THE SOCIETY OF RHEOLOGY

69TH ANNUAL MEETING PROGRAM AND ABSTRACTS

Hyatt on Capitol Square
Columbus, Ohio
October 19-23, 1997

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Meeting Schedule

Monday, October 20, 1997

8:30	S. Nagel (PL1)			
9:20	Coffee			
9:45	SL1	MT1	HT1	SP1
10:10	SL2	MT2	HT2	SP2
10:35	SL3	MT3	HT3	SP3
11:00	SL4	MT4	HT4	SP4
11:25	SL5	MT5	HT5	SP5
11:50	Lunch			
1:30	SL6	MT6	HT6	SP6
1:55	SL7	MT7	HT7	SP7
2:20	SL8	MT8	HT8	SP8
2:45	SL9	MT9	HT9	SP9
3:10	Coffee			
3:35	BS1	MT10	HT10	SP10
4:00	BS2	MT11	HT11	SP11
4:25	BS3	MT12	GN1	SP12
4:50	BS4	MT13		SP13
5:15	End			
7:00	Society Reception			

Tuesday, October 21, 1997

8:30	G. G. Fuller (PL2)			
9:20	Coffee			
9:45	FI1	MT14	SL10	SP14
10:10	FI2	MT15	SL11	SP15
10:35	FI3	MT16	SL12	SP16
11:00	FI4	MT17	SL13	SP17
11:25	FI5	MT18	SL14	SP18
11:50	Lunch			
1:30	FI6	MT19	FM1	SP19
1:55	FI7	MT20	FM2	SP20
2:20	FI8	MT21	FM3	SP21
2:45	FI9	MT22	FM4	SP22
3:10	Coffee			
3:35	MX1	MT23	FM5	BS5
4:00	MX2	MT24	FM6	BS6
4:25	MX3	MT25	FM7	BS7
4:50	MX4	MT26	FM8	BS8
5:15	End			
5:30	Business Meeting			
7:00	Awards Reception			
8:00	Awards Banquet			

Wednesday, October 22, 1997

8:30	P. T. Callaghan (PL3)			
9:20	Coffee			
9:45	FI10	MT27	FM9	BS9
10:10	FI11	MT28	FM10	BS10
10:35	FI12	MT29	FM11	BS11
11:00	FI13	MT30	FM12	BS12
11:25	FI14	MT31	FM13	BS13
11:50	Lunch			
1:30	FI15	LC1	FM14	BS14
1:55	FI16	LC2	FM15	BS15
2:20	FI17	LC3	FM16	BS16
2:45	FI18	LC4	FM17	BS17
3:10	Coffee			
3:35	FI19	LC5	FM18	NP1
4:00	FI20	LC6	FM19	NP2
4:25	FI21	LC7	FM20	NP3
4:50	FI22	LC8	FM21	NP4
5:15	End			
5:30	Poster Session & Refreshments			

Thursday, October 23, 1997

8:05	BL1	LC9	FM22	NP5
8:30	BL2	LC10	FM23	NP6
8:55	BL3	LC11	FM24	NP7
9:20	BL4	LC12	FM25	
9:45	Coffee			
10:10	MX5	LC13	SL15	GN3
10:35	MX6	LC14	SL16	GN4
11:00	MX7	LC15	SL17	GN5
11:25	MX8	LC16	SL18	GN6
11:50	MX9	LC17	SL19	GN7
12:15	End			

Session Codes

BL = Biological Systems
BS = Rheology and Flow-Induced Structure of Blends and Solutions
FI = Melt Flow Instabilities and Wall Slip
FM = Non-Newtonian Fluid Mechanics
GN = General Session
HT = Heterogeneous Systems
LC = Liquid Crystals: Structure and Rheology
MT = Molecular Theories for Polymer Dynamics
MX = Rheology and Mixing
NP = Novel Polymer Systems
PL = Plenary Lectures
SL = Rheology of Solids
SP = Suspensions

