUREMENTS

G rard Marin and Fr d ric L onardi

Laboratoire de Physique des Mat riaux Industriels, Universit  de Pau et des Pays de l'Adour, 64000 PAU, France

The idea of deriving the molecular weight distribution of polymers from linear viscoelastic measurements (i.e. from a distribution of relaxation times) has been applied by a large number of authors in the last few years. This method could prove to be very useful in a lot of applications (polymers with very large MWDs, non-soluble polymers...) due to the large sensitivity of rheological parameters on molecular weight and polydispersity. The starting point of these methods is a "mixing rule" which is either phenomenological or based on molecular models. The issue of mathematical inversion of this ill-posed problem may be considered as "solved" now, with very efficient methods which lead to a minimal loss of information. However, most of the calculations based on molecular models (basically the double reptation model or its derivatives) do not take into account correctly constraints release : such a simplification leads to a one-to-one correspondence between a relaxation time (or a set of relaxation times) and a given molecular weight, and does not take into account the shift in relaxation times in a polydisperse environment, leading to a wrong determination of the high molecular weight part of the distribution. This paper will present an efficient method to take into account constraint release in molecular models and show the improvement in the determination of the MWD of linear polymers, for a wide range of molecular species.

Tuesday 1:55 Hall of Ideas G

SG20

THEORY OF LINEAR VISCOELASTICITY OF CHIRAL LIQUID CRYSTALS

Alejandro D. Rey

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

The governing equations for monodomain isothermal cholesteric liquid crystals subjected to small amplitude oscillatory rectilinear shear have been derived for three representative helix orientations. The imposition of oscillatory flow excites splay-bend-twist deformations when the helix is aligned along the flow direction, splay-bend deformations when the helix is along the velocity gradient, and twist deformations when aligned along the vorticity axis. The different nature of the excited elastic modes as well as the anisotropic viscosities are reflected in the anisotropy of the linear viscoelastic material functions for small amplitude rectilinear oscillatory shear. When the helix is aligned along the flow direction, cholesteric viscoelasticity is strongest, and exists in a relatively narrow band of intermediate frequencies. When the helix is aligned along the vorticity direction cholesteric viscoelasticity is significant in a relatively broad range of intermediate frequencies. Finally, when the helix is aligned along the velocity gradient direction, cholesteric viscoelasticity is relatively insignificant and only exist in a narrow band of frequencies. The cholesteric pitch controls the location of viscoelastic region on the frequency spectrum, but only when the helix is not oriented along the vorticity axis.

Tuesday 2:20 Hall of Ideas G SG21
RHEOLOGY AND STRUCTURE IN MIXED SYSTEMS OF WORM-LIKE MICELLES AND NONIONIC POLYMER

Lynn M. Walker and My Hang Truong

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

We are quantifying the rheology and flow-induced structure of mixed systems of wormlike micelles and nonionic, aqueous polymer. Wormlike micelles exhibit a wide range of interesting behavior; dilute solutions of cationic surfactant exhibit a flow-induced transition to a viscoelastic, structured fluid while semidilute solutions act like model, single relaxation-time fluids. The transition and model behavior are well documented and several theories have been proposed for both. In this work, we utilize nonionic aqueous polymer to control the rheological behaviors of the micellar system and attempt to relate rheological behavior to physicochemical properties of the polymers. We have found significant differences in the rheology of mixtures of cetyltrimethylammonium tosylate (CTAT) and specific polymers; hydroxypropylcellulose (HPC) and poly(ethyleneoxide) (PEO). The flow-induced transition can be shifted to higher or lower values of critical stress through a careful choice of the nonionic polymer. We are using *in situ* small angle neutron scattering to probe the local structure of the micelle-polymer fluid and relate this to the observed rheology.

Tuesday 2:45 Hall of Ideas G SG22
SURFACE RHEOLOGY OF A DENDRITIC MONOLAYER

J. Patrick Kampf¹, Carlton F. Brooks¹, Curtis W. Frank¹, Gerald G. Fuller¹, Craig Hawker², and Eva E. Malmström²

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We have investigated the surface rheology of Langmuir monolayers of poly(benzyl ether) mono-dendrimers, which are covalently tethered to a poly(ethylene glycol) tail. Using an interfacial stress rheometer (ISR) [*Langmuir* **1999**, *15*, 2450] the surface storage and loss moduli could be measured for these films at the air-water interface. Increasing the molecular weight of the ethylene glycol tail of a 4th generation dendrimer from 90 to 1500 g/mol decreased the dynamic moduli, implying that the predominant resistance to flow arises from the dendrimer-dendrimer interactions. Increasing the hydrophilicity of the molecule, by increasing the ethylene glycol chain length, assists in screening these interactions. By varying the temperature, the principle of time superposition (TTS) was employed to probe dynamic time scales exceeding those that can be obtained with the present instrument. It was found that the temperature dependence of the shift factors was different depending on the number of generations of growth in the dendrimer. The 4th generation dendrimer exhibited Arrhenius behavior and the 5th generation dendrimer exhibited predominantly WLF behavior. At high temperature above the crossover point in the moduli, the shift factors of the 5th generation dendrimer had an Arrhenius dependence. The observed changes in rheological behavior are coincident with the suppression of the monolayer-bilayer transition below a critical temperature, T^* .

Tuesday 3:35 Hall of Ideas G SG23
RHEOLOGICAL PROPERTIES OF ASSOCIATIVE MODEL POLYMERS AND POLYOXYETHYLENE

Donald J. Plazek and Zane N. Frund, Jr.

Material Science and Engineering, University of Pittsburgh, Pittsburgh, PA 15261

Hydrophobically-modified polymers are composed of water soluble and insoluble (hydrophobic alkyl end-groups) components. They are referred to as associative polymers since their aqueous solutions exhibit enhanced viscosities due to the aggregation of their alkyl end groups into micelle-like structures. The aggregation is attributed to the rejection of the hydrophobic end-groups by the water. Most previous studies have been directed at determining the flow behavior of "end use", formulated solutions which contain the polyoxyethylene or hydrophobically modified polymers. Only a few studies have been carried out to determine the viscoelastic properties of the subject polymers. The rheological properties including the creep recovery behavior of associative model polymers were determined as function of molecular weight, solution concentration, shear rate, temperature and solvent type in this investigation. These polymers are composed of a linear water soluble polyoxyethylene backbone chain extended with isophorone diisocyanate and end-capped with hexadecyl alkyl groups, and have molecular weights ranging from 17,000 to

84,000 grams/mole. For comparison purposes, hydrogen end-capped and polyoxyethylene resins of various molecular weights were also evaluated.

Tuesday 4:00 Hall of Ideas G SG24
SIGNIFICANCE OF ROUSE SEGMENT IN VISCOELASTICITY OF BULK POLYMERS

Kunihiro Osaki and Tadashi Inoue

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Through comparison of stress and birefringence in oscillatory stretching of polymers, we revealed that the origin of stress in the glass-to-rubber transition zone was attributed to two modes of chain deformation. These are associated with different values of stress-optical coefficients, which may be theoretically estimated from the monomer polarizability tensor and assumed monomer orientation. Thus one can determine the chain deformation for each mode; one, named the glassy (G) mode is associated with the twist of chain, or the monomer rotation about the chain axis, and the other, rubbery (R) mode, with the orientation of chain axis. The viscoelastic function for the R mode could be fitted with a Rouse model. The size of the Rouse segment, as estimated from the instantaneous modulus of the R mode, was approximately equal to the literature values of the size of Kuhn statistical segment. The observed Rouse segment probably represents the flexible segment assumed as the basis of polymer chain model for rubber elasticity and viscoelastic liquids.

Tuesday 4:25 Hall of Ideas G SG25
DO DILUTE SOLUTION POLYMER DYNAMICS STUDIES PROBE DYNAMIC SPATIAL HETEROGENEITIES IN GLASS-FORMING SOLVENTS?

John L. Schrag

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Dilute-solution studies of polymer dynamics by means of viscoelasticity and oscillatory flow birefringence measurements have provided considerable insight into the dynamics of conformational change in macromolecules. The effects of molecular weight, polydispersity, branching, block copolymer architecture, excluded volume and solvent quality have, in general, corresponded closely to theoretical predictions if the actual solvating environment contribution is accounted for properly. However, there is one notable exception; the apparent chain flexibility deduced from these experiments is substantially less than expected from persistence length information from light scattering. Recently we have discovered that this flexibility "discrepancy" MAY be a result of unexpected solvent-generated restrictions of fairly local chain motions resulting from (dynamic) spatial variations in "solvent structure", and thus solvent mobility. The evidence supporting this hypothesis is still very limited in extent; it includes a significant decrease in the shortest relaxation time (global chain motions) at low chain molecular weight (shortest relaxation time normally independent of MW) for polystyrene/Aroclor solutions, remarkable variations at low MW in normally molecular-weight-independent quantities describing the concentration dependence of the time-temperature superposition parameter and the high frequency limiting value of the real part of the complex viscosity coefficient and, most notable, an astonishing large increase in apparent flexibility for polyisoprene in going from solution conditions to the melt. If these preliminary results are not anomalous, it may be possible to obtain solvent correlation length information via chain dynamics studies.

Tuesday 4:50 Hall of Ideas G SG26
THE DYNAMIC SCALING APPROACH TO GLASS FORMATION

Ralph H. Colby

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Experimental data for the temperature dependence of relaxation times are used to argue that the dynamic scaling form, with relaxation time diverging at the critical temperature T_c as $(T-T_c)^{-\nu z}$, is superior to the classical Vogel form. This observation leads us to propose that glass formation can be described as a simple mean-field limit of a phase transition. The order parameter is the fraction of all space that has sufficient free volume to allow substantial motion. Diffusion of this free volume creates random walk clusters that have cooperatively rearranged, for which we show that the distribution of cooperatively moving clusters must have a Fisher exponent $\tau = 2$. Dynamic scaling predicts a power law for the relaxation modulus $G(t) \sim t^{-2/z}$, where z is the dynamic critical exponent relating the

relaxation time of a cluster to its size. Andrade creep, universally observed for all glass-forming materials, suggests $z = 6$. Our analysis finds that there are multiple universality classes for the correlation length divergence exponent ν . Polymers appear to universally have $\nu z = 9$ (making $\nu = 3/2$). However, other glass-formers have unphysically large values of νz , strongly suggesting that other factors, such as local energetic barriers to motion, may be important.

Symposium SL Rheology of Solids

Organizers: Alan Wineman and Roderic S. Lakes

Tuesday 1:30 Hall of Ideas H SL6
CRITICAL EVALUATION OF A NONLINEAR VISCOELASTIC CONSTITUTIVE MODEL FOR GLASSY POLYMERS

Doug B. Adolf¹, Robert S. Chambers¹, Prashant Shrikhande², Grisha Medvedev², and James M. Caruthers²

¹Sandia National Laboratories, Albuquerque, NM; ²School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-1283

Over the last several years, we have developed a constitutive model that can address most of the viscoelastic relaxation behavior observed experimentally. The constitutive model is constructed using Rational Mechanics, where the material is assumed to relax on a material time scale t^* that depends upon the thermodynamic state history of the material. All constitutive relationships can be calculated from a single Helmholtz free energy functional, which depends upon the temperature and deformation histories. We have developed a number of models for how the rate of relaxation depends upon the state of the material; however, only when t^* depends upon the configurational part of the internal energy, does the model have the correct structure to describe the complete nonlinear mechanical behavior observed experimentally. To first order, these constitutive models are developed without resorting to adjustable intrinsically nonlinear parameters, instead relying only on linear viscoelastic properties.

In order to validate the constitutive model, arguably the most extensive set of multiaxial, nonlinear relaxation data ever generated for a polymeric material has been developed for a specific diethanol amine cured epoxy resin. The data set includes (i) complete linear viscoelastic characterization, (ii) isotropic volumetric and PVT behavior, (iii) multistep nonlinear loading and unloading experiments in extension, compression, and torsion at various strain rates, where in all cases the temperature history has been carefully controlled. The nonlinear constitutive model is able to quantitatively capture most features of the nonlinear behavior including yield - a feat that here-to-for has escaped alternative constitutive formulations - although the data does exhibit a more abrupt post-yield softening than is predicted theoretically. Potential reasons for the less than quantitative predictions of the post-yield softening will be discussed.

Tuesday 1:55 Hall of Ideas H SL7
MESO-SCALE MODEL INCLUDING FLUCTUATIONS TO DESCRIBE VOLUME RELAXATION IN POLYMERIC GLASSES

Grisha Medvedev and James M. Caruthers

School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-1283

In the classic data set of Kovacs (1958), poly(vinyl acetate) exhibited nonexponential, nonlinear, asymmetric, and overshoot volumetric behavior after single and two-step temperature jumps. Although the Kovacs data set has been available for 40 years, none of the existing models can quantitatively describe the complete data set. In order to describe the Kovacs data set we have developed a new model that explicitly acknowledges fluctuations in the density. Specifically, a single relaxation time constitutive equation is generalized to include a stochastic forcing function, where the nonlinearity is included via a relaxation time that depends upon the instantaneous temperature and specific volume. Both the free volume and Adam-Gibbs configurational entropy models have been used to specify the density dependence of the relaxation time. The form of the additional stochastic term is not arbitrary; specifically, the fluctuation dissipation theorem has been applied so that at equilibrium the resulting nonlinear

stochastic differential equation is stationary, which then yields the exact mathematical form of the stochastic term once a particular log(a) shift factor model has been chosen. There is only one new parameter - the size of the meso-domain, which we assume to be a function of temperature and volume consistent with the Adam-Gibbs model. In order to effect an efficient solution, the nonlinear stochastic differential equation has been transformed to a mathematically equivalent master equation for numerical solution, and the specific volume response to single and multiple step changes in temperature has been determined via solution of the master equation. The specific volume predictions can describe the experimental data set of Kovacs. It is significant that the fluctuation model predicts the width of relaxation spectra will evolve during the relaxation process (i.e. the response is thermorheologically complex) in agreement with recent experimental data.

Tuesday 2:20 Hall of Ideas H SL8

CONSTITUTIVE MODEL FOR PREDICTING THE STRESS RESPONSE OF SULFUR VULCANIZED RUBBERS DURING SIMULTANEOUS DEFORMATION AND CHEMICAL AGING

Prasenjeet Ghosh, Santhoji Katare, Priyan Patkar, and James M. Caruthers

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Elastomers are often used in applications where they are deformed while being challenged with chemical degradation. In order to predict the long time response of sulfur vulcanized elastomers, a quantitative kinetic model has been developed to describe the sulfur vulcanization of natural rubber, incorporating the mechanism for sulfur activation, the effects of retarders, and the reduction of polysulfidic crosslink structures. The model employs population balance methods to describe polysulfidic structures and their long time evolution. The vulcanization rate are determined using traditional oscillating disk cure data.

One must now connect the chemical kinetics with the mechanical properties. The vulcanization reaction can affect the stress response in two ways: (i) the degradation of polysulfidic crosslinks can release the contribution to the total stress from crosslinks that were generated at an earlier time and (ii) formation of new crosslinks can contribute to the total stress if the material is deformed subsequent to formation of these crosslinks. Proper accounting for the formation of new crosslinks is interesting, since it's stress free state can be a "deformed" state implying that there are a family of reference configurations. We have developed a full three-dimensional, tensorially valid constitutive equation that incorporates the simultaneous curing and deformation, including a family of reference configurations. The predictions of this model are currently being validated with experimental permanent set data for sulfur vulcanized rubbers.

Tuesday 2:45 Hall of Ideas H SL9

THE RELATIONSHIP BETWEEN THE ENERGY LANDSCAPE AND VISCOELASTIC RELAXATION FOR GLASSY MATERIALS

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The experimentally observed relaxation behavior for both polymeric and small molecule glasses extends over many orders of magnitude from nanoseconds to years. This time dependent behavior must obviously depend upon the molecular architecture of the glass as defined by the potential energy surface in configurational hyperspace. However, the rugged energy landscape as well as the extremely large number of local minima make even characterization of the potential energy surface difficult, while the extremely wide range of relaxation times makes prediction of the relaxation response by traditional molecular simulation methods problematic. As a first step, both the minima and transition states on the potential energy surface have been determined for a modified Lennard-Jones potential in a simulation cell with periodic boundary conditions. When the system is small (i.e. 30 molecules) and at a high density, the local minima and associated saddle points between minima have been exhaustively determined, where somewhat surprisingly there are only a small number (i.e. several 100 or less) of lower energy local minima. From this detailed map of the potential energy surface, the surface has been coarse-grained into an inter-connected graph of corrugated energy basins. The coarse-graining has been performed via the energy barrier for transition between neighboring minima, and we are currently statistically characterizing this coarse graining so that graph can be generated for larger, less dense systems and for more complex molecules like polymers, where exhaustive determination of all the minima and saddle points will not be possible. Using this potential energy graph that includes both minima and saddle points, a transition probability matrix governing the time evolution of the system

has been generated. The eigenspectra of the transition probability matrix extends over orders of magnitude, giving rise to KWW-like relaxation spectra. The extension of this initial work to polymeric glasses will be discussed.

Tuesday 3:35 Hall of Ideas H SL10

A MULTI-MECHANISM CONSTITUTIVE MODEL FOR CEREBRAL ARTERIAL TISSUE

Rachmadian Wulandana and Anne M. Robertson

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Past studies directed at predicting the mechanical behavior of cerebral aneurysms (localized protrusions of sections of blood vessel wall) model the aneurysm tissue using a hyperelastic constitutive equation for which the stress free reference configuration is either a spherical shell or an idealized aneurysm. Taking this approach, the aneurysm tissue is treated as a different entity than the arterial tissue from which it developed. The size, shape, thickness, anisotropy and inhomogeneity of the idealized aneurysm are specified. We have taken a different approach to the problem. Specifically, we use a multiple mechanism constitutive equation to model the microstructural changes which occur during the inelastic deformation of a section of cerebral arterial tissue into a cerebral aneurysm. This constitutive equation is motivated by mechanical and histological tests on cerebral arterial tissue which suggest that the development of cerebral aneurysms is tied to the recruitment of collagen fibers and breakage of elastin in the cerebral arterial tissue. Multi-mechanism constitutive models have previously been developed to model microstructural change associated with a number of complex physical phenomena. These include damage induced softening of rubber materials (e.g. Wineman and Huntley, 1994), twinning (Rajagopal and Srinivasa, 1995) and irreversible cyclic extension of human patellar tendons (see, e.g. Johnson et al., 1996).

Tuesday 4:00 Hall of Ideas H SL11

MODELING OF STEADY AND TIME DEPENDENT BEHAVIOR OF CROSSLINKED, FILLED POLYMERS

Arkady Leonov¹ and Prashant G. Joshi²

¹Department of Polymer Engineering, University of Akron, Akron, OH 44325; ²Organosilicones Group, Witco Corporation, Tarrytown, NY 10591

Filled polymer systems have been a subject of interest for rheologists since the past many decades. Their applications range from paints and pigments to high performance composite materials. Presently, there is a lack of complete understanding of the behavior of these materials under varying kinematic and dynamic conditions. Moreover, there is a lack of a comprehensive theory, which can simultaneously describe the rheology of filled rubbers, their chemorheology, and their behavior in the final fully cured state. The present work is aimed at capturing a wide range of rheological (viscoelastic and kinetic) properties of filled rubbers with one set of constitutive/kinetic equations and a flexible relaxation spectrum. The various experiments covered are yield-flow transition in creep, shear start up responses, and dynamic behavior in the melt state and the changes during the cure stage. In the post cure state, the manifestations in Mullins stress softening-hysteresis and recovery, large strain stress relaxations, and dynamic behavior are also demonstrated. Finally, the non-linearities during large strain dynamic deformations, accompanied by heavy non-isothermal, viscoelastic and structure effects are exemplified.

Tuesday 4:25 Hall of Ideas H SL12

SURFACE DEFORMATION OF CROSSLINKED POLYESTERS

Suresh K. Ahuja, Hui Chang, and Angela Strojny

Materials, Xerox Corporation, Webster, NY 14580

Surface deformation of polymer networks is of interest because of inhomogeneous structures arising out of variation in fractals and in voids through a layer. Bulk properties such as modulus and hardness are function of surface irregularities. Polyesters were crosslinked to different levels by using different crosslinker concentration at a fixed temperature and coated on smooth aluminum substrate. The polymer layers were subjected to different levels of forces using a diamond conical indenter. When the indenter reached a desired level of force, it was held for a certain time and then withdrawn from the surface. Modulus and hardness were calculated at different gel concentrations. Modulus increased as the gel concentration was increased to a certain threshold level. Beyond this critical level, modulus did not increase significantly. The results are analyzed in terms of the fractals and their distribution in the surface.