Contents

Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Governor's Ballroom PL1

GRANULAR GASES, FLUIDS AND SOLIDS

Sidney Nagel
University of Chicago

Sand in an hourglass, salt piles along the side of a highway, screes at the bottom of a mountain and sugar in a bowl are all examples of granular materials which are ubiquitous in our daily lives. Such materials play an important role in many industrial as well as geological processes. Yet, despite their pervasiveness, granular media behave in surprising ways, often having properties different from those commonly associated with solids, liquids or gases: in a large container of sand, sound will not propagate horizontally; during an avalanche, the "fluid" motion is confined to a thin boundary layer near the surface rather than throughout the bulk as in a liquid; in a gas of sand grains, the particles coalesce into long, thin, tendrils. Another example of exceptional behavior is found in a vibrated container filled with grains, where large particles separate from the smaller ones at the top surface despite the fact that entropy arguments favor complete mixing of the sizes. In such conditions, we also find convection rolls forming spontaneously. In this lecture, I will review a few of these unusual properties and describe some recent research on these fascinating materials.

Symposium SL
Rheology of Solids

Organizers: Gregory B. McKenna, Robert Shay and Omar A. Hasan

Monday 9:45 Senate SL1

THERMOVISCOELASTIC CONSTITUTIVE MODELS FOR DESCRIBING ENTHALPY RELAXATION IN AMORPHOUS POLYMERS

M.R. Hooker, P. Shirkhande and J.M. Caruthers
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-1283

For amorphous polymers in the glass transition region, nonlinear viscoelastic behavior is observed for a variety of phenomena, including volume and enthalpy relaxation. The effects of thermal history on both volume and enthalpy relaxation are traditionally described by the Narayanaswamy-Moynihan model, including the numerous variations in the specific forms of the relaxation spectra and the shift function. Although these models can qualitatively capture many features of the experimental data, several deficiencies exist including (i) different material parameters are needed to describe volume vs. enthalpy relaxation data, (ii) the material parameters vary with thermal history, and (iii) these models are unable to capture enthalpy and volume relaxation when the material is annealed for long times well below Tg and then reheated through the glass transition region. Using the Rational Mechanics Framework, thermoviscoelastic constitutive equations for amorphous materials that relax on a t* material timescale have recently been developed (Lustig, et al, J. Rheol. 1996). Both enthalpy and volume constitutive equations are determined from the same underlying nonequilibrium Helmholtz free energy in a self-consistent manner; thus, enthalpy and volume relaxation exhibit significant similarities, although the actual relaxation response are not identical. This approach

provides a logical methodology for comparing the differences/similarities in volume and enthalpy relaxation. Generalizing the postulate of Adam-Gibbs, it has been assumed that the log a shift function depends upon the configurational part of the entropic constitutive functional; therefore, the shift function exhibits memory in addition to the explicit dependence on the instantaneous volume and temperature. This inherent time dependence in log a accounts for some of the difficulties in the more traditional models in describing enthalpy relaxation data, where material parameters are observed to depend upon the details of the thermal history.

Monday 10:10 Senate SL2

VOLUME AND ENTHALPY RECOVERY OF POLYSTYRENE

S.L. Simon and D.J. Plazek
University of Pittsburgh, Pittsburgh, PA 15261

Volume and enthalpy recovery measurements were made on a polystyrene at isothermal aging temperatures near Tg. Volume and enthalpy both decrease during physical aging and level off at equilibrium. The temperature dependence of the shift factors used to reduce the volume and enthalpy recovery data and the times required to reach equilibrium for the two properties agree within experimental error. The shift factors appear to follow the VTF equation given for creep data in other work except at the lowest temperatures. Although the times required to reach equilibrium appear to be the same, the approach to equilibrium differs for the two properties, with volume recovering faster than enthalpy at short times.