Tuesday 4:50 Hall of Ideas H

SL13

A MODEL FOR STRESS EVOLUTION DURING THERMOSET CURE**Yuhai Mei¹, Alan S. Wineman¹, and Albert F. Yee²**¹Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109; ²Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109

A constitutive equation is presented which accounts for stresses developed during the curing of epoxy. The continuous creation of new cross links after the chemical gelation point forms new networks which can transmit stress. Each new network has a different reference configuration due to the volume changes of the previously formed networks. The mechanical response of each new network is assumed to be linear viscoelastic if the cure temperature is around T_g . The rate of formation of the new networks depends on the rate of curing. The total stress at any instant is the superposition of the stresses from each network formed from gelation until that instant. Using a curing rate based on experimental evidence, the model is used to determine chemical shrinkage under isothermal cure. Simulations are carried out for various assumed material parameters. The results are in qualitative agreement with experimental data.

Symposium FM Non-Newtonian Fluid Mechanics

Organizers: Michael D. Graham, Radhakrishna Sureshkumar and Lars Genieser

Tuesday 1:30 Hall of Ideas I

FM19

BIFURCATIONS AND TRANSITION TO CHAOS IN CONE-AND-PLATE FLOW**David O. Olagunju**

Mathematical Sciences, University of Delaware, Newark, DE 19702

It is well established that torsional flow of viscoelastic fluids in a cone-and-plate geometry is unstable if the Deborah number is sufficiently large. Linear stability analysis shows that as the Deborah number increases past a critical value, a pair of complex conjugate eigenvalues crosses the imaginary axis into the right half-plane. Using a weakly nonlinear analysis we study the dynamics of the flow just above criticality for a Maxwell fluid. We derive a Ginzburg-Landau equation that governs the dynamics of the flow for values of the Deborah number slightly above criticality. The complex Ginzburg-Landau equation is solved numerically using a pseudospectral method. Our results show bifurcations from a limit cycle to a torus, followed by a sequence of period-doubling bifurcations and chaos.

Tuesday 1:55 Hall of Ideas I

FM20

ROLE OF FLUID ELASTICITY AND DYNAMIC MODULATION ON STABILITY OF UNIDIRECTIONAL FREE SURFACE FLOWS**Chao-Tsai Huang and Bamin Khomami**

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

In this study we have theoretically investigated the effect of fluid elasticity and dynamic modulation on the stability of single and multilayer unidirectional free surface flows. Specifically, asymptotic and spectrally based numerical techniques in conjunction with Floquet theory has been used to investigate the linear stability of one and two layer viscoelastic flows down an inclined plane. Based on these analyses we have demonstrated that dynamic modulation with a frequency close to the inverse of the mean relaxation time of the polymeric fluid can significantly affect the interfacial and free surface stability/instability of single and multilayer viscoelastic flows down an inclined plane. It has also been shown that the effect of dynamic modulation on the stability/instability of this class of flows is significantly more pronounced when the fluids are viscoelastic. Moreover, in two layer flows it has been shown that the resonance between the free surface and the interface can occur giving rise to extremely rich dynamics. Finally, the mechanism(s) of interfacial and free surface instabilities in this class of flows in presence or absence of dynamic modulation has been determined based on a rigorous energy analysis.

Tuesday 2:20 Hall of Ideas I

FM21

STRESS/CONCENTRATION/SLIP INSTABILITIES IN COUETTE FLOW OF POLYMER SOLUTIONS**William B. Black and Michael D. Graham**

Chemical Engineering, University of Wisconsin, Madison, WI 53706

The existence of shear enhanced growth of concentration fluctuations in concentrated polymer solutions, has been known for some time. Theories of this phenomenon have focused on the bulk behavior (i.e. in an unbounded domain). In contrast, recent experimental observations of polystyrene solutions by Mhetar and Archer [Macromolecules, 31 (1998)] in plane Couette flow suggest that behavior near the boundaries may be important, namely: 1) they observe that the growth of concentration fluctuations is initiated near the boundaries of the flow cell, 2) the solutions exhibit slip at these boundaries at stresses far below the critical stresses for concentration fluctuation growth, 3) the wavelength of fluctuations is on the order of the extrapolation length for slip, and 4) modifying the surface properties changes the onset conditions for the growth of fluctuations. Motivated by these observations, we have analyzed the plane Couette flow of a solution of Hookean dumbbells, accounting for the interaction between stress and mass flux. If no-slip boundary conditions apply, the flow is linearly stable, though shear may induce enhancement of Brownian fluctuations. In contrast, if slip occurs, in the form of a simple Navier (shear stress dependent) slip boundary condition, a new mode of instability arises, with stress and concentration fluctuations localized near the boundaries. (This flow is stable if the dumbbell concentration is assumed constant.) The critical Weissenberg number for instability varies between 1 and 20, depending on the Peclet number. The critical wavelength of the most unstable fluctuation is on the order of the extrapolation length, in agreement with experiment. Time integration of the linearized equations shows that, irrespective of boundary conditions, initially delocalized concentration fluctuations evolve into structures localized near the boundary.

Tuesday 2:45 Hall of Ideas I

FM22

SHEAR BANDING IN THE JOHNSON-SEGALMAN MODEL WITH A DIFFUSION TERM**Ovidiu Radulescu¹, Peter D. Olmsted¹, and C-Y D. Lu²**¹University of Leeds, Leeds LS2 9JT, United Kingdom; ²Department of Physics, National Central University, Chung-li, Taiwan

We study the Johnson-Segalman (JS) model as a model system for complex fluids which are observed to phase separate, or "shear-band" in flow. We analyze the properties of this model in Couette flow conditions and demonstrate the clear history dependence inherent in the local JS model. We add a gradient term in the stress dynamics that has a rather general microscopic justification, and demonstrate how this term breaks the degeneracy of the local model and prescribes a much smaller (discrete, rather than continuous) set of banded steady state solutions. We investigate some of the effects of the curvature of Couette flow on the observable steady state behavior, and comment on the generality of the approach and results. We also present some preliminary results on kinetics and metastability.

Tuesday 3:35 Hall of Ideas I

FM23

ASYMPTOTIC STRUCTURE OF THE STRESS FIELD IN HIGH WEISSENBERG NUMBER FLOW PAST A CYLINDER**Michael Renardy**

Mathematics, Virginia Tech, Blacksburg, VA 24061-0123

We study the flow of an upper convected Maxwell fluid past a cylinder in the limit of high Weissenberg number. We make the simplifying assumption that the velocity field is given and similar to the Newtonian case (as will be explained, this assumption is almost certain to be wrong). We then consider the integration of the stress equations. The asymptotic behavior at high Weissenberg number leads to boundary layers along the edge of the cylinder as well as a stress concentration in the wake. The stresses in the boundary layer are of order W while the width of the boundary layer is of order W^{-1} . The stresses in the wake are of order W^3 , and the width of the wake is of order W^{-2} . Just outside the boundary layer and wake, there is a region of much higher stresses; these stresses are of order W^3 near the cylinder and of order W^5 along the wake.

Tuesday 4:00 Hall of Ideas I

FM24

ON FLOWS OF POLYMERS IN LONG CHANNELS AND DIES**Maxim Siline and Arkady Leonov**

University Of Akron, Akron, OH

The general nonexistence of steady rectilinear viscoelastic flows in long tubes causes secondary flows to occur. The early analytical and experimental studies of dilute polymer solutions and recent experiments and direct numerical simulations of polymer melts as well found the secondary flows to be very weak. It suggests that for many applications to polymer processing the secondary flow can either be neglected or when necessary, treated as a small disturbance relative to rectilinear flow component.

The study develops an approach based on partitioning flow in the main, quasi-rectilinear part and small disturbances. The formulated quasi-rectilinear flow problem is described by a second order nonlinear elliptic PDE that is close to simple shearing. The calculations of main axial velocity profiles employing this approach are successfully compared with recent experimental data. Using a perturbation procedure authors derive a fourth order linear PDE for secondary flow. Contrary to the quasi-rectilinear, computations of the secondary flow depend on features of viscoelastic constitutive equations. Scaling evaluations justifying above mentioned partitioning as well as example calculation of secondary flows showed that the stress and velocity fields related to the secondary flows are small.

Tuesday 4:25 Hall of Ideas I

FM25

NON-NEWTONIAN EFFECTS ON RIGID AND DEFORMABLE REVERSE ROLL COATING**Carlos Tiu¹, Lei Wang¹, and Ta-Jo Liu²**¹Chemical Engineering, Monash University, Clayton, Melbourne 3168, Australia; ²Formosa Advanced Coating Technologies, Inc., Chutung, Hsinchu 310, Taiwan

Reverse roll coating consists of two or more rolls in pair rotating in opposite directions to coat a liquid layer on substrate or provide sheet products. With a deformable roll, its surface is pressed onto a rigid roll, thus creating a negative gap called "nip". For deformable reverse roll coating no fluid can pass through the nip region hence the fluid transferred onto the metered roll surface is determined by the nature of feed flow only. Interactions of hydrodynamic forces with deformable solid boundaries are encountered in deformable roll coating system especially when the coating liquid is viscoelastic. Experimental results indicate that with the same minimum gap setting, the film behaviour in rigid roll coating system is influenced by roll speed ratio, Capillary number and fluid rheology. Whereas for deformable roll coating, a small non-uniform deformation of the elastic layer and the viscoelastic nature of the coating solution result in a different surface film behaviour. As the gap space between the rollers reduces to negative, the performance of the film is directly related to the hydrodynamic force generated in the nip area which is influenced by the liquid rheology, roll load, surface hardness and speed ratio. Capillary force has no significant effect on the film thickness. The viscoelastic nature of the liquid appears to improve the film stability. The maximum wipe ratios for viscoelastic liquids have been found to be about 50% larger than the corresponding values for inelastic liquids. The experimental results are presented and compared with existing theoretical predictions.

Tuesday 4:50 Hall of Ideas I

FM26

A NUMERICAL STUDY OF SIMPLE SHEARING FLOW OF FOAMS**Germán J. González-Santos¹ and Douglas A. Reinelt²**¹Matemáticas, Instituto Politécnico Nacional, México D.F., Distrito Federal 07738, Mexico;²Mathematics, Southern Methodist University, Dallas, TX 75275-0156

A numerical approach is presented to study the evolution and the bulk functions of a two-dimensional and doubly periodic array of deformable bubbles suspended in Newtonian fluid where the motion is driven by an external simple shearing flow.

When the thickness of the thin films separating individual bubbles is small compared to the bubble dimensions and the fluid motion caused by the external simple shearing flow is not too large, then the fluid motion is governed by the continuity and Stokes equations. These equations are coupled with the tangential and normal stress boundary conditions along the gas-liquid interface. The kinematic condition is used to advance the interface in time. To

prevent very thin films and to increase foam stability a stabilizing disjoining pressure that is inversely related to the film thickness is introduced.

The numerical method is based on the overlapping grid technique; a second order finite differences is used to approximate the equations and boundary conditions at the interior and interface boundary nodes respectively, and the solution at the interpolation points is approximate from another grid using interpolation.

The evolution of the foam structure and bulk functions depend on the Capillary number, Ca , bubble volume fraction, ϕ , and Hamaker's constant, A . When $A = 0$ and Ca is relatively small the foam develops a quasi-periodic motion during several periods of time before the thin film becomes so thin that is not longer possible to continue the numerical calculations. When $A \ll 0$ and Ca is relatively small the bubbles develop a periodic motion. For larger values of Ca the bubbles deform without limit and eventually coalesce. Also we examine a simplified quasi-static model $Ca = 0$, $A \ll 0$ with the thin films of constant thickness and Plateau borders of constant curvature.

Symposium MS Rheology of Polymer Melts and Solutions

Organizers: John L. Schrag and Faith Morrison

Tuesday 1:30 Hall of Ideas J

MS1

BROWNIAN DYNAMICS OF SINGLE DNA CHAINS IN STEADY AND TRANSIENT SHEAR FLOW

Joe S. Hur¹, Eric Shaqfeh¹, and Ronald G. Larson²

¹Dept. of Chemical Engineering, Stanford University, Stanford, CA 94305-5025; ²Dept. of Chem. Eng., University of Michigan, Ann Arbor, MI 48109

We have investigated the dynamics of single polymer chains in both steady and transient shear flow. In the first part of the talk, we present the results of large-scale Brownian dynamics simulations which have been used to examine the recent findings of Smith et al. (*Science* 283(99)) who studied a single DNA molecule in steady shear flow. We have used a series of different models - the Kramer's freely jointed chain, the Wormlike chain (Larson, *J. Rheol.* 43(99), *Phys. Rev. E* 55(97)), the Inverse Langevin chain, the Hookean dumbbell and the Rouse chain - to understand the experimental findings. The steady average molecular extension at various Weissenberg numbers is well predicted by the Kramer's chain with 150 beads whereas chains with fewer beads tend to overestimate it. Note the average molecular extension asymptotes quite surprisingly to nearly 1/2 even for extremely large Weissenberg number. We discuss this result on a physical basis. We have further examined the probability distribution of the extension at various Weissenberg numbers using the Kramer's chain and compared it to that of a single DNA molecule. By increasing the number of internal modes we again observe excellent agreement with the experiment. The Power Spectral Density (PSD) of molecular extension for three models (the Kramer's chain, the Wormlike chain and the Inverse Langevin chain) is directly compared to that from the experiments. Both qualitative and quantitative agreement is obtained. To understand the behavior of the PSD at various Weissenberg numbers, we have derived analytic solutions for the PSD for both the Hookean dumbbell and the continuous Rouse model. This analysis shows that the characteristics of the PSD at a given Weissenberg number depend critically on the number of internal modes and a single mode model can not capture the experimental observation. Three different frequency regimes in the PSD are demonstrated in the experiments, the simulations and in the analysis. We use our analytical results to explain these regimes. In the second part of the talk, we present simulation results for start-up shear flow with emphasis on the effect of the changes in the molecular configurations on the transient rheological response. We find that an overshoot in molecular extension is preceded by an overshoot in polymer shear stress. We analyze this in detail.

Tuesday 1:55 Hall of Ideas J

MS2

RHEOLOGY OF A C100 POLYETHYLENE MELT IN PLANAR COUETTE FLOW: A MOLECULAR DYNAMICS STUDY**Jonathan D. Moore¹, Shengting T. Cui¹, Peter T. Cummings², and Hank D. Cochran³**¹Department of Chemical Engineering, University of Tennessee, Knoxville, TN 37996-2200;²Chemical Engineering, Chemistry, and Computer Science, University of Tennessee, Knoxville, TN 37996-2200; ³Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6224

Utilizing a united atom potential model and rRESPA multistep dynamics, we have performed equilibrium and nonequilibrium molecular dynamics simulations of a monodisperse C100 polyethylene melt, including investigation of the transient rheological response to constant shear-rate start-up tests. The model polymer melt exhibits pronounced stress overshoot (dominated by bond-stretching and intermolecular-Lennard-Jones contributions) at the strain value predicted by the reptation model, in striking similarity to melts of longer, entangled polymer governed by reptation motion. At the maximum of shear stress overshoot, the molecular orientational order and the alignment angle are found to be mid-way between those characteristic of Newtonian flow and full alignment with the flow. Doi-Edwards theory is found to be applicable but only by taking into account the shear-rate-dependence of the reptation time. Using the Einstein relations for a fluid subject to a Couette strain field, we have determined self-diffusion coefficients as a function of strain rate and have found that diffusion is significantly enhanced under high shear, a possible explanation for the conjectured shear-rate-dependence of the reptation time.

Tuesday 2:20 Hall of Ideas J

MS3

STOCHASTIC SIMULATION OF A FULL-CHAIN REPTATION MODEL WITH CONSTRAINT RELEASE, CHAIN-LENGTH FLUCTUATIONS, AND CHAIN STRETCHING**Jesper Neergaard¹, Jay D. Schieber¹, and Chi-Chung Hua²**¹Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616; ²Chemical Engineering Department, National Chung Cheng University, Chia-Yi 621, Taiwan

A self-consistent reptation model that includes chain stretching, chain-length fluctuations, segment connectivity, and constraint release (CR) is used to predict transient and steady flows. Quantitative comparisons are made with entangled solution data. The model is able to capture quantitatively all features of experimental shear data considered, including overshoot in both shear and first normal stresses, the strain-rate dependence of the strain magnitude at maximum stress, the steady-state viscosity and first-normal-stress coefficient as functions of shear rate, the viscosity curves for different molecular weight, the transient and steady-state behavior of the extinction angle, and the stress relaxation in cessation of steady shear flow.

Tuesday 2:45 Hall of Ideas J

MS4

RHEOLOGICAL AND OPTICAL PROPERTIES OF ENTANGLED POLYMER UNDER SHEAR AND ELONGATIONAL FLOWS**Chi-Chung Hua and Hsiu-Hsien Chen**

Chemical Engineering Department, National Chung Cheng University, Chia-Yi 621, Taiwan

The rheological and optical properties of entangled linear polymer under shear and elongational flows are investigated via a rigorous full-chain reptation model that accounts for all important effects for entangled systems. The model is able to predict the stress-optical rule under soft flow conditions as well as saturation of birefringence under fast stretching flows. For shear flow, the consistent relation of the Cox-Merz rule and other empirical relations, such as the Laun's rule for the steady-state first normal stress difference and the Gleissl's mirror relation for the transient viscosity growth, are predicted. The model also exhibits a power-law index of 0.85 for the steady-state viscosity, in perfect agreement with various experiments on concentrated polystyrene solutions. For elongational flow, the model predicts strain hardening of the steady-state elongational viscosity, in contrast to the predictions of the original Doi and Edwards model.

Tuesday 3:35 Hall of Ideas J

MS5

QUANTITATIVE PREDICTIONS OF LVE RHEOLOGICAL PROPERTIES OF MONODISPERSE, BIDISPERSE AND POLYDISPERSE ENTANGLED POLYMERS**Cattaleeya Pattamaprom and Ronald G. Larson**

Dept. of Chem. Eng., University of Michigan, Ann Arbor, MI 48109

Recently, van Dyke and coworkers have presented an approximate treatment of constraint release processes that combines both "double reptation" and "tube dilution" concepts. The model does have the virtue that it is in principle equally applicable to linear and star polymers, whether monodisperse or polydisperse, and to mixtures of linears and mixtures of stars. In principle, it is also extendible to the nonlinear regime. In addition, this new model involves no parameters beyond the friction coefficient of Rouse theory and the plateau modulus of reptation theory. Thus, once these two parameters have been specified (for example by fits to data for monodisperse linear polymer of a single molecular weight), predictions can be made for linear polymers of other molecular weights, to stars of any molecular weight, or to polydisperse polymers, without needing to specify other parameters. Here, we test the approach of van Dyke and coworkers in the linear viscoelastic regime by using it to predict literature rheological data for monodisperse linear and star polymers. We use the literature values for the two parameters, monomeric friction coefficient and plateau modulus (where available). The behaviors of linear and star polymers have been correlated by using the same model parameters for both architectures having the same chemical compositions. This is the first time that linear viscoelastic properties are quantitatively predicted with absolutely no adjustable parameters for a variety of monodisperse, bidisperse and polydisperse polymers for both linear and star architectures.

References: Van Dyke T.J. et al. "on the concept of double diffusion an dynamic dilution" (to be submitted)

Tuesday 4:00 Hall of Ideas J

MS6

APPLICATION OF THE SIMPLIFIED CCR MODEL TO POLYDISPERSE LINEAR POLYMERS: TRANSIENT EXTENSIONAL VISCOSITY**Scott D. Mishler¹, Michael K. Lyon², David Mead¹, Ronald G. Larson³, and Masao Doi⁴**¹Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109; ²Exxon Chemical Company, Baytown, TX 77520; ³Dept. of Chem. Eng., University of Michigan, Ann Arbor, MI 48109; ⁴Applied Physics, University of Nagoya, Nagoya, Furo-cho 464, Japan

The DEMG theory can be extended to account for the destruction of binary chain-chain interactions via chain retraction in addition to reptation. This extension of the DEMG model is referred to as "convective constraint release" (CCR) and may be achieved without introducing any additional parameters. If the double reptation mixing rule is applied to this simplified CCR model, the theory can be extended to polydisperse linear systems. This simplified CCR model has been used to make both transient and steady state extensional viscosity predictions for polydisperse linear polystyrene systems under uniaxial extension. In the linear regime, this model collapses to the double reptation model. In the non-linear regime, this model is capable of predicting extension softening quantitatively while extension hardening may be predicted at least qualitatively. The accuracy of these extension hardening predictions is currently under investigation.

Tuesday 4:25 Hall of Ideas J

MS7

2D MAXWELL MODEL**Vyacheslav B. Birman¹ and Wieslaw K. Binienda²**¹Mechanical Engineering, The University of Akron, Akron, OH 44325-3903; ²Civil Engineering, The University of Akron, Akron, OH 44325-3905

Polymer was considered as ensemble of elastic elements with friction between them. Applicability of Newton's law was examined for high shear rate flow of this ensemble. Dependence of viscosity was analyzed and was shown that it decreases with elastic elongation of these elements. 2D Maxwell model was developed for low and high shear rate polymer flow using linear and nonlinear relationship between the shear deformation of the elements and shear stress. For the linear model, the analytical solution was obtained and for the higher order models numerical solution was demonstrated using MATHEMATICA software. Examination with respect to power law demonstrated that linear model is sufficient for the case of the power index approximately 0.5, while higher ordered models are needed for

the cases with power indices deviating significantly from 0.5. Pressure drop in the entrance and exit region of a die is qualitatively explained using this model.

Tuesday 4:50 Hall of Ideas J

MS8

EXPONENTIAL SHEAR FLOW OF POLYMER MELTS

David Venerus

Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616

Strong flows, or flows that tend to induce significant molecular stretching, have been of subject of considerable interest because they often produce rather dramatic rheological responses and can also provide critical tests of rheological constitutive equations. Extensional flows having a large constant Hencky strain rate are strong flows, but can also be difficult to achieve experimentally. Exponential shear flow, where the strain increases exponentially in time, has also been studied with regards to its flow strength classification and its relation to constant strain rate planar elongation flow. In this study, we examine the response of a low-density polyethylene melt in exponential shear and make comparisons with its behavior in constant rate planar elongation using data collected by Meissner and coworkers. New shear stress data and (for the first time) first normal stress difference data in exponential shear are obtained and used in several different material functions that have been previously proposed. Viscosities composed of principal stress differences for the two flows showed no correspondence suggesting that, contrary to previous assertions, exponential shear and constant rate planar elongation flows are fundamentally different. It is further suggested that the presence of vorticity makes exponential shear a weak, rather than strong, flow.

Wednesday Morning

Symposium PL Plenary Lectures

Wednesday 8:30 Lecture Hall PL3

EFFECT OF POLYMER COATS ON THE RHEOLOGY OF STABLE AND FLOCCULATED COLLOIDAL SUSPENSIONS

Jan Mewis

Department of Chemical Engineering, Katholieke Universiteit Leuven, Heverlee B-3001, Belgium

A polymer layer, either grafted or adsorbed on the surface of the particles, will affect the interparticle interactions. By pushing the particles further apart such a layer reduces the attractive forces and eventually can generate stable colloids. The polymer layer will, however, also alter the hydrodynamic forces between neighbouring particles. The interaction potential in polymerically stabilized systems cannot always be calculated directly. Its effect on the rheology is nevertheless quite well understood. Data on several systems are used to indicate the procedures that exist to scale or predict viscosity curves and to correlate them with the dynamic moduli. In this manner the data can be reduced quite accurately to those of Brownian hard spheres. Some differences with other stable systems, occurring at high volume fractions, are discussed. These include the structure during flow, e.g. the formation of bundles oriented in the flow direction. Shear thickening is highly sensitive to the hydrodynamic interactions between particles. This is illustrated by studying the effect of shrinking the polymer coat on this phenomenon. The results of shrinking the coat further, thereby inducing a weak flocculation, are also discussed.

Symposium BC Blends and Block Copolymers

Organizers: Timothy P. Lodge and Paula Moldanaers

Wednesday 9:45 Hall of Ideas G BC1

MORPHOLOGY PREDICTIONS FROM NORMAL STRESS MEASUREMENTS FOR DILUTE IMMISCIBLE POLYMER BLENDS

Mario Minale¹ and Pier Luca Maffettone²

¹Aerospace Engineering, Seconda Università di Napoli, Aversa, Caserta 81031, Italy; ²Material Science and Chemical Engineering, Politecnico di Torino, Torino 10129, Italy

The morphology of dilute blends is characterized by drops dispersed in a continuous matrix. If the blend is dilute enough, the hydrodynamic interactions between the droplets can be neglected; the study of the single drop problem is, therefore, of practical as well as of scientific interest. From the knowledge of the deformation of a single drop induced by the flow, the expression derived by Batchelor (1970), in the case of equi- viscous components, is used to calculate the interfacial contribution to the stress tensor given by the drops. Moreover, given the viscosity ratio, we derive a master curve for the interfacial stress tensor, as a function of the capillary number, where the interfacial stress of any dilute blend collapses. Once the master curve is known, either experimentally or numerically, it can be used to extract morphological information from rheometric measurements. Indeed, for example, known the interfacial first normal stress difference of a given blend at a certain shear rate, from the master curve a capillary number can be estimated, from which a characteristic dimension of the blend morphology is obtained. In addition to

this, the phenomenological model for the deformation of a single drop (Maffettone and Minale, 1998) gives the possibility to have information on the whole state of deformation of the drop, i.e. its orientation angle and the dimensions of its three major axis, once the capillary number is known. A comparison of both the stress and the morphological predictions with experimental data gives satisfactory results.

G. K. Batchelor, *J. Fluid Mech.* 41, 545, (1970).

P. L. Maffettone and M. Minale, *J. Non-Newtonian Fluid Mech.* 78, 227, (1998).

Wednesday 10:10 Hall of Ideas G

BC2

DROPLET VORTICITY ALIGNMENT IN MODEL POLYMER BLENDS UNDER SHEAR

Kalman B. Migler

Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8542

The shear induced deformation of polymeric droplets in an immiscible polymeric matrix is studied using a transparent rotating plate-plate device. We consider the case where the viscosity ratio of the two phases is near unity, but the elasticity ratio of the droplet to the matrix is of order 100. This is achieved by using a matrix of PDMS and a droplet of a PIB based Boger fluid. In the limit of weak shear and small droplets, the droplet alignment is along the shear direction, whereas for strong shear and large droplets, the alignment is along the vorticity direction. There is a range of conditions for which alignment can be along either axis. For droplets aligned along the vorticity axis, the distribution of aspect ratios is broad. The transformation from flow alignment to vorticity alignment upon commencement of shear flow has been observed and correlates with the time scale for development of normal forces in the Boger fluid.

Wednesday 10:35 Hall of Ideas G

BC3

RHEOLOGY OF A VISCOELASTIC EMULSION WITH A LIQUID CRYSTALLINE POLYMER DISPERSED PHASE

Heon Sang Lee and Morton M. Denn

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The steady-shear viscosity and first normal stress difference and the dynamic storage and loss moduli have been measured for an immiscible blend consisting of a thermotropic liquid crystalline polymer dispersed in a thermoplastic fluoropolymer matrix. The components are immiscible and nonreacting. Consistency with the Palierne emulsion theory for viscoelastic blends is possible if and only if the interfacial tension is assumed to become very small for droplets that are comparable in size to a domain or smaller, while retaining the bulk value for larger droplets. Steady shear results are approximately described by the scaling of the Doi-Ohta theory, but there is a significant reduction in the excess shear stress over a finite shear-rate range for the lowest concentration, which contains the smallest droplets.

Wednesday 11:00 Hall of Ideas G

BC4

AN ADAPTATION OF THE DOI-OHTA THEORY TO THE PREDICTIONS OF DROPLET SHAPE CHANGES AND STRESSES IN THE FLOW OF IMMISCIBLE BLENDS

Abdulwahab S. Almusallam, Ronald G. Larson, and Michael J. Solomon

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This study reports a phenomenological model for emulsion and polymer blend rheology for a suspension of Newtonian droplets in a Newtonian liquid. The Doi-Ohta theory [*J. Chem. Phys.* 95: 1242 (1991)] can be adapted to blends with a discontinuous minor phase by replacing its relaxation function with a new function of invariants of the droplet anisotropy tensor. This new function approximately reflects the constancy of droplet volume under conditions in which breakup and coalescence of droplets do not occur. Experiments performed on the relaxation of a single droplet of polybutadiene (PBd) in polydimethylsiloxane (PDMS) after shear step-strain at equi-viscosity conditions confirm observations made earlier by Yamane et. al. [*J. Rheol.* 42: 567 (1998)] that a flat extended droplet relaxes to an axisymmetric shape followed by a slow relaxation to isotropy. The model is designed to predict

these major characteristics of the relaxation of such flat extended droplets. Stress predictions of the model were compared to experimentally obtained shear stress data for start-up and step-strain flows of concentrated blends.

Wednesday 11:25 Hall of Ideas G BC5
MORPHOLOGICAL DEVELOPMENT OF IMMISCIBLE POLYMER BLENDS IN COMPLEX FLOWS

Brian E. Priore and Lynn M. Walker

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Continued growth and expansion of the use of polymer blends for commercial applications hinges on our ability to control morphology of the melt during processing. Our work focuses on the fact that the shear and elongational flows found in these operations have inherently different effects on phase deformation and break-up. To quantify these effects, a slit flow cell with several different contraction ratios has been constructed. The cell provides a non-homogenous, shear dominated flow field with variable amounts of transient elongational pulses. Blend structure was probed through a combination of small angle light scattering and microscopy. For this study, polyisobutene/polydimethylsiloxane blends, in which each component is a room temperature melt that displays Newtonian-like behavior, were utilized. Use of this system allowed comparison to a large volume of data available on morphological changes in simple shear. The morphological findings for flow approaching an abrupt contraction have been examined. Specifically, the effects of viscosity ratio, volumetric flow rate, and contraction geometry (i.e. elongational intensity and duration) were quantified. This analysis provides a better understanding of the effect of transient elongational flow on blend morphology and provides a basis for comparison to investigations involving more complex phenomena including droplet break-up and phase deformation in viscoelastic blends.

Symposium HT Heterogeneous Systems

Organizers: Daniel De Kee, Lisa Mondy and Mike Solomon

Wednesday 9:45 Hall of Ideas H HT1
EFFECTS OF ORDERING IN THE NEAR-WALL REGION ON THE APPARENT VISCOSITY OF SUSPENSIONS

Jason G. Kralj, Allen E. Kaiser, James R. Abbott, Alan L. Graham, and Jeremy W. Leggoe
 Chemical Engineering, Texas Tech University, Lubbock, TX 79409

The objective of this study was to investigate the effect of wall induced structure on the properties of concentrated suspensions of monomodal, neutrally buoyant spheres in Newtonian liquids. In these experiments, falling balls are used as momentum tracers to investigate suspension properties and falling ball behavior at locations ranging from the centerline to the walls of the containing cylinder. The principle experimental parameters are the relative geometries of the suspended spheres, falling spheres, and the containing cylinder, and the concentration of suspended particles. Experimental results for pure Newtonian fluids are in excellent agreement with existing numerical and analytical predictions. Concentrated suspensions, however, have been found to exhibit markedly different behavior. The data indicate that in the near-wall region the ball velocity is less than would be expected in a pure fluid of the same effective viscosity. Effects deriving from wall induced particle ordering appear to be responsible for an increase in effective viscosity in the near-wall region. These wall effects extend much further into the suspension and are much larger in magnitude than expected for a pure fluid.

Wednesday 10:10 Hall of Ideas H HT2
CONCENTRATED SUSPENSION FLOW INTO A CONTRACTION

Jeffrey F. Morris and Ryan M. Miller

Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100

The flow of a concentrated suspension undergoing two-dimensional channel flow with a contraction of the available flow width has been examined through bulk flow modeling. Contractions in flow diameter of 2:1 and 4:1 ratio

(before:after contraction) are considered. The bulk flow model is based upon the suspension balance approach, with a rheological model for the suspension which includes shear-induced viscous normal stresses. Emphasis is placed in this study upon the maldistribution of particles caused by the flow, especially accumulation in the lip vortex and the subsequent change in structure of this vortex.

Wednesday 10:35 Hall of Ideas H HT3
SHEAR-INDUCED NORMAL STRESSES AND DIFFUSIVITIES IN A DILUTE SUSPENSION OF NON-BROWNIAN HARD SPHERES

Isidro E. Zarraga and David T. Leighton

Department of Chemical Engineering, University of Notre Dame, Notre Dame, IN 46556

The complete set of normal stresses in a dilute suspension of hard spheres undergoing simple shear at low Reynolds number is calculated using a path integration approach for the cases where the concentration is uniform and where a small gradient in concentration is present. As expected, the normal stresses are seen to be a strong function of $e_s = 2(b-a)/a$, where b is the hard sphere radius and a is the particle radius. The normal stress differences N_1 and N_2 , as well as the osmotic pressure P , are all negative, with $|P|/|N_2|$ and N_1 approaches 0 as e_s approaches infinity. For $e_s \ll 1$, the asymmetry in the pair distribution function due to a depletion of particles in the extensional side of a pair interaction leads to $|N_1|/|N_2|$. On the other hand, for e_s approaching infinity, the additional stresslet induced when hard sphere radii touch dominates the stress generated in the suspension, and N_2 becomes the prevailing normal stress difference. The self and gradient diffusivities are calculated using da Cunha and Hinch's [J. Fluid Mech. 309, 211 (1996)] trajectory method. Numerical results for the diffusivities are in agreement with those obtained by da Cunha and Hinch for $e_s < 0.08$ while matching the analytically obtained diffusivities for large e_s . Finally, we calculate the normal stress in the presence of a small concentration gradient and compare two models of migration for this case, namely the suspension balance model of Nott and Brady [J. Fluid Mech. 275, 157 (1994)] and the diffusive flux model first introduced by Leighton and Acrivos [J. Fluid Mech. 181, 415 (1987)]. The results show that although the two models equally describe migration in the presence of a concentration gradient for the case where $b \gg a$ (or e_s approaches infinity), the two models are shown to be quantitatively different when near-field hydrodynamics are relevant.

Wednesday 11:00 Hall of Ideas H HT4
FRAME-INVARIANT MODELS FOR SUSPENSION FLOWS

Zhiwu Fang¹, Andrea A. Mammoli¹, John F. Brady², Marc S. Ingber¹, and Lisa A. Mondy³

¹Mechanical Engineering, University of New Mexico, Albuquerque, NM 87131; ²Chemical Engineering, California Institute of Technology, Pasadena, CA 91125; ³Sandia National Laboratories, Albuquerque, NM 87185

Models to describe the transport of particles in suspensions flows have progressed considerably during the last 10 years. In one class of models, the motion of particles within the suspension is described through a diffusion equation based on shear rate gradient. In the other main class, the stress in the particle phase is described by a constitutive equation, and particle transport is driven by gradients in this stress. Neither type of model provides a complete description of the anisotropy of the particle interactions, which results in anisotropic diffusion in the former models, and in normal stress differences in the latter. Because of this, the prediction of steady-state particle concentration in torsional flow between parallel plates does not match experimental data. Here, the diffusive flux model is re-written with respect to a frame-invariant tensor, which is a function of the local flow field. The particle stress model is modified in a similar manner. Using this new formulation, the shortcomings of the unmodified models are eliminated in a unified manner. Results that are in excellent agreement with experimental data are obtained for consistent sets of empirical constants, without the need for ad hoc additional terms.

Wednesday 11:25 Hall of Ideas H

HT5

RHEOLOGICAL PROPERTIES OF CONCENTRATED SUSPENSIONS OF NON-COLLOIDAL PARTICLES**Frederic Cotton, Pierre J. Carreau, and Michel Perrier**

Center for Applied Research on Polymers, Ecole Polytechnique, Montreal, QC H3C3A7, Canada

Although considerable efforts have been devoted to the determination of the rheological properties of concentrated suspensions, the behavior of concentrated suspensions of non-colloidal particles is still far from being understood. A new approach has been developed with the help of the newest generation of high precision rheometers. Instead of using the traditional shear rate sweep method, that is quite disruptive or even destructive for the particle arrangement in suspensions, softer measurement strategies (low stress creep tests and low strain oscillatory measurements) have been used for elucidating phenomena encountered in concentrated suspensions. These strategies have been tested on model suspensions (hollow glass beads and plastic particles in a low molecular weight polybutene). The rheological measurements are shown to be sensitive to sample preparation and conditioning using small amplitude oscillatory shear must be applied prior to any rheological determination. The results for concentrated suspensions show that a structure is induced at strain values around 1. A simple mechanistic model is proposed to explain the results. Finally, the non-linear viscoelastic behavior is discussed in light of Lissajou figures and higher harmonics in the stress or strain responses for oscillatory shear experiments.

Symposium SF Shear-free Flows

Organizers: John Wiest, Kurt W. Koelling and David James

Wednesday 9:45 Hall of Ideas I

SF1

AN INTERLABORATORY COMPARISON OF MEASUREMENTS FROM FILAMENT-STRETCHING RHEOMETERS USING COMMON TEST FLUIDS**Shelley L. Anna¹, Gareth H. McKinley¹, D. A. Nguyen², Tam Sridhar², Susan J. Muller³, Jin Huang⁴, and David F. James⁴**¹Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139;²Department of Chemical Engineering, Monash University, Clayton, Victoria, Australia;³Department of Chemical Engineering, University of California - Berkeley, Berkeley, CA 94720;⁴Mechanical and Industrial Engineering, University of Toronto, Toronto M5S 3G8, Canada

Following the development of a filament-stretching extensional rheometer at Monash University, similar rheometers were designed and built in other laboratories - instruments based on the same concept but realized in different ways. To help validate the basic technique, a collaborative program was undertaken to compare results from several of the instruments. First, three test fluids were prepared at Berkeley; they were characterized in steady and transient shear flows there and at MIT, and then tested in extensional rheometers at MIT, Monash and Toronto. Each fluid was a constant-viscosity solution of a narrow-distribution polystyrene in oligomeric polystyrene. The molecular weights of the solutes were 2, 7, and 20 million, and the polymer concentration in each fluid was the same, 0.05 wt%. From linear viscoelastic measurements and normal stress relaxation data, the Zimm relaxation times of the fluids were found to be 4, 32 and 155 seconds respectively. The scaling of relaxation times with molecular weight indicates better than theta solvent quality, a finding consistent with independent intrinsic viscometry measurements of equilibrium coil size. Each fluid was tested in the three filament stretching rheometers at the same Deborah numbers, spanning a range of extensional rates. Despite the variations in instrument design and the general difficulty of the technique, plots of the transient Trouton ratio versus strain from the three instruments are in good agreement.

Wednesday 10:10 Hall of Ideas I

SF2

BIREFRINGENCE AND STRESS IN UNIAXIAL EXTENSION OF POLYMER SOLUTIONS**Tam Sridhar¹, D. A. Nguyen¹, and Gerald G. Fuller²**¹Department of Chemical Engineering, Monash University, Clayton, Victoria, Australia;²Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025

Simultaneous measurements of extensional stresses and birefringence are rare, especially for polymer solutions. This paper reports such measurements using the filament stretching rheometer and a phase modulated birefringence system. Both the extensional viscosity and the birefringence increase monotonically with strain and reach a plateau. Estimates of this saturation value for birefringence, using Peterlin's formula for birefringence of fully extended polymer chain are much higher than observed. Similarly estimates of the saturation value of the extensional viscosity using Batchelor's formula for suspensions of elongated fibres are much higher than observed. Reasons for the inability of the flow field to fully unravel the polymer chain are examined using published Brownian dynamics simulations.

Simultaneous measurements of stress and birefringence during relaxation indicate that the birefringence decays much more slowly than the stress. The stress-birefringence data show a pronounced hysteresis as documented by Spiegelberg and McKinley. The failure of the stress optic coefficient in strong flows is noted.

Experiments were also performed wherein the strain was increased linearly with time, then held constant for a short period before being increased again. The response of the stress and birefringence in such experiments is dramatically different and can be traced to the different configurations obtained during stretching and relaxation. The results cast doubt on the appropriateness of pre averaging the non-linear terms in the constitutive equations.