Monday 10:35 Senate SL3

THE EFFECT OF LOCAL DENSITY FLUCTUATIONS ON VOLUME RELAXATION IN THE GLASS TO RUBBER TRANSITION REGION

G.A. Medvedev, R. Bhatia, H.S. Lackritz and J.M. Caruthers
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-1283

It has been traditionally assumed in models for volume relaxation of amorphous glasses that the rate of volume relaxation depends upon the temperature and density (or some other descriptor of the nonequilibrium state like the fictive temperature, etc. that depends upon the density), where the density is an average of the local density that must exhibit spatial and temporal fluctuations. A stochastic term has been added to the well-known single relaxation time model of Kovacs so that the rate of relaxation depends upon the instantaneous and local density rather than the average density. The form of the stochastic term is not arbitrary, but is completely specified by the fluctuation-dissipation theorem once the size of the local domain is set. The macroscopically observed volume response to a given thermal history is determined for the complete set of thermal histories reported by Kovacs (1963). The single relaxation time stochastic model predicts the experimental data, which exhibits highly non-exponential decay; in addition, the stochastic model is able to predict the volume response for long annealing times well below Tg--results which cannot be predicted using the traditional models for volume relaxation. A key consequence of the stochastic model is that it naturally predicts the relaxation spectrum associated with an ensemble of realizations is thermorheologically complex.

Monday 11:00 Senate SL4

STRUCTURAL RECOVERY IN PLASTICIZED EPOXY: FIRST EVIDENCE OF A MOISTURE INDUCED MEMORY EFFECT

W.H. Han and G.B. McKenna
Polymers Division, NIST, Gaithersburg, MD 20899

The glass transition temperature Tg of a polymer glass, e.g., epoxy, can be easily lowered by 20 K or more in the presence of only a few percent moisture. We have studied the impact of moisture on the structural recovery and physical aging responses of a model epoxy network. We first demonstrate a strong analogy between humidity and temperature by showing the existence of a humidity glass transition Hg in isothermal dilatometry experiments. Furthermore, at constant temperature, we performed relative humidity (RH)-jump experiments in which the creep response of thin films of the epoxy was measured as a function of the time after the RH-jump. The use of 0.06 mm film thicknesses makes possible the separation of the aging times from the diffusion times, the latter being much longer than the equivalent thermal diffusion time in T-jump experiments. RH up- and down-jumps in isothermal conditions showed asymmetry of the approach to equilibrium observed by Kovacs in classical T-jump experiments in glasses. Furthermore, aging only part-way towards equilibrium leads to the first evidence of a plasticizer-induced memory effect--the creep compliance showed a maximum following the two-step RH-jump. Volumetric measurements under the same sorts of humidity histories are also examined and the results compared to the viscoelastic measurements.

Monday 11:25 Senate SL5

PREDICTION OF THREE-DIMENSIONAL DEFORMATIONS FOR POLYMER SOLIDS IN THE GLASS TRANSITION REGION USING A NONLINEAR THERMOVISCOELASTIC CONSTITUTIVE EQUATION

R.S. Chambers*, J.M. Caruthers and D.B. Adolf***

*Sandia National Laboratories, Albuquerque, NM 87185-5800 and **School of Chemical Engineering, Purdue University, West Lafayette, IN 47907

Three dimensional finite element code has been developed for a recently proposed nonlinear thermoviscoelastic constitutive equation, where the relaxation occurs on a t* material timescale that depends upon the configurational part of the time dependent entropy (Lustig, et al, J. Rheology, 1996). Three dimensional stress/strain fields have been determined for a variety of deformation conditions that are employed to experimentally measure the nonlinear mechanical behavior of polymer solids, including uniaxial extension, uniaxial compression, torsion of a rod, and torsion of cylinder, where experimentally realizable boundary conditions have been utilized. The resulting kinematic/stress fields can exhibit significant spatial dependence even for these relatively simple deformation situations. Specifically, since the rate of relaxation is a sensitive function of the local density, very small spatial variations in density can lead to large variations in the stress field, and in certain situations these spatial variations can propagate into zones of large deformation like necking in uniaxial extension, shear banding, etc. For example, if a cylinder is subjected to a finite torsional deformation, the material at the surface of the cylinder is effectively in biaxial extension with significant dilation so that the material may be close to the yield condition, while the material at the center of the cylinder is will experience a significant hydrostatic stress which acts to inhibit yield. Similar complex spatial fields have been determined for all the test geometries that have been investigated. These results clearly show that it will be exceedingly difficult to infer nonlinear viscoelastic material behavior from the traditional analysis of experimental data, which implicitly assumes idealized kinematics. The need for large-scale, three-dimensional finite element calculations in order to connect the predictions of nonlinear viscoelastic constitutive equations with experimental data is clearly demonstrated.