Wednesday 10:35 Hall of Ideas I

SF3

THE EFFECT OF A KNOWN PRESHEAR HISTORY ON THE TRANSIENT STRESS GROWTH IN UNIAXIAL ELONGATIONAL FLOWS OF DILUTE POLYSTYRENE SOLUTIONS**Shelley L. Anna¹, Minwu Yao², and Gareth H. McKinley³**¹Division of Engineering and Applied Science, Harvard University, Cambridge, MA 02139;²Goodyear Technical Center, Akron, OH 44309-3531; ³Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

We investigate the effect of imposing a controlled pre-shear history on the transient uniaxial elongational stress growth in a dilute polystyrene solution. We use a Filament Stretching Rheometer (FiSER) modified to apply either a steady shear flow perpendicular to the direction of uniaxial stretching, or an oscillatory shear flow parallel to the direction of stretching, immediately before applying a transient uniaxial elongational flow. The ideal elastic test fluid we study consists of a dilute solution (0.025 wt.%) of high molecular weight monodisperse polystyrene ($MW = 2.25 \times 10^6$ g/mol) dissolved in a Newtonian styrene oil. This constant-viscosity Boger fluid has been fully characterized using standard cone-and-plate rheometry, and the small-amplitude oscillatory shear data is well described by a Zimm spectrum of relaxation times. We compare the measured transient stress growth profiles for the uniaxial elongational flow with no pre-shearing to similar profiles obtained after imposing known, controlled pre-shear histories of the types described above. For a fixed uniaxial elongation rate or Deborah number, we observe that the onset of strain hardening and the transient stress growth characteristics change significantly as the Weissenberg number characterizing the strength of the pre-shear flow increases, but that the final, steady-state Trouton ratio is only weakly affected. We also investigate the role of fluid memory of this preshear history on the long-time behavior of the fluid column by studying the filament breakup behavior after cessation of stretching as a function of this Weissenberg number and the imposed Hencky strain. Finally, we compare the transient stress growth profiles for both modes of pre-shear to corresponding predictions for FENE-type dumbbell models using both time-dependent finite-element simulations and also a one-dimensional theory derived from a slender filament approximation.

Wednesday 11:00 Hall of Ideas I

SF4

A NEW MODEL SUITABLE FOR FLOWS WITH STRONG EXTENSIONAL COMPONENTS**Indranil Ghosh¹, Gareth H. McKinley², Robert A. Brown¹, and Robert C. Armstrong¹**¹Chemical Engineering, M.I.T., Cambridge, MA 02139; ²Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

Recent work [1] has shown that experimentally observed hysteresis effects in elongational flows can be qualitatively captured by the FENE dumbbell and the Kramers chain. However, quantitative comparisons between the two models [2], reveal that the FENE force law, which assumes that each segment of the chain is in pseudo-equilibrium, does not hold in strong extensional flows. In fact, the end-to-forces are shown to exceed FENE levels, and the extent of the deviation increases with strain. This insight explains why the FENE dumbbell predicts a slower stress growth than the Kramers chain. It also explains the absence of configurational hysteresis effects in the FENE dumbbell model.

As described above, the Kramers chain captures much more physics than the FENE dumbbell in elongation, but Kramers chain simulations are very computationally intensive and cannot be used for complex flow calculations in a CONNFESSITT- type context. This work aims to satisfy the need for a one-mode model that incorporates the fine scale physics of Kramers chains, but is amenable to complex flow calculations. We develop a constitutive equation that views the molecule as a set of identical segments that are each small enough to be stretching reversibly. The resulting model gives very good predictions of stress growth and hysteresis.

We also investigate more complex flow kinematics such as mixed shear and elongation and extend the new model to agree with Kramers chains simulations under these flow conditions. The final constitutive equation is therefore capable of modeling polymer behavior in more general flows.

[1] Doyle P.S., Shaqfeh E.S.G., McKinley G.H., and Spiegelberg S.H., JNNFM 76(1-3),81 (1998)

[2] Ghosh I., McKinley G.H., Brown R.A. and Armstrong R.C., preprint, (1999).

Wednesday 11:25 Hall of Ideas I

SF5

KINEMATIC DEPENDENT ANISOTROPY IN STRONG FLOWS OF DILUTE POLYMER SOLUTIONS**John M. Wiest**

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

Shearfree components are significant in many technologically important flows. Furthermore, elongational flow experiments are becoming much more accurate and less ambiguous. These flow experiments are elucidating behavior that is not captured by simple molecular models. This, in turn, is stimulating the development of more detailed molecular models that incorporate a wide variety of ideas (e.g., multiple links, nonlinear spring forces, internal viscosity). The constitutive equations obtained from these models tend to be quite complicated, but numerical analysis of complicated flow requires relatively simple constitutive relations. There is a need for relatively simple models that capture the most significant behavior of the molecules. Dumbbell models yield sufficiently simple constitutive equations, but they do not describe all of the observed behavior - primarily because they admit only one fundamental time scale. Here we explore an alternative dumbbell model that attempts to address the fact that each 'bead' of the dumbbell represents half of the polymer molecule and can be deformed by the flow. This gives rise to an anisotropic drag on the bead that depends upon the kinematics of the flow.

Symposium MS Rheology of Polymer Melts and Solutions

Organizers: John L. Schrag and Faith Morrison

Wednesday 9:45 Hall of Ideas J MS9

ON THE CONSTITUTIVE MODELING OF LDPE MELT I

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LDPE Melt I is, rheologically, perhaps the most well characterized polymer. Different batches of the same resin referred to as IUPAC A and IUPAC X, have virtually indistinguishable rheological properties. This polymer, with its long side branches, has also proven to be most difficult for viscoelastic modeling. The first successful modeling the rheological properties of LDPE Melt I was attempted in paper [1], however with the use of a thermodynamically inconsistent and Hadamard unstable model. The second attempt to model the rheological behavior of LDPE Melt I was undertaken in paper [2] where the stable constitutive equations were used. In this paper, all the shearing and simple elongational experiments available have been well described. However, the authors of [2] were unaware of hardening effects in planar elongation experiments, which their simplified model could not predict. This report demonstrates the new version of a stable rheological modeling proposed generally in paper [2]. This modeling is capable to describe all the available data for the LDPE Melt I. They include hardening effects for both simple and planar elongation flows, and irreversible phenomena related to mechano-degradation of the material, which have been reported and roughly modeled in paper [3].

References: 1. M. H. Wagner and H. M. Laun, *Rheol. Acta*, 17, 138-148 (1978); 2. M. Simhambhatla and A. I. Leonov, *Rheol. Acta*, 34, 259-273 (1995); 3. A. I. Leonov and A. N. Prokunin, *Rheol. Acta*, 22, 137-150 (1983).

Wednesday 10:10 Hall of Ideas J MS10

DIAGNOSING LONG-CHAIN BRANCHING IN POLYETHYLENES

Jay Janzen¹ and Ralph H. Colby²

¹Phillips Petroleum Co., Bartlesville, OK 74004; ²Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802-5007

We describe a novel method for assessing sparse long-chain branching in synthetic polymers such as high-density polyethylene at levels far below the limits of detectability by the usual methods of solution viscometry, size-exclusion chromatography, and NMR spectrometry on solutions. The new method exploits the extreme sensitivity of melt Newtonian viscosity to random branching architecture, along with the systematic phenomenological description thereof developed recently in fundamental studies by Lusignan, et al. The method satisfies the only validation criterion presently available to us: it finds long-branch contents in quantitative agreement with stoichiometric yields calculated for several series of linear precursor polyethylenes treated with very low levels of peroxide.

Wednesday 10:35 Hall of Ideas J MS11

THE EFFECT OF PRESSURE ON THE VISCOSITY OF LONG CHAIN BRANCHED METALLOCENE POLYETHYLENES

Stewart A. Mcglashan, Paula M. Wood-Adams, and John M. Dealy

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The pressures reached in some plastics forming processes, particularly injection molding, are high enough to have a strong effect on the rheological properties of molten polymers. But because of the difficulty of making measurements at high pressures there have been very few reports of rheological properties at these conditions. A recently developed high pressure sliding plate makes it possible to study the effect of pressure on the response of molten polymers to a wide range of shearing deformations. Both the pressure and the shear strain are uniform.

This study concentrated on the effect of pressure on the viscosity of long chain branched polyethylenes. Measurements were made at 170C over a range of pressures from atmospheric to 70MPa. A series of constrained

geometry catalyzed polymers (a class of mPE) was studied. mPEs were ideally suited to this type of study because of their unique and precisely controlled molecular structure. This series of mPEs consisted of four homopolymers with increasing degrees of long chain branching. Using these materials it was possible to study the effect of degree of long chain branching on viscosity at several pressures while keeping constant the molecular weight and polydispersity.

The results reveal that the sensitivity of viscosity to pressure is significantly influenced by degree of long chain branching and that the magnitude of this influence depends on the level of branching. The range of shear rates achievable was limited on the high end by melt flow instabilities such as slip and cavitation and at the low end by low stress signals.

Wednesday 11:00 Hall of Ideas J

MS12

THE RHEOLOGY OF POLYMERIC FLUIDS AT ELEVATED PRESSURES

David M. Binding, Mark A. Couch, and Ken Walters

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Accepted wisdom, and recent experimental data support the view that multigrade oils are more efficient lubricants than their single-grade counterparts, (over and above the obvious viscosity/temperature improvement) but there has been a long running and, often, contradictory debate as to the most likely cause for the improvement. In this debate, pressure has been increasingly seen as one potentially important variable. Our background studies have revealed that existing rheometrical work on the pressure dependence of viscoelasticity in polymeric liquids is somewhat contradictory, with no clear picture emerging on the scale of any effect.

To help clarify this situation, a capillary rheometer is adapted to permit measurements of the rheological properties of lubricants at elevated pressures (up to 80MPa). The pressure drop in the capillary section of the rheometer is used to provide shear viscosity data and the 'entrance pressure loss' in the contraction flow before the capillary section is used to estimate the extensional viscosity, employing ideas pioneered by Cogswell and Binding.

Experimental results on single grade oils (which are near-Newtonian in response) are used to validate procedures, and attention is then given to multigrade oils in the 15W/40 category, both in a virgin and a degraded state. A substantial pressure dependence of the Trouton ratio for the virgin oils is demonstrated, and this is shown to be greatly reduced in the degraded samples. The relevance of the data to the performance of multigrade oils in practical Journal-Bearing situations is emphasised.

The present experiments have shown conclusively that pressure has a stronger influence on the viscoelastic properties of multigrade oils than would be anticipated on the basis of shear viscosity alone. One consequence of this is that, in a practical bearing situation, one can anticipate an enhanced effect of viscoelasticity over that predicted for ambient pressure conditions.

Wednesday 11:25 Hall of Ideas J

MS13

DYNAMICS OF SULFONATED STYRENE-ETHYLENE-BUTENE RANDOM IONOMER MELTS

Neena K. Tierney and Richard A. Register

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The melt flow behavior of ionomers (polymers that contain a small amount of covalently bound ionic functionality) is dramatically affected by the ionic aggregates that are formed within the hydrocarbon matrix. These aggregates act as reversible crosslinks that retard the motion of the polymer chains at short times, resulting in orders-of- magnitude increases in viscosity and terminal relaxation time of the polymer over those of its nonionic counterpart. We investigate a series of sulfonated styrene-ethylene- butene random ionomers of varying molecular weights and number of ionic groups per chain. Random styrene-butadiene copolymers with low polydispersities were synthesized via anionic polymerization, from which ionomers were prepared by selective hydrogenation of the butadiene units, followed by partial sulfonation of the styrene units. By conducting rheological measurements over a wide range of temperatures, we are able to access the rubbery and terminal flow regions. All ionomers show two peaks in the loss modulus, but the two relaxation mechanisms do not have the same dependence upon temperature; thus, all ionomers studied exhibit thermorheological complexity. In addition, we find that the zero-shear viscosity

Wednesday Morning

increases by up to 6 orders of magnitude with the addition of a few ionic groups, and it has an exponential type dependence on the number of ionic groups per chain.

Wednesday Afternoon

Symposium BC Blends and Block Copolymers

Organizers: Timothy P. Lodge and Paula Moldanaers

Wednesday 1:30 Hall of Ideas G

BC6

MONITORING BLEND COALESCENCE VIA PARTICLE SIZE DISTRIBUTION AND RHEOLOGY

Suping Lyu, Frank S. Bates, and Christopher W. Macosko

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High density polyethylene (HDPE) was dispersed in polystyrene (PS) melts at high shear rate. The shear rate was then decreased and coalescence of the HDPE drops monitored by quenching and dissolving away the PS matrix with methylene chloride. The HDPE particles were filtered out, redispersed in toluene and their size distribution measured by light scattering (LS 230, Coulter). Increasing HDPE volume fraction increased coalescence rate, while increasing the ratio of HDPE-PS viscosity slowed it slightly. Adding a small amount of PS-PE diblock copolymer greatly suppressed coalescence. Steady shear viscosity and the dynamic moduli were measured during coalescence and correlated to the evolving particle size distribution.

Wednesday 1:55 Hall of Ideas G

BC7

THE INFLUENCE OF BLOCK COPOLYMER ON THE PHENOMENA OF COLLISION AND FILM DRAINAGE GOVERNING DROPLET COALESCENCE IN IMMISCIBLE BLENDS

Steven D. Hudson, Alex M. Jamieson, Ica Manas-Zloczower, Anthony R. Ramic, Julia C. Stehlin, Brian E. Burkhart, and Wararat Sophanowong

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Shear-induced droplet breakup and coalescence in binary and emulsified polymer blends were investigated by optical microscopy during simple shearing. Coalescence consists of two steps: first, droplet collision and then drainage of the matrix film between the droplets. Analysis of coalescence kinetics reveals that the coalescence rate may be limited by one or both of these processes. When the droplets are much smaller than their steady state size, coalescence is collision limited, and the droplets grow exponentially with increasing shear strain. The growth rate is also proportional to the dispersed phase concentration and the so-called collision efficiency. Therefore, under these conditions, the collision efficiency, and the effect of hydrodynamic interaction between droplets, can be evaluated. When the droplets become larger, film drainage also becomes important. The departure from the collision limit is independent of composition, because to first order it stems from binary droplet interactions. Therefore, for the first time, an experimental procedure and analysis method have been developed that are able to measure the effect of collision efficiency and film drainage independently.

For mixtures containing a block copolymer, the amount of copolymer adsorbed to the interface was calculated according to Semenov's theory. These calculations predict a relative reduction in interfacial tension that is consistent with application of the Taylor equation to the observed breakup behavior. As expected, a relatively large amount of copolymer adsorbed to the interface is required to reduce interfacial tension significantly. Most strikingly, a much smaller amount of copolymer adsorbed to the interface is dramatically effective in suppressing coalescence. It does so by effectively decreasing both collision and film drainage efficiencies.

The authors gratefully acknowledge the financial support of the Goodyear Tire and Rubber Co., GE plastics, and NSF grant CTS-9731502.

Wednesday 2:20 Hall of Ideas G

BC8

A NEW STRESS-OPTICAL RELATION IN TWO-PHASE LIQUID/LIQUID MIXTURES

Peter Van Puyvelde, Paula Moldenaers, and Jan Mewis

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In a flowing two-phasic fluid mixture, the contribution of the interface to the stress tensor is proportional to an interfacial anisotropy tensor. Here it is demonstrated experimentally that scattering dichroism under various flow conditions is also proportional to this anisotropy tensor. The flow conditions studied include steady state shear flow, sudden changes in shear rate, relaxation after cessation of flow and oscillatory shear flow. These flow histories lead to a wide variety in morphologies of the dispersed phase ranging from a perturbed spherical shape, over undulating liquid threads to highly elongated droplets. For all morphologies the same proportionality factor is obtained between the scattering dichroism and the interfacial anisotropy. As scattering dichroism is not only governed by the shape of the dispersed phase but also by its size, a size correction for the proportionality constant is proposed in order to extend the applicability of this relation to a wide range of shear rates. In addition, for sudden changes in shear rate the proportionality between stresses and dichroism could be obtained on a theoretical basis by combining calculations of the dichroism from a scattering theory with calculations of the dichroism based on the interfacial anisotropy tensor. In summary the experiments and the theoretical result provide evidence for a stress-optical relation between scattering dichroism and stresses in two-phase fluid/fluid mixtures.

Wednesday 2:45 Hall of Ideas G

BC9

EXAMINING THE DYNAMIC RHEOLOGICAL BEHAVIOR OF AN LCST POLYMER BLEND IN THE TWO-PHASE REGION

Diana B. Hess and Susan J. Muller

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

The phase separation of three different blends of moderate-molecular weight polystyrene (PS) and polyvinylmethylether (PVME) has been studied under oscillatory shear in a Rheo-SALS device which combines a rheometer with a small-angle light scattering (SALS) assembly. For each blend, three compositions at different fixed distances from the critical point were chosen for study. Frequency sweeps were performed at several temperatures on both sides of the cloud point curve. A number of interesting behaviors were perceived in the two-phase region. As predicted by the Paliarne model, an augmentation in the low-frequency G' response, with no corresponding increase in G'' , was observed for all blends. A loss of time-temperature superposition over the entire frequency range was also seen in both G' and G'' at the higher temperatures and volume fractions of PVME. Under the conditions when time-temperature superposition with the single-phase curves was observed, the shift factors for the two-phase blend always displayed a positive deviation from those predicted from the single-phase WLF fit. The Paliarne model semi-quantitatively describes the observed rheology when the PVME-rich phase is the major constituent, but it fails when the PS-rich phase is the major constituent. SALS and microscopy results will also be presented.

Wednesday 3:35 Hall of Ideas G

BC10

STRESS-INDUCED MORPHOLOGICAL TRANSITION IN THE BODY-CENTERED CUBIC PHASE OF BLOCK COPOLYMER MELTS

John M. Sebastian, Chiajen Lai, Richard A. Register, and William W. Graessley

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The rheology of polystyrene-polyisoprene and polystyrene-poly(ethylene-*alt*-propylene) block copolymer melts having a body-centered cubic (BCC) morphology has been studied under steady shear with a controlled stress rheometer. Testing at temperatures below the order-disorder transition (ODT) and at low stresses ($< 10^3$ dyne/cm²) indicates that both diblock and triblock copolymer systems manifest extremely large ($\sim 10^8$ Poise) but finite Newtonian viscosities. Corresponding small-angle x-ray scattering (SAXS) indicates that at these low deformation rates the BCC lattice remains intact, suggesting that the flow mechanism is due to the motion of large-scale structures such as grains. This Newtonian region ends abruptly when a critical shear stress ($\sim 2 \times 10^3$ dyne/cm²) is

reached, and the viscosity plummets by almost four orders of magnitude with only a factor of three increase in stress. Upon further increase in shear stress, the viscosity reaches a weakly shear-thinning regime very similar to the disordered state that is obtained by heating the block copolymer above its ODT. SAXS patterns of samples quenched from this high-stress region reveal the absence of any BCC lattice order, reflecting a "shear-disordering" process has occurred. If the polymer is held at a low ($< 10^3$ dyne/cm²) or zero shear stress after being shear-disordered, it will return to its original rheological and morphological state, following kinetics identical to the ordering process which occurs after a thermal quench from above the ODT. Shear-disordering, therefore, produces a metastable state identical to that generated by thermal disordering.

Wednesday 4:00 Hall of Ideas G

BC11

STRUCTURE AND DYNAMICS OF GIANT BLOCK COPOLYMER MICELLES

Dimitris Vlassopoulos¹, Reinhard Sigel¹, George Fytas¹, Stergios Pispas², and Nikos Hadjichristidis²

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Using specially synthesized ultra-high molecular weight asymmetric diblock copolymers of styrene and isoprene in selective solvents for either block, we create giant polymeric micelles of typical diameter of 700 nm and aggregation number of 2000. These ultrasoft model colloidal spheres exhibit liquid-like ordering with a structural peak in the range of light scattering wave vectors (q), thus allowing the exploration of their dynamic structure factor $S(q,t)$ and identification of the contributing relaxation mechanisms using photon correlation spectroscopy and small amplitude oscillatory shear rheology. The main findings are: (i) At the structural peak the collective density fluctuations do not exhibit the anticipated slowing down, in sharp contrast to the respective behavior of hard colloidal spheres and diblock copolymer solutions. (ii) The long-time diffusion coefficient follows the same concentration dependence as the zero-shear viscosity at concentrations below the crystallization transition, in analogy to the behavior of hard spheres. We propose that polymeric-layer mediated repulsive steric forces, affecting the system's mobility, govern the physics of this unexpected behavior. These layers give rise to extra dynamic processes, typically grafted arm relaxation, which are not present in hard sphere suspensions and differ from block copolymer solution behavior.

Wednesday 4:25 Hall of Ideas G

BC12

ORIENTATION OF POLYMERIC HIERACHICAL NANOSTRUCTERS BY OSCILLATORY SHEAR FLOW

Karin de Moel¹, Riikka Mäkinen², Janne Ruokolainen², Olli Ikkala², and Gerrit ten Brinke¹

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Self-organized supramolecular polymeric materials show nanoscale order at multiple length scales. This allows the preparation of functional materials, as shown recently by us by complexing block copolymers with tailored amphiphiles(1). Here we report on the first efforts to macroscopically orient these hierarchical self-organized block copolymer-amphiphile structures by imposing oscillatory shear flow. We characterize the structures using small angle X-ray scattering, in combination with an area detector, with simultaneous rheology.

References: 1. J. Ruokolainen, R. Mäkinen, M. Torkkeli, R. Serimaa, T. Mäkelä, G. ten Brinke and O. Ikkala, Science 280, 557, 1998

Wednesday 4:50 Hall of Ideas G

BC13

RHEOLOGY OF LAYERED SILICATE BASED BLOCK COPOLYMER NANOCOMPOSITE

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The rheology of layered silicate based block copolymer nanocomposites is investigated using linear viscoelastic measurements in oscillatory shear with small strain amplitudes. Two different kinds of SBS(polystyrene-block-polybutadiene-block-polystyrene) copolymer with varying amounts of layered silicate(montmorillonite) are examined. The storage(G^*) and loss (G^{**}) moduli for intercalated and exfoliated nanocomposites increase at all frequencies with increasing silicate loading, consistent with previous findings with conventionally filled polymer systems. But, the power-law dependence of storage(G^*) and loss (G^{**}) moduli of intercalated nanocomposites in the terminal zone is different from that observed in SBS block copolymer and decreases with increasing silicate loading. The rheological behaviors of polymer chains either in exfoliated hybrids or in close proximity(intercalated hybrids) to the host surfaces are discussed relating their microstructure. The microstructural evolution of nanocomposites (from immiscible state to intercalated state or to exfoliated state) can be also monitored by viscoelastic measurement in oscillatory shear mode.

**Symposium HT
Heterogeneous Systems**

Organizers: Daniel De Kee, Lisa Mondy and Mike Solomon

Wednesday 1:30 Hall of Ideas H

HT6

SIMULATION OF MONODISPERSE SUSPENSION FLOW

Amy Sun and Rekha Rao

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A major goal of modeling concentrated suspension flow is the ability to predict transient evolution of particle migration under various flow configurations. Using a two-dimensional finite-element program (GOMA), this work first examines the transient behavior of neutrally buoyant particle migration in concentric Couette as well as torsional flow geometries.

While theoretically we expect invariance w.r.t. flow fields, the particle-flux model based on the Couette studies of Phillips (1992) and Leighton & Acrivos (1987) has not yet yielded results consistent with parallel-plate and cone-and-plate rheometer studies. Through the differences in the model parameters regressed from individual Couette and torsional flow experiments, we have examined the degree of inconsistency and considered additional mechanisms in the model. For non-neutrally buoyant particles, the particle-flux equation is further complicated by the gravitational field. The results of validation studies for floating particles will also be discussed.

Wednesday 1:55 Hall of Ideas H

HT7

HIGH FREQUENCY RHEOLOGY OF CONCENTRATED CHARGE-STABILIZED POLYMER DISPERSIONS

Johan Bergenholtz¹, Frank M. Horn², Walter Richtering², Norman J. Wagner³, and Norbert Willenbacher⁴

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The high frequency viscoelastic properties of charge-stabilized PS latexes have been characterized by means of torsional resonance oscillation and are compared to steady high shear as well as low frequency oscillatory shear data from rotational rheometry. The dependence of the rheological properties on particle size a , salt content and volume

fraction ϕ is discussed. It is demonstrated that the high frequency viscosity η'_{inf} is always lower than the high shear viscosity η_{inf} , this can be traced back to the shear alteration of the microstructure. Nevertheless, both quantities are dominated by hydrodynamic interactions as evidenced by their insensitivity to particle size and salt concentration. The plateau modulus G_0 determined by low frequency oscillatory shear underestimates the true high frequency modulus G'_{inf} as determined by torsional resonance oscillation. The apparent colloidal surface charges extracted from the G'_{inf} data fall onto a master curve independent of particle size and increase systematically with increasing κ^*a . The results are compared with electrophoretic mobility data, critical coagulation concentration (ccc) measurements. Finally, an effective surface charge is deduced by comparing the effective particle diameter calculated from perturbation theory to the corresponding data extracted from a hard sphere mapping of the zero shear viscosity of the charged latexes.

Wednesday 2:20 Hall of Ideas H

HT8

THE RHEOLOGY AND MICROSTRUCTURE AT THE SHEAR THICKENING TRANSITION FOR NEAR HARD SPHERE COLLOIDAL DISPERSIONS

Brent Maranzano and Norman J. Wagner

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Accurate predictions of the rheology for hard sphere colloidal dispersions are industrially important, especially with regards to predicting the onset of shear thickening. Predictions of the rheology for concentrated dispersions are aided by understanding the relationship between the microstructure and the rheology. In this work we investigate the microstructure evolution of near hard sphere colloidal dispersions in the vicinity of the shear thinning - shear thickening transition. The microstructure is studied using several rheo-optical techniques: Flow Small Angle Light Scattering and Flow Small Angle Neutron Scattering are used to measure the structure factor under flow, which reflects the increasing order or disorder of the suspension and can be related to the formation of hydro-clusters. Flow dichroism experiments are used to probe structural anisotropy, which can be connected to the stresses resulting from the interparticle potential. The effect of particle size on the rheology and the onset of shear thickening is tested by varying the particle diameter from 100 nm to 1mm and determining a scaling law for the prediction of the shear thickening transition as a function of particle size. The effects of polydispersity on the rheology is also studied by mixing suspensions of various particle sizes. The results demonstrate the direct relationship between microstructure and rheology and suggest possible methods to modify the rheology of near hard sphere colloidal dispersions.

Wednesday 2:45 Hall of Ideas H

HT9

STRUCTURAL EVOLUTION DURING COLLOIDAL GEL FORMATION: POWER LAW RELAXATION AND SUPERPOSITION OF VISCOELASTIC SPECTRA

Robert J. Butera

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Previously we have shown that flocculated colloidal fluids can pass through a power law relaxation regime that is phenomenologically similar to that exhibited by crosslinking polymers at the gel point. Further work has shown that the observed power law exponent is a function of the flocculation conditions, suggesting that this parameter is related to the microstructure of the fluid. In addition, the viscoelastic spectra recorded at different extents of gelation can be superposed to form a master curve, similar to behavior predicted and observed for crosslinking polymers (D. Adolph and J.E. Martin, *Macromolecules*, 23, 3700-3704 (1990)). This superposition suggests that the underlying structure of the fluid does not change as it passes through the gel point. Rather, the connectivity of the clusters present in the fluid increases smoothly as the gelation proceeds, and the gel point is reached when the last connection is made between clusters of finite size to form the "infinite" cluster which spans the volume of the sample.

Wednesday 3:35 Hall of Ideas H

HT10

A SMALL-ANGLE LIGHT SCATTERING STUDY OF THE GELATION OF THERMOREVERSIBLE COLLOIDAL SUSPENSIONS**Priya Varadan and Michael J. Solomon**

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

The effect of volume fraction, temperature and shear flow on the structure factor of colloidal particulate gels formed by net-attractive interparticle interactions has been investigated by means of small-angle light scattering. A recent study has reported the existence of long-range microstructure and fractal scaling of the structure factor in low volume fraction ($\phi < 0.003$) aqueous suspensions of aggregating colloidal polystyrene (Carpinetti and Giglio, Phys. Rev. Lett., 70, 3828 (1993)). The effect of temperature on the structure factor of concentrated ($0.007 < \phi < 0.1$) thermoreversible gels of organophilic silica in hexadecane has also been studied (Chen and Russel, J. Colloid Inter. Sci., 141, 565 (1990)). To better understand the relationship between microstructure and gelation, we have quantified the structure factor of organophilic colloidal silica ($a = 40$ nm) in hexadecane for $0.02 < aq < 0.2$ by means of small-angle light scattering. Here a is the particle radius and q is the scattering vector. The design of the device is based on the work of Cumming et al. (Phys. Rev. A., 45, 885 (1992)). By varying volume fraction ($0.01 < \phi < 0.1$) and temperature ($20^\circ\text{C} < T < 60^\circ\text{C}$) the change in structure factor which accompanies macroscopic gelation is determined. The effect of an applied shear flow on the scattered light intensity is also reported. The light scattering results are discussed in the context of the Baxter model of adhesive spheres, the theories of diffusion and reaction-limited colloidal aggregation, and recent rheological studies of thermoreversible colloidal gels.

Wednesday 4:00 Hall of Ideas H

HT11

STOKESIAN DYNAMICS SIMULATIONS OF THE RHEOLOGICAL BEHAVIOR OF RIGID SPHERES SUSPENDED IN A VISCOELASTIC MEDIUM**Henny M. Schaink¹, Johan J. Slot², Rob J. Jongschaap¹, and Jorrit Mellema¹**¹Rheology Group, Faculty of Applied Physics, University of Twente, Enschede 7500 AE, The Netherlands; ²Department for Physical Chemistry, DSM Research, Geleen 6160 MD, The Netherlands

An extensive Stokesian Dynamics study is presented of the rheological behavior of suspensions of rigid spheres subjected to an oscillating shear strain. Two types of suspensions are considered: 1) rigid spheres in a viscous medium, and 2) rigid spheres in a viscoelastic medium. For this last system we need to extend the Stokesian Dynamics method, which was originally developed by Brady and Bossis for particles suspended in a viscous medium. The derivation of the necessary equations for these extended Stokesian Dynamics simulations is given. In this derivation we use the well known correspondence principle and apply it to the set of equations for the hydrodynamic forces and stresslets that are valid for spheres suspended in a viscous medium. Then using Fourier transformation we obtain differential equations for these forces and stresslets in the viscoelastic case. The contribution of the Brownian motion of the spheres to the bulk stress is found to be independent of the viscoelastic properties of the suspending medium. As an example of a viscoelastic medium we have chosen the Maxwell fluid. In our computer simulations we have calculated both elastic and viscous moduli and compared these results with experimental data. For the case of spheres suspended in a viscous medium we find that the elastic modulus reaches a plateau at high frequencies. Finally we present a simple analytical model which reproduces accurately the hydrodynamic contribution to the viscosity of spheres suspended in a Maxwell medium. This model is used to interpret the experimental results of Aral and Kaylon (Aral and Kaylon, 1997) that were obtained at Peclet numbers currently inaccessible to Stokesian Dynamics simulations.

Wednesday 4:25 Hall of Ideas H

HT12

A STUDY OF FLOW INDUCED STRUCTURES WITHIN AN ELECTORRHEOLOGICALLY ACTIVE SUSPENSION UNDER STEADY SHEAR FLOW**Steve W. Henley and Frank E. Filisko**

Macromolecular Science and Engineering, University of Michigan, Ann Arbor, MI 48105

We present the experimental results on the formation of various structures under steady shear flow using temperature regulated rheometers equipped with both parallel disc and couette devices. The suspension consisted of

Amberlite 200 particles suspended in melted paraffin wax. This allowed the procurement of solidified samples with the corresponding structures remaining intact. It was found that the structures varied with the type of rheometric device used, couette or parallel disc. It was also found that the structures varied with time sheared, concentration of ER active particles, applied field, and gap width of the rheometric device. The shear stress was also recorded as a function of the time sheared. The interaction of small amounts of inactive secondary particles with the active ER matrix was also studied along with the shear stress of the biparticulate system.

Wednesday 4:50 Hall of Ideas H

HT13

A MODEL SYSTEM FOR THE STUDY OF ELECTORRHEOLOGICAL BEHAVIOR IN GELS

Bo Liu¹ and Montgomery T. Shaw²

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We developed a model electrorheological (ER) gel system of silicone elastomers with iron particles. A magnetic field was used to introduce the alignment of particles during the cure of the liquid prepolymer, and the gap between the particles was controlled by swelling the crosslinked material with silicone oil. The shear rheology of the model system was studied under the electrical fields of various intensities. The dependence of ER effect on particle dispersion structures was investigated experimentally using rheometry and dielectrometry. These results were compared with the numerical simulations. The ER effect was found to decrease with the increase of the gap between the particles, as expected. It was also predicted that the uniaxial chain structure of particles would give maximum positive ER effect for displacement gradients along the alignment direction.

**Symposium SF
Shear-free Flows**

Organizers: John Wiest, Kurt W. Koelling and David James

Wednesday 1:30 Hall of Ideas I

SF6

STRESS AND BIREFRINGENCE MEASUREMENTS DURING THE UNIAXIAL ELONGATION OF POLYMER MELTS

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The measurement of flow-induced birefringence is frequently exploited to study the flow of polymer liquids. Using the well-known stress-optic rule, stress fields for complex flows can be inferred from the birefringence. There is evidence, however, that the stress-optic rule fails in strong flows, or flows that tend to induce significant chain stretching. In this study, a rheometer for generating uniaxial elongations in molten polymers (RME) has been modified to allow for the simultaneous measurement of stress and birefringence. Tensile stress and birefringence data in flows at constant strain rates up to one 1/s were collected on a polydisperse, polystyrene melt at temperatures of 160°C and 170°C. From these data, the stress-optic rule was followed for stresses below roughly one MPa. For stresses less than one MPa, the stress-optic coefficient was found to have a value of 4.8×10^{-9} 1/Pa, which was independent of strain, strain rate and temperature. At stress levels higher than one MPa, the stress-optic coefficient decreased indicating a failure of the stress-optic rule. A criteria for failure of the stress-optic rule was formulated using simple arguments from network models and characteristic times suggested by the reptation model. This criteria, which is based on the hypothesis that failure of the stress-optic rule is the result of significant chain stretching, was found to be consistent with the data reported in this study and with data from previous studies on polymer melts.

Wednesday 1:55 Hall of Ideas I

SF7

RESULTS OF A ROUND-ROBIN EXPERIMENT TESTING LLDPE EXTENSIONAL VISCOSITY ON COMMERCIAL RME RHEOMETERS

Jonathan S. Schulze¹, Timothy P. Lodge², and Christopher W. Macosko¹

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In a previous effort to compare the performance of available extensional rheometers, the transient extensional viscosity of linear low density polyethylene (LLDPE) was measured using the original (ETH, Zürich)¹ and the commercial (Rheometric Scientific) versions of the RME and the Münstedt² tensile rheometer. The commercial RME indicated a significant strain hardening of the LLDPE, especially at a strain rate of 1 s^{-1} ; whereas the Münstedt rheometer and the original RME showed the LLDPE to be only slightly strain hardening. This artificial strain hardening effect in the commercial RME resulted from the strain rate applied to the sample being up to twenty percent less than the set strain rate. A round-robin experiment was subsequently conducted on seven commercial RMEs in Germany, England, Italy, and the United States using samples of the same LLDPE. All but one of the commercial RME's indicated a deviation of set and applied strain rate of at least ten percent, especially at strain rates above 0.1 s^{-1} . A partial solution to the problem involves the exact determination of L_0 , the effective distance between the clamps that extend the sample. In addition, the upper pair of belts may not sufficiently grip the sample as the strain rate is increased.

1. Meissner, J. and J. Hostettler, *Rheol. Acta* **33**, 1-21 (1994).

2. Münstedt, H., *J. Rheol.* **23**, 421-436 (1979).

Wednesday 2:20 Hall of Ideas I

SF8

INFLATION AND INSTABILITY OF A POLYMERIC MEMBRANE

Jesper Neergaard¹ and Ole Hassager²

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We consider an axisymmetric polymeric membrane inflated by a uniform pressure difference acting across the membrane. The polymeric material is described by an arbitrary combination of a viscoelastic and a purely viscous component to the stress. Some viscoelastic materials described by a Mooney-Rivlin model show a monotone increasing pressure during inflation of a spherical membrane. These materials develop a homogeneous membrane thickness in agreement with the Considère-Pearson condition. Molecularly based models such as the neo-Hookean, Doi-Edwards or Tom-Pom model show a pressure maximum when inflated. Membranes described by these models develop a local thinning of the membrane which may lead to bursting in finite time.

Wednesday 2:45 Hall of Ideas I

SF9

ATOMIZATION: CONTROL OF DROP SIZE DISTRIBUTION BY RHEOLOGY

Vera Romagnoli¹, Phil Felton², and Robert K. Prud'homme¹

¹Chemical Engineering, Princeton University, Princeton, NJ 08544; ²Mechanical Engineering, Princeton University, Princeton, NJ 08544

When solutions are sprayed from a nozzle, a distribution of drop sizes is formed. Control of drop size distributions is of concern in agricultural spray applications, aerosol science, and paint or coating applications. The droplet size spectrum can be controlled by mechanical means such as nozzle design or chemical means such as fluid properties. This work examines several techniques for controlling drop size chemically. The ability of extensional thickening polymers and Newtonian fluids to alter the drop size is investigated by using Boger fluids. In general these systems tend to broaden the drop size distribution compared to water. An investigation of emulsions and elastic gel microbeads have identified two methods of narrowing the drop size distribution.

Symposium GN General Session

Organizers: Dave S. Malkus and Donald G. Baird

Wednesday 3:35 Hall of Ideas I GN1

DYNAMICS OF INDIVIDUAL FLEXIBLE POLYMERS IN A SHEAR FLOW

Denis Wirtz¹, Philip Leduc², Charbel Haber¹, and Gang Bao²

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²Mechanical Engineering Department, Johns Hopkins University, Baltimore, MD

The dynamics of macromolecular solutions and melts in shear flow is typically studied using bulk experimental methods, including light and neutron scattering and birefringence. Yet, due to the lack of basic conformational information, the impact of shear on the dynamics of individual polymers is not well-understood. Using fluorescently-labeled DNA molecules, we observed the real-time dynamics of individual, flexible polymers under a shear flow. Sheared polymers exhibit multiple, extended conformations with an overall orientation ranging from parallel to perpendicular compared to the flow direction. The relative population of these two major types of conformations is controlled by the rate of the shear flow, but at shear rates much smaller than the inverse of the relaxation time of the molecule. These surprising results reveal a new and fundamental insight into the behavior of individual polymers under shear and question the adequacy of the assumptions made in models of polymer dynamics.

Wednesday 4:00 Hall of Ideas I GN2

EVIDENCE FOR A STRESS-THERMAL RULE IN DEFORMING POLYMERS

David Venerus, Jay D. Schieber, Job D. Guzman, and Hadjira Iddir

Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616

Polymer processes invariably involve strongly coupled velocity, stress and temperature fields. While a great deal of effort has focused on developing mechanical, or rheological, constitutive equations, much less is known about energy transport in deforming polymer systems. Recently, both experimental and theoretical activity on energy transport in deforming polymeric materials has increased significantly. Theoretical hypotheses suggest that the thermal conductivity in such systems is anisotropic, and support, analogous to the well-known stress-optic rule, the validity of a stress-thermal rule where the thermal conductivity and stress tensors are linearly related. In this study we have developed a technique to measure the thermal diffusivity in deforming polymers. The optical technique, known as Forced Rayleigh Scattering, is shown to be sensitive and non-invasive and capable of quantitative measurements of anisotropic thermal diffusivity in both static and dynamic (relaxing) polymers subjected to deformations. Results will be presented for a polymer melt in step-shear strain flows and a cross-linked elastomer in uniaxial extension. Thermal diffusivity data are complemented by measurements of stress and birefringence so that evaluations of the stress-optic and stress-thermal rules can be made. We find that the thermal diffusivity is enhanced in the flow (or stretch) direction compared to the equilibrium value and that the stress-thermal rule is valid for the modest deformations achieved in this study.

Wednesday 4:25 Hall of Ideas I GN3

THE JAUMANN DERIVATIVE: AN INTERPRETATION FROM WITHIN THE BODY MANIFOLD OF LODGE

Alan D. Freed

Polymers Branch in the Materials Division, NASA's John Glenn Research Center, Cleveland, OH 44135

In *Elastic Liquids*, the classic textbook by Arthur Lodge, the Jaumann derivative of a Cartesian tensor field is shown (pg. 330) to result from the transfer of a special body tensor field to Cartesian space. First, we state that the transfer of field from body to Cartesian space is many to one. In an Eulerian transfer of field, where the covariant and contravariant descriptions of a body tensor field both map to the same Cartesian space tensor field, the average of the rates of these two body fields, using the metric tensor to pull down the indices of the contravariant rate, will map

to Cartesian space as the Jaumann derivative. As a point of reference, the simple time derivative of a body field maps to space as Oldroyd's convected derivative, which retains all information of weight and kind arising from the originating body field even though Cartesian tensors have no sense of kind and are boolean in their ability to sense weight.