Symposium MT
Molecular Theories for Polymer Dynamics

Organizers: Ralph H. Colby and Michael Rubinstein

Monday 9:45 Executive MT1

THEORY OF SPIN CORRELATIONS IN POLYMERIC NETWORKS AND ENTANGLED LIQUIDS

Sergei Panyukov*, Alexander Deshkovski and Michael Rubinstein****

*P.N.Lebedev Physics Institute, Russian Academy of Sciences, Moscow, Russia; ** Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290

Kinetics of spin relaxation in polymeric networks and entangled liquids is studied on the basis of the Rouse and reptation models. We derive analytical expressions and carry out numerical simulations for a sine correlation function, which is sensitive to modulations of nuclear interactions caused by slow molecular reorientations. The predictions of the theory can be directly tested by the nuclear magnetic resonance experiments.

Monday 10:10 Executive MT2

KINETICS OF SOLVENT ABSORPTION IN A HIGHLY SWELLABLE ELASTOMERIC NETWORK

Benoit Barriere* and Ludwik Leibler**
*LEM, Centre d'Etudes, de Recherche et de Developpement Elf Atochem, 27170 Serquigny, France; **Unit Mixte de Recherche CNRS-Elf Atochem, Centre d' Applications de Levallois, 95 rue Danton, 92303 Levallois-Perret Cedex, France.

In order to model a polymer gel or an elastomer undergoing a large change in volume under the action of a solvent diffusing in or out of it, a theoretical approach based on an elastohydrodynamic point of view is proposed. Drawing a parallel between the polymer network/solvent system of interest and a liquid flowing through a porous medium, the friction between the polymer and the solvent is described phenomenologically. An equation that couples the large elastic deformations undergone by the polymer network and the diffusion process is then derived and solved numerically in numerous cases. Special emphasis is placed on the influence of the shear elasticity during the diffusion process. In particular during the swelling process, a non-zero shear modulus induces a non-isotropic swelling at the surface that is responsible for the sigmoidal shape of the mass uptake of solvent with the square root of time, as well as for the presence of a front in the concentration profile of the solvent when the latter diffuses inside the network.

Monday 10:35 Executive MT3

ELASTICITY OF POLYMER NETWORKS

Michael Rubinstein* and Sergei Panyukov**
*Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290; **P.N. Lebedev Physics Institute, Russian Academy of Sciences, Moscow, Russia 117924

We demonstrate that the origin of non-linear elasticity of polymer networks is in the non-affine deformations of these networks. We introduce the affine length, which separates the solid-like elastic deformations on larger scales from liquid-like non-affine deformations on smaller scales. This affine length grows as 3/2 power of elongation and decreases as square root of compression. The behavior of networks on scales up to this affine length is that of stretched or compressed individual chains (we call them affine strands). The affine strands are stretched in the elongation direction and confined and folded in the effective tubes in the compression direction. The fluctuations of the affine strands determine the diameters of confining tubes, which change non-affinely as square root of network deformation. Our model gives a unified picture of deformation of both phantom and entangled networks and leads to stress-strain relation which is in excellent agreement with experiments.