Because the transfer of tensor field from the body to Cartesian space is many to one, the above field transfer presented by Lodge is not unique. In my talk I will present an alternative transfer of field that also yields the Jaumann rate in Cartesian space. I will begin by defining a new derivative over the body manifold. I call it the *intrinsic derivative* because it is only sensitive to change occurring within the field itself. Specifically, the intrinsic derivatives of the covariant and contravariant body metric tensors and their determinants are all zero. A characteristic property of the intrinsic derivative is that whenever this derivative vanishes, so too will vanish the time derivative of the magnitude of that tensor. This is not true, in general, of the simple time derivative of a body tensor field. The intrinsic derivative of all body tensors possessing the same rank (independent of weight and kind) map into Cartesian space as a single Jaumann rate that is only dependent on rank.

Wednesday 4:50 Hall of Ideas I

GN4

STRUCTURAL RHEOLOGICAL MODEL: APPLICATIONS TO BIOFLUIDS

Ning Sun and Daniel De Kee

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Materials such as suspensions, biofluids, etc. are heterogeneous on the microscale and this is responsible for rather complex rheological behavior. In addition, the rheological measurements are function of the shear history as well as of the thermal history of the sample. In the case of a suspension, for example, the flow properties will depend on the particle size, on the particle size distribution, on the particle shape, on the particle concentration, and on the rheological properties of the suspending medium. This can result in measurements of properties such as shear-thinning, shear-thickening, thixotropy, antithixotropy, yield stress and non-linear viscoelasticity. The amazing part is the all of these properties can be measured on the same material, depending on the type of excursion, one subjects the sample to.

In particular, biofluids such as blood, exhibit behavior such as shear thinning, thixotropy and viscoelasticity. Most likely, blood also exhibits yield stress behavior. Earlier theoretical work ranges from qualitative explanation to quantitative modeling, bridging micro and macro blood rheology. A generalized Maxwell model has been used to explain equilibrium state rheology. To study transient flows and hysteresis behavior of blood, a structural parameter has been introduced.

A structural model proposed by Soong and Shen, and further developed by De Kee and Chan Man Fong, is able to describe the behavior of complex structured fluids. Here we look at the applicability of this type of model to describe the behavior of biofluids such as blood and a penicillin suspension.

Symposium MS **Rheology of Polymer Melts and Solutions**

Organizers: John L. Schrag and Faith Morrison

Wednesday 1:30 Hall of Ideas J

MS14

RHEOLOGY OF SHEAR THICKENING WATER-SOLUBLE ASSOCIATING POLYMER SOLUTIONS

Sharon X. Ma¹ and Stuart L. Cooper²

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It has been observed that certain associating polymers in selective solvents exhibit shear thickening behavior over a limited range of concentration. It is generally caused by shear-induced changes in the structure of the material;

however, the details of the mechanisms of shear thickening in various systems are quite diverse and often poorly understood. Telechelic polymers (i.e. polymers with "sticker" groups at both ends) have been synthesized and used as model systems to investigate the mechanism of shear thickening of associating polymer solutions. The response of hydrophobically end-capped poly(ethylene oxide) in aqueous solution to both steady shear and oscillatory shear was determined. The effects of temperature and solvent viscosity on shear thickening have been studied. The experimental results were quantitatively compared with a non-Gaussian chain stretching theory.

Wednesday 1:55 Hall of Ideas J

MS15

A PHENOMENOLOGICAL MODEL FOR SHEAR-THICKENING

Jacqueline L. Goveas

Chemical Engineering, Rice University, Houston, TX 77005

Recently, experiments by Pine et al. observed shear-thickening in solutions of worm-like micelles. The viscosity increase in these solutions occurred above a critical stress, and was concomittant with the growth of a gel-like phase. The stress-strain curve for was non-monotonic, and certain states under stress-controlled experiments could not be accessed under strain-control. We give a simple phenomenological model to explain this behavior. We consider a fluid micellar phase, which can undergo reactions above a critical stress. The reaction product is insoluble and forms a solid-like phase within which there is no flow. The solid-like phase can break and revert to the micellar phase. We show that with these dynamics, it is possible to produce the experimental stress-strain observations. Assuming that the fluid phase viscosity is concentration dependent reproduces the non-monotonicity in the stress.

Wednesday 2:20 Hall of Ideas J

MS16

DYNAMIC RESPONSE OF FUNCTIONALIZED STAR POLYMER MELTS

Dimitris Vlassopoulos¹, Tadeusz Pakula², George Fytas¹, Marinos Pitsikalis³, and Nikos Hadjichristidis³

¹Institute of Electronic Structure & Laser, FO.R.T.H., Heraklion, Crete 71110, Greece; ²Max-Planck Institute for Polymer Research, Mainz 55021, Germany; ³Department of Chemistry, University of Athens, Athens 15701, Greece

We investigate the structure and dynamics of model mono-, di-, and tri- \bar{u} -functionalized three arm star polybutadiene melts. By using X-ray scattering, dynamic rheological measurements and dielectric relaxation, we find that functionalization of the arm ends can lead to distinctly different supramolecular structures and material behavior. The mono-functionalized samples behave like multiarm nonionic star-like dendrimers, whereas the di-functional stars resemble a transient network consisting of highly branched structures with a very broad relaxation spectrum. On the other hand, the tri-functional stars seem to develop an unusually regular structure of dominant intramolecularly aggregated functional groups leading to collapsed star conformations, resembling soft spheres, and a well defined terminal relaxation. These results suggest that by tailoring the telechelic functionalization of regular star polymers, a route to design and obtain a wealth of controlled supramolecular structures exhibiting a rich and variable dynamics could open.

Wednesday 2:45 Hall of Ideas J

MS17

THE EFFECTS OF MOLECULAR VARIABLES AND ARCHITECTURE ON THE RHEOLOGICAL BEHAVIOR OF DENDRITIC POLYMERS

Ibrahim Sendjarevic and Anthony J. McHugh

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Comparisons of simple shear, oscillatory, and creep flow rheological behaviors are presented for several poly(propylenimine) dendrimers (DAB), hyperbranched (HBP) polyesters, and poly ether-imide (PEI) HBPs. Variables examined include molecular weight, degree of branching, nature of peripheral groups, and molecular architecture. In simple shear, DAB dendrimers and HBP polyesters exhibited a Newtonian behavior and both showed a similar relationship between zero shear rate viscosity, η_0 , and molecular weight, M_w . In oscillatory experiments amine end-capped DAB dendrimers and HBP polyesters exhibited Newtonian behavior, while the nitrile end-capped DAB dendrimers showed a Rouse-like frequency dependence of both moduli. A fit of Fox and Flory theory to the fractional free volume data obtained by WLF analysis of DAB dendrimers suggests that the volume free fraction of

end-groups is independent of generation number. The data on PEI HBPs suggest that at the lowest molecular weight ($M_n \sim 4,301$) the rheological behavior is Newtonian, however, the higher molecular weight solutions showed shear thinning and normal stress effects, both of which increased with the decrease in the degree of branching (DB). From the concentration dependence of storage and loss moduli, it is observed that intermolecular interactions of PEI HBPs are dominated by hydrodynamics at low concentrations (30 wt.%), by coil overlap at intermediate concentrations (~35 wt.%), and by entanglements at higher concentrations (40 wt.%).

Wednesday 3:35 Hall of Ideas J

MS18

MELT RHEOLOGY OF POLYLACTIDE BLENDS

John R. Dorgan¹, Hans J. Lehermeier¹, Daniel Knauss², and Michael Mang³

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Poly(lactic acids) or polylactides (PLAs) are a family of polyesters available via fermentation from renewable resources and are the subject of considerable recent commercial attention. Cargill-Dow Polymers plans to produce 300 million pounds annually of this new thermoplastic by 2003 yet little is known about the fundamental rheological properties of this material. In this study, the melt rheological properties of a family of PLA star polymers are investigated and compared to the properties of the linear material. For polymers made from a 98:2 ratio of the L to D enantiomeric monomers it is found that the entanglement molecular weight is approximately nine-thousand grams per mole ($M_e \approx 8,700$ g/mol). Results suggest that PLA is a semi-stiff polymer in accordance with other recent findings. The increase in zero shear viscosity for the branched materials is measured and quantified in terms of appropriate enhancement factors. Relaxation spectra show that the transition zone for the linear and branched materials are nearly indistinguishable while the star polymers have greater contributions to the terminal regime. The effects of chain architecture on the flow activation are found to be modest implying that small scale motions in PLA homopolymers largely control this phenomenon. Good agreement is found between the dynamic data and many aspects of the theory of star polymers, however, a dependence of the zero shear viscosity on the number of arms is observed. The rheological properties of blends of linear and branched PLAs are also discussed.

Wednesday 4:00 Hall of Ideas J

MS19

EFFECT OF STARCH PACKING ON VISCOSITY OF HIGHLY STARCH-FILLED POLY(HYDROXY ESTER ETHER) COMPOSITES

Genwen Zhou¹, J. L. Willett¹, and Craig J. Carriere²

¹Plant Polymer Research, NCAUR/ARS/USDA, Peoria, IL 61604; ²Biomaterials Processing Research Unit, USDA ARS NCAUR, Peoria, IL 61604

This research focuses on the flow behavior of highly starch-filled poly(hydroxy ester ether) (PHEE) composites. In this paper the effect of starch volume fraction on the composite viscosity is presented. Corn starch (Buffalo 3401)/PHEE (Dow Chemical) were extruded using a Leistritz twin screw extruder with starch volume fractions from 0.27 to 0.66. The starch was dried to a moisture content of 0.7% to minimize moisture effect on composite rheology. Dynamic frequency sweep measurements were carried out using an ARES Rheometer (Rheometric Scientific) at 120°C and 1% strain. The maximum packing fraction of the starch (in ethanol) was determined to be 0.61 with a Quanta Chrome Autotap. Starch volume fraction dependence of melt viscosity is well described using Maron & Pierce, Frankel & Acrivos, and Mooney equations when starch packing fraction is below the maximum packing fraction. Reasons are discussed for the deviation of composite viscosity from the models and extrusion processability of the composite at starch volume fraction above the maximum packing fraction. This research was conducted under CRADA 58-3K95-8-0635 between the Agricultural Research Service and Biotechnology Research and Development Corporation.

Wednesday 4:25 Hall of Ideas J

MS20

PREDICTION OF RHEOLOGICAL PROPERTIES OF HARD WHEAT FLOUR USING NONLINEAR DIFFERENTIAL VISCOELASTIC MODELS**Muthukumar Dhanasekharan and Jozef L. Kokini**

Department of Food Science, Rutgers University, New Brunswick, NJ 08901

To understand complex viscoelastic flows of wheat flour dough that occur in manufacturing unit operations such as extrusion, dough sheeting etc., it is important to characterize wheat flour doughs using viscoelastic models. Previous studies show those integral viscoelastic models, such as Doi-Edwards, KBKZ and Bird-Carreau can predict rheological properties of dough. However, integral viscoelastic models are not amenable to be used in numerical simulation of complex flows, due to high computational costs involved in tracking the history of the stresses. Therefore the objective of this research is to test the applicability of several differential viscoelastic models such as White Metzner, Phan-Thien-Tanner, and Giesekus-Leonov, in studying the rheological properties of hard wheat flour dough. The choice of these models was based on molecular basis of the models and the models have one or two adjustable parameters. Steady and Transient Shear properties and extensional properties of hard wheat flour dough was predicted by using differential models such as Phan Thien-Tanner model, Giesekus model and White-Metzner model. Phan Thien-Tanner gave good zero shear viscosity prediction, but overpredicted the shear viscosity at higher shear rates. It also overpredicted the transient and extensional properties. Giesekus model gave similar predictions to Phan Thien-Tanner, but the extensional viscosity was not well predicted. White-Metzner model gave good predictions of the steady shear viscosity and first normal stress coefficient. However, it was unable to predict the uniaxial extensional viscosity as it exhibited an unbound behavior in the tested extensional rates. The transient shear properties were predicted with reasonable accuracy in the transient phase, but very well predicted at higher times.

Wednesday 4:50 Hall of Ideas J

MS21

NONLINEAR RHEOLOGY OF ENTANGLED POLYMERS**Lynden A. Archer**

Chemical Engineering, Texas A&M University, College Station, TX 77843-3122

Nonlinear rheology of entangled polymers is investigated theoretically and experimentally using a series of well-characterized entangled polystyrene solutions and 1,4-polybutadiene melts. Polymers in both series are selected to maintain fixed entanglement spacing over a broad range of polymer molecular weights. Several new results are uncovered in step and steady shearing deformations. First, in steady shearing at modest rates, entangled polymers are found to manifest a defined limiting orientation angle beyond which shearing is incapable of producing further molecular alignment, at steady state. Consequences of a plateau in molecular orientation for the universality of the Doi-Edwards orientation tensor, Q , are addressed. Second, using a new procedure we present a method for directly estimating the amount of molecular stretching from steady shear flow measurements. For well entangled polymers ($N/Ne > 20$), this procedure reveals a cross-over from complete retraction to partial retraction of polymer contour length, as entanglement density and/or shear rate increases. Finally, we reconsider the requirements for a factorizable nonlinear shear relaxation modulus in step shear experiments. The experiments suggest that for polymers with ($N/Ne > 20$) the fundamental physical requirements for factorable or nonfactorable relaxation moduli are only subtly different. This last finding will be discussed in the context of modified reptation theories, in which the tube diameter itself may be altered by flow.

Thursday Morning

Symposium BC Blends and Block Copolymers

Organizers: Timothy P. Lodge and Paula Moldanaers

Thursday 8:05 Hall of Ideas G BC14

LINEAR RHEOLOGY OF LAMELLAR DIBLOCKS COMPARED TO THEIR HETERO-FOUR-ARM STAR BLOCK COPOLYMER ANALOGS

D. Martin A. Buzza¹, Adnan F. Fzea², Jurgen B. Allgaier², Ronald N. Young², David J. Groves¹, and Tom C. Mcleish¹

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The linear shear rheology of symmetric styrene-isoprene (PS-PI) diblock copolymers with three different molecular weights is compared to that of their hetero-four-arm star counterparts. For both the linear and star samples, the low, intermediate and high molecular weight samples had PS and PI arm molecular weights of $M_a=10\text{kg/mol}$, 20kg/mol , 60kg/mol respectively. Both the disordered and ordered lamellar phase were accessible for the lowest molecular weight linear and star samples while only the ordered lamellar phase was accessible for the higher molecular weight samples. Due to the widely differing timescales of PS and PI relaxations, three distinct regions in the rheological spectrum could be identified, namely mesoscopic relaxations at low frequencies, PS relaxations at intermediate frequencies and PI relaxations at high frequencies. The PI relaxations were experimentally accessible only for the highest molecular weight linear and star samples. Qualitative differences in the molecular relaxation spectra were observed between the linear and star samples for all three molecular weights. For star samples with $M_a=10\text{kg/mol}$ and 20kg/mol , an additional shoulder (absent in linear samples) was observed in both G' and G'' at frequencies around the Rouse terminal relaxation time of the PS chains. For linear and star samples with $M_a=60\text{kg/mol}$, the star appears to have a higher PS plateau modulus compared to the linear. We show that these differences can be explained by the difference in Rouse spectra for chains with linear and star architectures (i.e., free chain vs. tethered chain). In addition, for both $M_a=10\text{kg/mol}$, 20kg/mol , a PS entanglement plateau is discernable in the star systems which is absent in the linear systems. This is consistent with existing data on star homopolymers, which show that star polymers become entangled when the molecular weight (i.e., two times M_a) exceeds M_c , the critical molecular weight for entanglements (for PS, $M_c=30\text{kg/mol}$).

Thursday 8:30 Hall of Ideas G BC15

SIMULATION OF DIBLOCK COPOLYMER MELTS BY DISSIPATIVE PARTICLE DYNAMICS

Kai Zhang, Guoai Pan, and Charles W. Manke

Dept. Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202

Dissipative Particle Dynamics (DPD), a recently developed mesoscopic simulation technique, is used to model the morphology and dynamical behavior of short-chain diblock copolymer melts. The copolymer melt model is constructed by filling a 3 dimensional periodic simulation box with 20-bead polymer chains consisting of DPD particles connected by FENE springs. The two blocks, A and B, of the copolymer chain are represented by particles of different DPD "phases", and composition is varied by varying the number of beads in each block. As composition is varied in 5% increments from 0-50% A, the predicted morphology changes, progressively, from a disordered system to spherical domains of A, and then to cylindrical domains and lamellae. These predicted phase structures are

in good agreement with experimental and theoretical results from the literature. The effects of phase-separated morphology on linear viscoelasticity are investigated by measuring the decay of the shear stress autocorrelation function during equilibrium (non-flow) DPD simulations. The stress relaxation functions $G(t)$ calculated from the stress autocorrelation functions show different long-time decay responses for each phase structure. Steady shear flow is simulated by means of Lees-Edwards boundary conditions to investigate the effect of shear flow on morphology, and to evaluate viscosity and normal stresses under shearing.

Thursday 8:55 Hall of Ideas G

BC16

PHASE TRANSITION IN A TRIBLOCK-DIBLOCK COPOLYMER BLEND

Adriana Silva and Ramanan Krishnamoorti

Department of Chemical Engineering, University of Houston, Houston, TX 77204-4792

We have investigated the nature of the order-disorder phase transition in a block copolymer blend using linear viscoelastic rheological measurements and small-angle neutron scattering. The system studied consisted of a polystyrene-polyisoprene diblock blended with a polystyrene-polyisoprene-polystyrene triblock copolymer. The effect on blending on the order-disorder transition is studied as a function of concentration. We observed a dramatic reduction and concentration dependence of the order-disorder transition temperature which can not be satisfactorily modeled by either multi-component RPA or self-consistent field theory.

Thursday 9:20 Hall of Ideas G

BC17

DYNAMICS OF MODEL MISCIBLE POLYOLEFIN BLENDS

Jai A. Pathak¹, Ralph H. Colby¹, George Floudas², Ramanan Krishnamoorti³, Lewis J. Fetters⁴, and Rudi Faust⁵

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We report results on terminal and segmental dynamics of two model miscible polyolefin blends: head-to-head polypropylene (hhPP)/polyisobutylene (PIB) and head-to-head polypropylene/ poly(ethylene-propylene) (PEP), measured by oscillatory shear and dielectric spectroscopy, respectively. The presence of a small fraction (~6%) of asymmetric structures in hhPP gives it higher specific polarizability than PIB and PEP. The terminal relaxation of each component has been clearly resolved in the blends. While all pure components uphold the time-temperature superposition principle, the terminal relaxation of both components cannot be superposed simultaneously in either blend. Our findings are consistent with the observation of distinct temperature dependences of the tracer diffusion coefficients of hhPP and PEP in their blends, observed by Gell and her co-workers. However, their assessment of thermorheological simplicity in the linear viscoelastic response of hhPP/PEP blends is revised. In hhPP/PIB blends, a series of blends with the same composition of the more entangled component, but varying chain lengths have been studied. The relaxation peak of the higher T_g component (hhPP) shifts much faster than that of the low T_g component (PIB), resulting in thermorheological complexity. In both hhPP/PEP and hhPP/PIB blends, the impact of composition fluctuations at the segmental level is felt on relaxations at both segmental and terminal length scales.

Thursday 10:10 Hall of Ideas G

BC18

SCALING OF THE RELAXATION TIMES FOR DIFFERENT RELAXATION MECHANISMS IN IMMISCIBLE POLYMER BLENDS

Paula Moldenaers, Peter Van Puyvelde, and Jan Mewis

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Recently, it has been shown that both linear conservative dichroism and small angle light scattering are powerful techniques to investigate microstructural changes under flow conditions in immiscible polymer blends. In this investigation the morphological changes upon cessation of flow are studied. The instantaneous structure and the shape relaxation of the droplets can be deduced from dichroism relaxation curves and the corresponding SALS patterns. Both techniques clearly reflect the mechanism of relaxation, i.e. retraction, end-pinch and relaxation by

Rayleigh instabilities. By systematically adjusting the flow conditions, droplets of various aspect ratios can be created before they are allowed to relax. An important information that follows out of these experiments is the time scale of the relaxation process. These time-scales, associated with the different relaxation mechanisms, have been mapped out in detail. When comparing different blend systems, the effect of viscosity ratio as well as concentration needs to be taken into account. Therefore, a new scaling relation will be proposed incorporating the effects of these parameters. It has been shown that the scaling relation holds for concentrations of the dispersed phase between 1 and 10%.

Thursday 10:35 Hall of Ideas G

BC19

MONOMERIC FRICTION FACTORS IN POLYMER MIXTURES

Timothy P. Lodge and Jodi M. Milhaupt

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431

All chain dynamics properties depend on the timescale of conformational rearrangements at the segmental level, usually discussed in terms of the monomeric friction factor. In polymer mixtures (blends, copolymers, etc.) the friction factor of each component acquires a composition dependence about which little is known. Furthermore, in spatially heterogeneous systems (phase separating blends, ordered block copolymers, etc.) the friction factors may depend on spatial location. We have been exploring this phenomenology in two immiscible polymer systems, styrene/isoprene and styrene/methylmethacrylate. The former is notable for the wide difference in glass transition temperatures between the two components, but rather simple mixing rules for the resulting friction factors, whereas the latter pair have very similar glass transition temperatures but apparently more complicated mixing rules. Comparisons to various models will also be made.

Thursday 11:00 Hall of Ideas G

BC20

ON THE BLENDS OF HYPERBRANCHED POLYMERS WITH LINEAR POLYMERS

Michael E. Mackay¹, Ye Hong², Justin J. Cooper-White², Craig Hawker³, and Eva Malmstrom⁴

¹Chemical, Biochemical and Materials Engineering, Stevens Institute of Technology, Hoboken, NJ 07030; ²Chemical Engineering, University of Queensland, Brisbane, Queensland 4072, Australia; ³IBM Almaden Research Center, San Jose, CA 95120-6099; ⁴Polymer Technology, Royal Institute of Technology, Stockholm, Sweden

We have extrusion, melt blended hyperbranched polymers (HBPs) with linear low density polyethylene to show that the HBP rapidly phase separates to the interface between the die and linear polymer. At this point it is not known why this phase separation occurs so rapidly. The separation is not dependent on the extruder since it occurred on both a small scale extruder and a large scale extruder used to manufacture blown film. The HBP used was modified with alkane groups of varying length, however, the alkane length did not make a significant change in the phase separation. Yet, the phase separation is important since it allows a processing aid effect to take place even at low loadings (approximately 0.1wt%) and perhaps, more importantly, produces surface modification of the linear polymer. Thus, it may be possible to change the surface properties, keep the bulk physical properties and extrude faster. In this work we present further results on the phase behavior.

Thursday 11:25 Hall of Ideas G

BC21

RHEOLOGICAL STUDY OF THE EFFECT OF MOLECULAR PARAMETERS AND TEMPERATURE ON THE MISCIBILITY OF POLYETHYLENE BLENDS

Ibnelwaleed A. Hussein and Michael C. Williams

Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2G6, Canada

The influence of molecular weight, comonomer type, and mixing temperature on the miscibility of LLDPE and LDPE is discussed. Adequate amounts of antioxidants were added during melt blending. Dynamic and steady shear measurements were carried out in a Rheometrics Mechanical Spectrometer 800. The mixing temperatures were chosen to dovetail with the recently reported high-temperature transitions in polyethylene (Hussein and Williams, *Macromol. Rapid Commun.*, 19, 323-325, 1998).

Blends of low-Mw LLDPE (butene) and LDPE are likely miscible as revealed by the dependence of their rheological properties on blend composition. Blends of high-Mw LLDPE (butene) and LDPE mixed at 190°C are only partially miscible; immiscibility is likely to occur around the 50/50 composition and in the LDPE-rich blends. Blends are likely miscible in the LLDPE-rich range. Blends of high-Mw LLDPE (butene) and LDPE mixed at 220°C are almost immiscible. Miscibility is likely to occur for the 70% LLDPE blend. Increasing the branch length from butene to octene slightly increased the miscibility of LLDPE/LDPE blends. It is suggested that the molecular order (see Hussein and Williams, *J. Non-Newtonian Fluid Mech.*, in press, 1999) and mismatch of the molecular conformations of different polyethylene structures provide an explanation for the immiscibility of polyethylenes. Agreement of the measurements of dynamic viscosity as function of composition and theoretical predictions of two-phase models (e.g., dilute emulsion model) was observed.

Thursday 11:50 Hall of Ideas G

BC22

ELASTIC BEHAVIOR OF THERMOPLASTIC POLYURETHANES PROBED BY RHEO-OPTICAL FTIR SPECTROSCOPY

Rangaramanujam Kannan and Gerald Hofmann

Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48375

Synthesis and processing of complex microstructured polymeric materials demands a clear insight into the viscoelastic response at the individual molecular, interfacial, and the microstructural level. Such understanding can provide unique ways to optimize macroscopic properties. We have developed a novel rheo-optical FTIR spectrometer to gain insights into responses at such length scales, by combining conventional mechanical testing with step-scan FTIR spectroscopy. Using polarization-modulation scheme, we monitor the dichroism spectra of the complex polymer over a wide range of conditions (temperature, deformation, deformation rate, observation time scales). Structure-property relationships in polyurethanes are motivated by their technological importance, rich chemistry, and the diverse requirements for different products. In thermoplastic polyurethanes, the high degree of elasticity is suggested to arise from the complex morphology. By varying the relative amounts of the soft segments (polyol), and the hard segments (isocyanate), the morphology and the elastic character of the sample can be manipulated. Using rheo-optical FTIR, we explore the origin of the elastic behavior by monitoring the orientation response of the soft segment (wavenumber: 2940 cm^{-1}), hard segment (wavenumber: 1640 cm^{-1}), and the interface (wavenumber: 1730 cm^{-1}) simultaneously, over a wide range of deformation conditions. Preliminary experiments reveal that: at small strains, the soft segments and the hard segments orient nearly independently, and in different directions with respect to strain; at high strains, they show stronger orientation correlation, as revealed by 2D-IR spectroscopy. Results will be presented for different chemical compositions, temperatures and strain histories, to elucidate the role of each of the parameters on the elastic behavior.

Symposium HT Heterogeneous Systems

Organizers: Daniel De Kee, Lisa Mondy and Mike Solomon

Thursday 8:05 Meeting Room L-M

HT14

THE EFFECT OF SURFACE CHEMISTRY ON NONLINEAR CONDUCTION IN ELECTORRHEOLOGICAL SUSPENSIONS

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¹Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706;

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One of the primary limitations to the commercialization of electrorheology is the poor understanding of and inability to control the conduction processes in these materials. In particular, nonlinear conduction processes increase suspension conductivity and reduce stress transfer, which are detrimental to commercial applications. Previous work has suggested that nonlinear conduction originates in the interfacial region between surfaces. In this presentation, we will report results from an experimental investigation of the effect of surface chemistry on nonlinear conduction and

the rheological properties of electrorheological suspensions. Particle and electrode surfaces are modified by a variety of methods, such as grafting chemical species or coating thin films. The effect of such surface treatments on the conduction behavior is determined by analyzing the current passing through the suspension when it is subjected to an ac electric field. The degree of nonlinear conduction is quantified by the amplitude and phase shift of the harmonics of the current. Preliminary results indicate that the particle surface chemistry only weakly affects the degree of nonlinear conduction, while treating the electrode surfaces can dramatically alter the nonlinear conduction processes. These results suggest that nonlinear conduction is controlled by injection processes at the electrode surfaces. We will describe how these injection processes and their manifestations in the suspension electrical and rheological properties are affected by electrode, particle, and continuous phase chemical properties.

Thursday 8:30 Meeting Room L-M HT15
ELECTORHEOLOGICAL FLUIDS CONTAINING PARTICULATE AND LIQUID DROPLET BI-DISPERSED PHASE

Byung Doo Chin and O Ok Park

Center for Advanced Functional Polymers & Dept.Chem.Eng., Korea Advanced Institute of Science and Technology, Taejon 305-701, Republic of Korea

The electrorheological behaviors of multi-phase dispersed materials were considered which serve as a composite substrate in electrorheological fluids. Immiscible oils with different electrical conductivity and dielectric constant were employed as the complex medium. Selecting of the lower-conductive oil for the carrier fluid would induce a "new type" ER performance when both the higher-conductive oil and ER-active particles form the dispersed phase. Additional liquid phases in ER suspension induced the extraordinary dispersion with synergistic effects on ER response. Furthermore, the rheological properties of the electrorheological fluids under electric field can be explained by the change in relative composition of liquid droplet phases. Both experimental analysis as well as theoretical study on the yield stress behaviors and structural changes of multiphase ER materials were performed. These results would be possibly applied for enhancing the performance of conventional ER suspension without facing the increase of the bulk current density of ER fluids.

Thursday 8:55 Meeting Room L-M HT16
A CONTINUUM APPROACH TO ELECTRO- AND MAGNETORHEOLOGY

Yuri M. Shkel and Daniel J. Klingenberg

Chemical Engineering, University of Wisconsin, Madison, WI 53706

An equilibrium thermodynamic approach is employed to derive a continuum-level expression for the electric or magnetic field-induced stress in uniaxial anisotropic materials. Although this model is developed specifically to describe electro- and magnetoactivity of particulate suspensions and elastomers, it also applies to other uniaxial materials such as nonpolar nematic liquid crystals, biaxially oriented polymer films, and paper. This model introduces new electro- and magnetostriction coefficients, which are material parameters that describe the strain dependence of the dielectric and permeability tensors, as well as the field-induced stresses. Rheological properties can thus be predicted once these parameters are known. Experimental techniques for measuring the electro- and magnetostriction parameters are described, and preliminary results for magnetorheological suspensions will be presented. An idealized microscopic model is presented to illustrate the relationships between microscopic parameters and the macroscopic electro- and magnetostriction coefficients. The model is used to determine the stresses in common applications; predictions from the continuum approach agree with direct calculations from a microscopic approach for the normal stress and static shear modulus of electrorheological suspensions.

Thursday 9:20 Meeting Room L-M HT17
ELASTIC-PLASTIC DEFORMATION OF A SOFT SOLID BY AN EXPANDING BUBBLE

Phillip A. Gauglitz, Terrones Terrones, Donny P. Mendoza, and Chris A. Aardahl

Environmental Technology Division, Pacific Northwest National Laboratory, Richland, WA 99352

High-level radioactive waste has been stored in 177 underground tanks at the U.S. Department of Energy's Hanford Site in Washington State since 1944. Flammable gases such as hydrogen and ammonia are generated in the waste creating a flammable gas hazard. Previous studies have established that the waste level of these tanks responds to

barometric pressure changes, the compressibility of retained bubbles accounts for the level changes, and the volume of retained gas can be determined from the measured waste level and barometric pressure changes. However, interactions between the gas bubbles and the rheologically complex waste cause inaccurate retained gas estimates and are not well understood.

The objective of this work is to gain a fundamental understanding of the interactions between gas bubbles and the rheologically complex tank waste during barometric pressure fluctuations. This presentation will discuss modeling results from a solid mechanics viewpoint and associated experimental results. The solid mechanics modeling considers how a smooth external pressure fluctuations affects the deformation history of a single bubble imbedded in a compressible elastic-perfectly plastic isotropic medium of infinite extent. The problem is approached by solving an outer elastic and an inner plastic problem for each compression and decompression sweep of the pressure cycle, then matching the deformations and stresses at the location of the elastic-plastic boundary. The general case was considered in which yield and yield-in-reverse zones alternate with each pressure cycle. The experimental studies focus on quantifying the effect of small pressure changes on the volume of a single non-spherical bubble in a waste simulant while also visualizing the changes in bubble shape. Experimental and modeling results for bubble volume and shape during pressure cycles, which clearly show bubble/waste interactions, will be compared to the modeling results.

Thursday 10:10 Meeting Room L-M

HT18

SIMPLE SHEARING FLOW OF A DRY SOAP FROTH WITH RANDOM STRUCTURE

Andrew M. Kraynik¹ and Douglas A. Reinelt²

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We analyze the microrheology of a dry soap froth with random cell structure that is subjected to quasistatic simple shearing flow. The 'jammed' state causes solid-like response under static conditions where energy minimization determines foam geometry. All of the foam structures that we describe are calculated with the Surface Evolver, a computer program developed by K.A. Brakke. The relationship between macroscopic stress and microscopic, cell-level geometry will be emphasized. Dry foams, which contain negligible liquid, satisfy Plateau's laws. Random foams are derived by minimizing the surface area of Voronoi polyhedra; various algorithms are used to produce the Voronoi seeds. We will focus on the stress-strain curves for the viscometric functions. Regardless of whether the foams are 2D or 3D, ordered or random, the stress-strain curves are piecewise continuous, which corresponds to elastic-plastic behavior; each branch of the curve represents large-deformation elastic response of a foam with fixed topology; and each branch terminates when the foam structure violates Plateau's laws. Stability is restored by a cascade of local topology changes called T1s that result in a stable foam structure with different cell neighbors. We will compare and contrast the behavior of 2D and 3D systems with cell structure ranging from perfectly ordered to random.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under contract DE-AC04-94AL85000.

Thursday 10:35 Meeting Room L-M

HT19

RHEOLOGY OF POLYAMPHOLYTE (GELATIN) STABILIZED LATEX

K. Abe Vaynberg¹, Brent Maranzano², and Norman J. Wagner³

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Polyampholytes, (e.g. gelatin) are widely used to stabilize colloidal dispersions in the photographic, food, and pharmaceutical industries. In this work we connect the rheology of gelatin stabilized colloidal dispersions to the interparticle potential due to adsorbed gelatin. The adsorbed gelatin layer is characterized by measurements of adsorption isotherms, intrinsic viscometry, SANS and DLS. SANS measurements of the structure factor are inverted to yield pair potentials in qualitative agreement with surface forces measurements. The potential can be adequately modeled by a superposition of a steric contribution typical of uncharged polymer with an added electrostatic repulsion. The flow curve of gelatin stabilized acrylic latex is measured on a stress rheometer as a function of particle concentration for a fixed gelatin adsorbed layer. Complementary flow dichroism and birefringence, as well

as DLS measurements are performed to examine the structure, characteristic relaxation times, and homogeneity of the dispersion. The flow curves are modeled by a recently proposed extension of hydrodynamic preaveraging and Brownian Dynamics simulations, where all of the input parameters are determined independently. Shear stability is probed at shear rates approaching 10^6 1/sec in a pressure driven capillary viscometer. Comparing prediction with experiment provides insight into the remarkable stabilizing ability of adsorbed gelatin.

Thursday 11:00 Meeting Room L-M

HT20

LONG-TIME NON-PRE-AVERAGED DIFFUSIVITY AND SEDIMENTATION VELOCITY OF CLUSTERS: APPLICATIONS TO MICELLAR SOLUTIONS

Venkat Ganesan and Howard Brenner

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Calculations are presented for the long-time diffusivity and sedimentation velocity of *associating colloids*. Examples of the latter are micellar solutions and microemulsions. The analysis incorporates the role of reversible association-dissociation processes accompanying the physical-space transport of these clusters through the solution. This is accomplished without the need for pre-averaging by transforming the association-dissociation processes into equivalent "size-space" diffusional processes, which are then embedded into the simultaneous physical-space transport processes occurring in three-dimensional space so as to obtain a four-dimensional convective-diffusion equation governing transport of the clusters in both the physical and size spaces. A generic "projection" scheme framework based on generalized Taylor dispersion theory is then applied to the problem, thereby reducing the four-dimensional transport equation to a coarse-grained three-dimensional *physical-space* convective-diffusion equation. Effects arising from the existence of a distribution of cluster sizes are accounted for in the latter formulation governing the *mean* transport process by the appearance of three coarse-grained phenomenological coefficients whose values depend *inter alia* upon the cluster-size distribution. These "macrotransport" coefficients include a mean sedimentation velocity vector arising from the action of external forces (if any), a mean molecular diffusivity dyadic, and an additional diffusive-type contribution to the diffusivity corresponding to a convective ("Taylor") dispersivity. The generic framework developed is illustrated by applications to two classes of micellar solutions: (i) solutions comprised of spherical micelles; (ii) solutions comprised of cylindrical or worm-like micelles (so-called "living polymers"). Possible applications and potential extensions of the generic framework are outlined.

Thursday 11:25 Meeting Room L-M

HT21

DO FATS ACT AS LUBRICANTS IN FOODS?

Suzanne Giasson¹, Imane Lahlou², Sumana Chakrabarti³, Tonya Kuhl⁴, and Jacob Israelachvili⁴

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Rheological behaviors of foods are important for developing food products, both for texture perceptions as well as for processing purposes. One of the major challenges in food development work has been in understanding the role of fats in the control of food properties such as texture, flavors, mouthfeel, etc. It has been conjectured that fats provide lubrication and thus alter the perception of texture. In general, food products containing fats are also easier to process, presumably for the same lubricating effects. However, this reasoning has been a hypothesis only, as bulk rheological testing has not been effective in differentiating between products with or without fat. Using the Surface Forces Apparatus (SFA) technique and FEKO optical interferometry, we have characterized the thin-film morphology and measured the tribological and other interfacial properties of different food systems. We plan to show that fats do, indeed, act as lubricants and that the SFA experiments capture those lubricating processes very well. Data for flour /water batter systems as well as for a series of different mayonnaises will be presented. The results reveal new tribological properties that help to uniquely differentiate between different food samples and provide a new mechanistic hypothesis for sensory perceptions which cannot be deduced from bulk properties.

Thursday 11:50 Meeting Room L-M

HT22

COLOUR RHEOLOGY OF LIQUID PAINT DURING AND AFTER SHEAR

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This paper is concerned with experimental observation on the colour change of an acrylic resin based paint both during and after shear. Research on dry paint films has shown that colour strength is dependent on the distribution of the pigment particles, which result from flocculation of the particles (1). Shear can effect the state of agglomeration of particles and consequently shear can influence both the rheology and colour of wet paint.

In order to investigate the effect of shear on flowing paint, shear was applied to a full-shade wet paint using a Multi-pass Rheometer (2), and the corresponding colour change was measured using a fibre optic probe attached to an X-Dap Spectrophotometer (3). This experiment enabled the observations of colour changes to be made both during and after shear. During shear, results show that the magnitude of colour change increases with increasing shear rate. In addition, colour relaxes to a no-shear quiescent value with a characteristic time constant that is independent of the initial shear rate.

Further studies of pigment flocculation after shear were also made using the CSS optical shearing cell (4). It is possible to make direct optical observations of diluted pigment particles and observe the way in which these particles flocculate on cessation of shear. Qualitatively, optical results follow a shear induced deflocculation model and colour changes appears to be more sensitive to microstructure changes in the liquid paint than to the rheology

- 1) U. Kaluza, Prog. Org. Coating, 10, 289-330(1982)
- 2) M. R. Mackley, R. T. J. Marshall, Smeulders. J Rheol. 39, 1293-1309(1995)
- 3) D. B. Judd, G. Wyszecski, Colour in Business, Science and Industry (1975)
- 4) M. R. Mackley, S. Wannaborwon, P. Gao, F. Zhao, Microscopy and Analysis, 25-27(1999)

**Symposium GN
General Session**

Organizers: Dave S. Malkus and Donald G. Baird

Thursday 8:05 Meeting Room P-Q

GN5

**MORPHOLOGY VARIATIONS AND FLOW ANOMALIES IN EXTRUSION OF
POLYPROPYLENE-EP RUBBER BLENDS**

Krishnamurthy Javaraman¹, Jonathan Lopez¹, Sang-Yoon Kang¹, and Chi-Chang Shu²

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Cross-stream variations in disperse phase volume fraction have been investigated in axisymmetric Poiseuille flow of molten blends of polypropylene and ethylene-propylene copolymer over apparent shear rates ranging from 100 to 12,000 s⁻¹ and at different flow lengths. These blends were prepared with two different EP grades dispersed at about 20 volume percent in the same PP grade as matrix. Flow curves obtained from dies of different diameters show a complex geometry dependence that may be explained with the help of results on drop migration and the morphology observations. These results are also compared with other results by Bousmina et al. for blends with crosslinked rubber particles as the disperse phase.