Monday 11:00 Executive MT4

ON THE ELASTICITY OF POLYSOAPS

A. Halperin* and O. Borisov**
*ICSI-CNRS, 15 rue Jean Starcky, 68057 Mulhouse, France; **Department of Physical and Collod Chemistry, Wageningen Agricultural University, 6703HB Wageningen, The Netherlands

Polysoaps comprise of a water-soluble backbone incorporating, at intervals, covalently bound amphiphilic monomers. In water, the polymerised amphiphiles self assembled into micelles of various geometries. This induces a dramatic modification of the spatial configurations of the polymers. What were featureless random coils now exhibit intramolecular, hierachial self organisation. Due to this self organisation it is necessary to modify the description of the large scale behaviour of these polymers: Their configurations, dimensions and elasticity. Understanding the behaviour of these polymers is of practical interest because of the wide range of their industrial applications, It is of fundamental interest because polysoaps are characterized by a rugged free energy landscape that is reminiscent of complex systems such as proteins and glasses. The talk will summarize theoretical considerations concerning the deformation behaviour of a linear string of intrachain micelles. In particular (i) The extension behaviour of a single chain. For intermediate extensions the force law exhibits a plateau associated with coexistence of dissociated and micellised amphiphiles The nature of the force law and its relation to the one dimensional character of the system will be discussed.(ii) The effect of free surfactants on the extension behaviour. Addition of free surfactants is expected to give rise to a "critical point" in the fR diagrams. (iii) The confinement behaviour of polysoaps. In this

case no coexistence regime is expected. However, the coupling to the micellar structure does give rise to a novel force law.

Monday 11:25 Executive MT5

PERISTALTIC INSTABILITY OF CYLINDRICAL GELS

Benoit Barriere*, Ludwik Leibler, and Ken Sekimoto*****

*LEM, Elf Atochem, 27170 Serquigny, France; **Unit Mixte de Recherche CNRS-Elf Atochem, 95 rue Danton, 92303 Levallois-Perret Cedex, France; ***Yukawa Institute for Theoretical Physics Kyoto University, Kyoto 606-01, Japan.

We investigate the stability of a polymer gel of a cylindrical shape, swollen in a solvent and subject to a strong surface tension. The criterion for the occurrence of a peristaltic instability - induced by the surface tension but resisted by the shear elasticity of the gel - is derived. The dynamics of the gel/solvent system are then described within the frame of linear elasticity. This allows to determine the preferred wavelength at which the instability develops initially. Shrinking gels may show such an instability, as has been reported by Matsuo and Tanaka [Nature 358, 482 (1992)]. Considering approximate values of the relevant parameters, we find results in qualitative agreement with their experiments.

Symposium HT
Heterogeneous Systems

Organizers: Joe Goddard and Andrew M. Kraynik

Monday 9:45 Judicial HT1

LIGHT SCATTERING AND RHEOLOGY OF A MODEL FOAM

U. Nobbmann, F. Dorri-Nowkoorani, and B.J. Ackerson

Department of Physics, Oklahoma State University, Stillwater, OK 74078

Static and dynamic light scattering and rheological measurements have been conducted on a commercially available shaving cream as a function of time. The samples are highly multiple scattering, and the transmitted intensity is used to measure the mean scattering length or average bubble size. The mean bubble size increases as the square root of elapsed time and is used to reduce dynamic light scattering data and characterize the crossover time between thermal fluctuations and bubble rearrangement regimes. The elastic modulus is characterized by three different methods using creep, creep recovery, and stress oscillation experiments. It follows the same power law behavior in all three measurements. The elastic modulus is expected to be inversely proportional to the bubble size, but we find the exponent to be -2/3. Yield stress measurements do indicate values inversely proportional to the bubble size and a yield strain of approximately 0.07 independent of bubble size.

This research is supported by the National Science Foundation grant DMR 9501865.