Thursday 8:30 Meeting Room P-Q

GN6

MICRORHEOMETRY FOR POLYMER MELTS AND CONCENTRATED SOLUTIONS**Gavin J. Braithwaite and Gareth H. McKinley**

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In recent years there has been increasing interest in the behavior of macromolecules near surfaces. The perturbed interfacial conformations of the molecules result in markedly different responses when compared to the behavior of the same polymer molecules in the bulk. This can give rise to effects such as an apparent slip at the interface, and can affect the bulk processing characteristics or lead to complex dynamical features such as melt extrusion instabilities. However, although much significant experimental work has been performed at the nanometer scale using devices such as the SFA, or at millimeter dimensions using standard rheometers, few systems have been studied with micrometer sized gaps which begin to approach the characteristic scales of the macromolecules.

We discuss the design and fabrication of a "microrheometer" using a cantilever spring system and optical flats to generate an ideal viscometric shear flow. Interferometry allows absolute gap and alignment measurements to be made and the sample is optically accessible throughout the experiment. The kinematics of the device are easy to determine, and inertia & instrument compliance are easy to calibrate out of the final results. In this paper we will describe the study of various model room temperature melt systems over a large range of plate separations. Predominantly, we present results in the small amplitude oscillatory regime, so here slip is not the primary concern. However the proximity of the molecules to the walls results in changes in the relaxation time spectrum which can be detected in the linear viscoelastic results. The gap in the device can be varied from ~200 - 3 microns and the sample volume is very small (~1 microliter). The experimental technique is thus also useful for probing the rheology of other materials as diverse as specialized lubricants or foodstuffs at scales more relevant to the usual end-use application, but beyond the range usually accessible in bulk rheometry.

Thursday 8:55 Meeting Room P-Q

GN7

SIMULATION OF FLOW OF DILUTE POLYMERIC SOLUTIONS THROUGH A 4:1:4 AXISYMMETRIC CONTRACTION/EXPANSION GEOMETRY USING CONSTITUTIVE EQUATIONS BASED ON THE ELASTIC DUMBBELL MODEL**Bin Yang and Bamin Khomami**

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In recent years, a number of studies have focused their attention on evaluating the predictive capability of constitutive equations derived based on the elastic dumbbell model to describe flow of dilute polymeric solutions in complex geometries [Yang and Khomami, JNNFM, 82(1999); Li et al., JNNFM, in press]. These studies have shown that dumbbell based models can at best qualitatively describe the experimental measurements. A number of different reasons have been put forward to rationalize the quantitative differences between experimental findings and simulations results. One of the suggested explanations is that dumbbell based constitutive equations such as the Chilcott-Rallison (CR) and the FENE-P models under predict the dissipative stresses of a polymer chain. These additional dissipative stresses have been recently modeled by a number of investigators [Verhoef et al., JNNFM 80(1999); Rallison, JNNFM 68(1997); Hinch, JNNFM, 54(1994)]. Our objective in this study was to investigate whether the differences observed between numerical predictions and experimental observations in flow of dilute polymeric solutions in complex geometries can be accounted for by these additional dissipative stresses. Hence, we have performed simulations in a 4:1:4 axisymmetric contraction/expansion geometry with a number of dumbbell based constitutive equations with or without the additional dissipative stress term. A Comparison of simulations results with the experimental observations of [Rothstein and McKinley, JNNFM, in press] clearly show that dissipative stresses are not the main cause of the discrepancy between the experimental and simulation results. Hence, other explanations such as the accuracy of an entropic spring force law in strong flows as well as intramolecular interactions must be considered to explain the differences between simulation and experimental results.

Thursday 9:20 Meeting Room P-Q

GN8

POST-DIE EXTRUSION OF PLASTIC PIPE

Aaron J. Hade¹, Alan J. Giacomini¹, John C. Slattery², and David N. Githuku³

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In continuous plastic pipe extrusion, melt emerges from an annular die and is then freely drawn down into a sizing sleeve. Here, we investigate this extensional flow with and without an internally applied pressure. For the case without internal pressure, an analytic solution is derived. For the case with internal pressure, a numerical solution is presented, where differential equations for the melt cone shape are derived from a force balance. Design curves are then constructed from the solutions to these models. These curves are helpful in predicting pipe extrusion operating conditions for the post-die region.

Thursday 10:10 Meeting Room P-Q

GN9

ON LOSS OF EXISTENCE AND UNIQUENESS OF PERTURBATION SOLUTIONS FOR STEADY, FULLY DEVELOPED FLOWS OF VISCOELASTIC FLUIDS IN CURVED PIPES

Anne M. Robertson

Department of Mechanical Engineering, University of Pittsburgh, Pittsburgh, PA 15261

Beginning with the work of Dean in 1927, regular perturbation methods have been used to study flows of Newtonian, generalized Newtonian and viscoelastic fluids in curved pipes of circular cross section. In these studies, the perturbation parameter is the curvature ratio: the cross sectional radius of the pipe divided by the radius of curvature of the pipe centerline. Closed form perturbation solutions for steady fully developed flows in curved pipes have previously been obtained for viscoelastic fluids with *zero* second normal stress coefficient including Oldroyd B' fluids, Upper Convected Maxwell (UCM) fluids, Oldroyd-B fluids, and second order fluids with the second normal stress coefficient set to zero. When this coefficient is non-zero, either an additional perturbation expansion has been introduced in order to obtain closed form solutions or the perturbation equations have been solved numerically for specific combinations of non-dimensional parameters.

We will discuss closed form solutions for the perturbation equations for the second order fluid and a four constant Oldroyd-B model, both with *non-zero* second normal stress coefficient. We show that for a countable number of combinations of non-dimensional parameters a perturbation solution exists but is not unique. For other combinations of parameters a perturbation solution does not even exist. This latter result implies that for these parameter values there does not exist a steady, fully developed solution for flow in curved pipes which is a perturbation of the straight pipe solution, regardless of the magnitude of the curvature ratio. We emphasize that these singular points do not arise when the second normal stress coefficient is zero.

Thursday 10:35 Meeting Room P-Q

GN10

ELONGATIONAL RHEOLOGY OF POLYMER MELTS AND SOLUTIONS USING HYPERBOLIC DIES

John Collier¹, Simioan Petrovan¹, and Bijan Seyfzadeh²

¹Chemical Engineering Department, University of Tennessee, Knoxville, TN 37996; ²Chemical Engineering Department, Louisiana State University, Baton Rouge, LA 70803

The elongational rheology of polymer melts and solutions is being determined using hyperbolically converging dies in a capillary rheometer at processing elongational strain rates. The effects of elongational strain rate, Hencky strain, temperature, composition for solutions, and molecular parameters such as chemical structure, molecular weight, and branching content will be presented. The polymers considered are high density and metallocene polyethylenes, polypropylene, and lyocell solutions. Comparison of the results with shearing rheology from capillary and rotational rheometers and with the Cogswell approximation will be shown.

Thursday 11:00 Meeting Room P-Q

GN11

DETERMINATION OF THE MEMORY FUNCTION OF A CONSTANT VISCOSITY VISCOELASTIC FLUID (BOGER FLUID) IN EXTENSIONAL FLOW BY TIKHONOV REGULARISATION

Leong Y. Yeow

Chemical Engineering, The University of Melbourne, Parkville, Victoria 3052, Australia

The filament stretching experiment is now a well-established flow field for studying the behaviour of polymer solutions and melts in extension. An attractive feature of filament stretching is the complete stress and strain history generated by such an experiment. This presentation describes a computational procedure, based on Tikhonov Regularisation, for extracting the memory function of polymer solutions and melts from filament stretching data. The method is demonstrated by applying it to the stress-strain history of a constant viscosity viscoelastic filament (a Boger fluid) taken from the recent literature.

Thursday 11:25 Meeting Room P-Q

GN12

THE EFFECT OF RHEOLOGY IN FILM CASTING

Evan Mitsoulis¹ and Michel Beaulne²

¹Department of Mining Engineering & Metallurgy, National Technical University of Athens, Athens 157-80, Greece; ²Plastics Engineering, ABC Plastics, Toronto, Ontario, Canada

The film-casting process is used industrially to manufacture plastic films that are uniaxially or biaxially oriented. The process is a shear-free process described in terms of the draw ratio, the thickness reduction, and the neck-in. The rheology of the material must be taken into account through some appropriate constitutive equation that describes well the response of the material in extensional flows.

In this work, the film-casting process of polymer melts is examined under isothermal and non-isothermal conditions. The stresses within the film are expressed by an integral constitutive equation of the K-BKZ type, which fits well experimental data for the shear and extensional viscosities and the normal stresses measured in shear flow.

The dimensionless governing equations used to simulate the film-casting process extend from the equations of conservation of mass and momentum using a quasi two-dimensional approach. The simulation results corresponding to experiments for a polypropylene (PP) melt under non-isothermal conditions agree well for both the thickness of the film as well as its temperature variation. The results show that the K-BKZ integral constitutive equation describes well the behaviour of polymer melts for the film-casting process. Parametric studies are undertaken that show the response of the material in the process assuming different extensional viscosities as predicted by the K-BKZ model.

Thursday 11:50 Meeting Room P-Q

GN13

NOVEL APPLICATION OF SYNERGISTIC GUAR/NON-ACETYLATED XANTHAN GUM BLENDS IN HYDRAULIC FRACTURING

Reinaldo C. Navarrete¹, Christine C. Fischer², **Mitchell D. Coffey**³, and **Vernon G. Constien**²

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Non-acetylated xanthan is a variant of xanthan gum which when combined with guar in solution develops a synergistic interaction that generates superior viscosity and particle transport at low polymer concentrations. These water-base fluids have improved low shear viscosity when compared to fluids viscosified using a single viscosifier such as guar or xanthan gum. The blends can be crosslinked to provide enhanced viscosity at higher temperatures. The synergistic blends of non-acetylated xanthan and guar provide better particle transport using less polymer, which makes them ideally suited as fracturing fluids. Fracturing fluids have been traditionally viscosified with guar and guar derivatives. In the hydraulic fracturing process a fracture is created in an oil reservoir by pumping a viscous fracturing fluid under pressure in order to generate a highly conductive path for oil and gas to flow through. Sand particles, called proppants, are suspended in the fluid and transported into the fracture to prop it open once the pumping pressure is off. The effect of different parameters on the rheology of the blends will be shown, such as the

Thursday Morning

ratio of guar to non-acetylated xanthan, the effect of salts, temperature and high shear rates. A video of scaled slot flow proppant transport tests will be shown to illustrate the transport capability of the blend with respect to pure guar fluids.

Symposium MS Rheology of Polymer Melts and Solutions

Organizers: John L. Schrag and Faith Morrison

Thursday 8:05 Hall of Ideas J MS22

A NONLINEAR FLUID STANDARD REFERENCE MATERIAL - SRM 2490: PROGRESS REPORT

Carl R. Schultheisz and Gregory B. McKenna

Polymers Division, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899

A new NIST Standard Reference Material (SRM 2490 - Nonlinear Fluid for Rheological Measurements) demonstrates shear thinning and normal stresses typical of polymeric fluids. SRM 2490 consists of polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane (pristane), giving a stable fluid with a wide temperature range. NIST will certify the linear viscoelastic behavior and the shear-rate dependence of the viscosity and first normal stress difference between 0 °C and 50 °C. NIST will also use the fluid in a round robin to help the polymer community recognize sources of variability in rheological measurements. Here we report progress on the project, and compare solutions of varying concentration.

Thursday 8:30 Hall of Ideas J MS23

RHEOLOGY OF POLYMERIC SOLUTIONS: ZERO-SHEAR CONDITIONS

Vacheslav Yasnovsky

Rheology Associates, Nyack, NY 10960-1712

Current polymer characterization methods include preparation of dilute solutions of a polymer and determination of intrinsic viscosity from which one can calculate the polymer DP using pre-established literature data on a and K values of a semi-empirical Mark-Houwink equation. This method is tedious and often ambiguous; in addition, large volumes of waste solvents are generated. This work opens a way for a single-point DP determination of moderately concentrated solutions minimizing chemical waste.

If viscosity is a rate process, usual thermodynamic relations should describe it. Logically, zero-shear viscosity is a function of enthalpy while shear-thinning is a function of entropy of flow. It will be shown that a modified Mark-Houwink equation provides a functional form for the change in enthalpy of flow with the system composition:

$$RT \ln \eta_R = \Delta H = K * B\phi M^n / (1 + B\phi M^n)$$

Where:

Logarithm of viscosity does increase with the concentration and polymer's molecular weight but in a Langmurian fashion.

K represents a change in enthalpy of viscous flow from a pure solvent to a pure polymer at the same temperature or from a polymer of low M_w to higher M_w , and has the dimensions of energy, (e.g. J/mole) because the ratio $B\phi M^n / (1 + B\phi M^n)$ is dimensionless.

ϕ is the volume fraction of a polymer in solution (concentration units can be used in dilute solutions), and

B is a scaling constant; at $B\phi M^n \gg 1$, $\ln \eta_R = K/RT$

The equation describes published data on the Zero shear viscosity of four polar and non-polar polymers in nine solvents with $R^2 > 0.98$. At low polymer concentrations the equation can be simplified to the Mark-Houwink equation.

Thursday 8:55 Hall of Ideas J

MS24

SHEAR ENHANCED CONCENTRATION FLUCTUATIONS IN A POLYMER SOLUTION**Grant T. Templin and David J. Pine**

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

Light scattering was utilized to study the structure of a semidilute polymer solution under uniform laminar shear flow. A quantitative comparison has been made between experimental results and dynamical theories of shear enhanced concentration fluctuations. The structure factor was obtained for several shear rates while varying both concentration and temperature. Important parameters to the theory including the concentration dependence of the viscosity, normal stress, and characteristic relaxation times were measured independently under the same conditions using standard quasielastic light scattering and rheological techniques. In addition, osmotic compressibility was measured. As the solvent quality increased with increasing temperature, the enhancement of fluctuations by shear was observed to diminish.

Thursday 9:20 Hall of Ideas J

MS25

STRETCHING AND BREAKUP OF ENTANGLED POLYMERIC LIQUIDS**Anubhav Tripathi¹, Stephen H. Spiegelberg², and Gareth H. McKinley²**¹Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139; ²Dept of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

We study the role of the transient extensional viscosity in governing the stretching and breakup of filaments of entangled viscoelastic fluids. Such experiments probe the non-Newtonian fluid rheology in a strong flow far from the near-equilibrium configurations typically studied in shear flows, and provide insight into heuristic concepts such as 'tackiness' and 'spinnability'. Measurements are performed during imposed uniaxial elongation and also following the cessation of stretching in a Filament Stretching Rheometer in which the temperature and environmental surroundings can be controlled. We consider four different classes of entangled polymer liquids that are of importance commercially including (i) pressure sensitive adhesives, (ii) branched and linear polymer melts, (iii) concentrated polymer solutions and (iv) aqueous solutions of associating polymers such as HEUR (Hydrophobically modified urethane-ethoxylate). In contrast to Newtonian liquids in which breakup is governed by surface-tension-driven instabilities, the failure mechanisms of non-Newtonian liquid filaments undergoing extension are more complex. We show that the breakup dynamics in these liquids depend on the extensional viscosity, on molecular parameters such as the chain-length & entanglement density and on external factors such as solvent volatility. For example, pressure sensitive adhesives are elastically stabilized against breakup and are 'tacky' if the solvent evaporation rate is significantly larger than the stress relaxation rate whereas they are 'non-tacky' and undergo capillary breakup if the evaporation rate is much slower than the viscoelastic capillary necking rate. In the case of associative polymers, the breakup mechanism also depends on the concentration of micelles and on ionic or surfactant concentrations. We conclude by comparing our experimental results with simple numerical predictions of appropriate constitutive models for each class of fluid.

Thursday 10:10 Hall of Ideas J

MS26

EFFECT OF DIE GEOMETRY ON THE ONSET OF GROSS MELT FRACTURE**Seungoh Kim and John M. Dealy**

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

Several criteria have been proposed for the onset of gross melt fracture (OGMF), but these depend on the procedure used to for measuring them and are thus not material properties. We propose the use of a critical extensional stress as a criterion for OGMF. This stress is estimated using the entrance pressure drop analyses proposed by Cogswell and by Binding. We used orifice dies to eliminate the complication arising from the presence of a capillary and varied the entrance angle and contraction ratio.

Materials used were a conventional linear low density polyethylene and two new polyethylenes produced by metallocene and constrained geometry catalysts. It was found that critical extensional stress is independent of contraction ratio for a given polymer. It is also independent of entrance angle, as long as this angle is equal to or

greater than 90 degrees. These results support the view that gross melt fracture originates in the die entrance region. The effects of particulate additives (boron nitride and carbon black) and the treatment of the orifice entrance region with fluoropolymer were also investigated.

Thursday 10:35 Hall of Ideas J MS27

EXCESS EDGE EFFECT IN ROTATIONAL PARALLEL PLATE RHEOMETRY

David W. Giles

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

Standard rotational parallel plate geometry involves two plates of equal diameter with the sample sandwiched between them. The ideal sample shape is a cylindrical disk with axially straight sides and diameter equal to that of the plates. In practice, it can be difficult to achieve this ideal shape, due to high viscosity, for example, and some sample excess may protrude beyond the edge of the plates. We studied the effect of this excess edge material on the viscosity or modulus measurement. The error can exceed 10% for a typical geometry of 1 mm gap, 25 mm diameter, and it follows a linear relationship with the gap/diameter ratio. This linear relationship agrees with findings of a previous study (Vrentas et al., Chem. Eng. Sci. 46, 33 (1991)) utilizing a plate-cup geometry simulating a sea-of-fluid on the lower plate. Using larger gaps is thus shown to involve a significant penalty in accuracy, if excess edge material is present and not accounted for. Use of an accounting and correction for excess edge material is examined.

Thursday 11:00 Hall of Ideas J MS28

FLOW ENHANCEMENT DURING THE EXTRUSION OF LLDPE MELTS

José Pérez-González¹ and Morton M. Denn²

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Two linear low-density polyethylenes with nearly the same molecular weights and polydispersities, one a butene copolymer and one a hexene copolymer, were extruded through identical dies of different materials over a wide temperature range. Extrudate appearance and die pressure drop were dependent on the die material and startup conditions, and the two polymers showed qualitative differences in flow behavior. Flow enhancement consistent with a possibly flow-induced phase change was observed under some processing conditions.

Thursday 11:25 Hall of Ideas J MS29

INFLUENCE OF THE RESIDENCE TIME IN THE UNSTABLE FLOW OF CETYLTRIMETHYLAMMONIUM TOSILATE (CTAT) AQUEOUS SOLUTIONS

Lourdes De Vargas¹, José Pérez-González¹, Arturo F. Méndez-Sánchez¹, Sergio Hernández-Acosta², A. González-Alvarez², and O. Manero³

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The capillary and cone and plate flow of micellar aqueous solutions at different concentrations was studied in this work. The experiments were performed above the Kraft temperature by using capillaries of different length to diameter ratios and also different diameters. It was found that flow instabilities associated with a plateau in the flow curve are developed at residence times longer than a critical value, regardless of concentration. At high shear rates and residence flow times less than the critical one, the expected upturn of the flow curve is observed, however, the flow curves become diameter dependent in a contrary fashion as in the case of apparent slip. The upturn is definitively associated with the flow time as evidenced by the cone and plate studies. Finally, at very long residence times in the capillary rheometer, a dramatic spurt flow was observed, which is consistent with a flow-induced structuring. Video images of the spurt flow are presented. L. de Vargas and J. Pérez-González are COFAA fellows, A. Méndez-Sánchez has CONACyT scholarship.

Thursday 11:50 Hall of Ideas J

MS30

POLYETHYLENE MELT ADSORPTION AND DESORPTION IN FLOW: FLUORESCENCE CHARACTERIZATION OF POST-EXTRUSION DIE WALLS

Justin R. Barone and Shi-Qing Wang

Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106

In this paper we report new experimental evidence that supports the previously proposed molecular mechanism for "cohesive" wall slip of polyethylene (PE) on highly adsorbing surfaces, involving disentanglement of adsorbed chains with unbound chains. This is done by pre-coating a slit die wall made of a silicon wafer with a thin layer of fluorescent dye-labeled polyethylene and then extruding through the slit die a non-fluorescent polyethylene both below and beyond the interfacial stick-slip transition (SST). Using a laser confocal microscope, the post-extrusion die walls were examined to show that the pre-adsorbed fluorescent PE chains were still present after the stick-slip transition. In contrast, slit die walls made of brass became weakly adsorbing after an induction period and could not retain any adsorbed chains at a stress level of 0.1 MPa, as evidenced by the absence of pre-adsorbed fluorescent PE upon flow.

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