Monday 10:10 Judicial HT2

MICROMECHANICS OF CLOSED-CELL FOAMS

Andrew M. Kraynik and Michael K. Neilsen

Engineering Sciences Center, Sandia National Labs, Albuquerque, NM 87185-0834

We analyze the micromechanics of low-density foams with closed cells, e.g. rigid polyurethane foam. The foams are modeled as spatially periodic structures composed of thin cell walls and range in complexity from perfectly ordered Kelvin cells to tetrahedrally close-packed (tcp) foams, which have crystal symmetry, to random structures based on Voronoi polyhedra. Macroscopic behavior is determined from cell-level forces and distortions of representative foam volumes under periodic boundary conditions. Finite element methods are used to calculate large-deformation response. Shell elements are used to model closed-cell foams and beam elements are used for open-cell foams. We focus on connections between macroscopic response of foams and cell-level geometrical features. We compare and contrast the behavior of open-cell and closed-cell foams, as well as predictions based on 2D and 3D models of foam structure. This work performed at Sandia National Labs with support from the U.S. Department of Energy under contract #DE-AC04-94AL85000 and from the Dow Chemical Company under a CRADA.

Monday 10:35 Judicial HT3

ANALYSIS OF AN EMULSION YIELDING WITH A NEW POSITION ECHO TECHNIQUE

P. Hebraud*, F. Lequeux*, J.P. Munch and D.J.Pine****

*Laboratoire de Dynamique des Fluides Complexes, 3 rue de l'Universite, 67070 Strasbourg FRANCE; **Departments of Chemical Engneering and Materials, University of California, Santa Barbara, CA 03106

We analyse the motion of the particles in concentrated emulsions submitted to a periodic strain. We use diffusing wave spectroscopy to detect the echoes of particle positions after times equal to multiples of the strain period. We observe that some droplets are rearranged, so that they experience a chaotic motion, while others experience a purely periodic motion. It appears that the volume fraction of the rearranged droplets grows like the square of the strain amplitude. We show that the mechanical yielding is clearly related to the echo attenuation.

Monday 11:00 Judicial HT4

ELASTOPLASTIC ARCHING IN 2D GRANULAR HEAPS

J.D. Goddard, F. Cantelaube and A.K. Didwania

Dept. of Applied Mechanics and Engineering Sciences, University of California, San Diego, La Jolla, CA 92093-0411

A theory is given for the stress distribution in deep, two-dimensional static granular heaps or "wedges", modeled as isotropic linear-elastic continua subject to Mohr-Coulomb yielding. For symmetric heaps, with both surfaces inclined at the usual angle of repose, we find three distinct symmetric solutions. One solution exhibits a central minimum or "dip" in the vertical normal stress, corresponding to the experimentally observed "arching" that has become the subject of recent literature on "sandpile physics" [1].

As an extension of our previous work [2], we consider asymmetric heaps or "berms" with one face inclined at the angle of repose. Here, we find a multiplicity of solutions, including continuous families as well as isolated solutions. The continuous families extend to the limit of symmetric heaps, representing asymmetric states. We discuss some possible rheological resolutions to this problem of static multiplicity.

1. A. Watson, "Searching for the Sand-Pile Pressure Dip", Science, 273, 579 (1996).

2. F. Cantelaube and J.D. Goddard, "Elastoplastic Arching in 2D Granular Heaps", in Powders and Grains '97, R. Behringer et al., eds., Balkema, 1997.

Monday 11:25 Judicial HT5

PRESSURE DISTRIBUTION IN SILOS AND DEEP EARTH: THE JACKI LAW FROM QUASI-STATIC RHEOLOGY OF SOIL

Pierre Evesque

Lab. MSSM, URA 850 CNRS, Ecole Centrale Paris; F-92295 Châtenay-Malabry, France

We propose a new theoretical model to calculate the ratio $k_o= s_h/s_v$ between horizontal s_h and vertical s_v stresses in deep earth or in an oedometer test. It assumes that granular material obeys the Rowe equation and that it reaches a stabilized state. This last point imposes in particular that small stresses are reversible and controlled by the Rowe equation. This model gives a k_o value whose dependence as a function of the angle of solid friction j is close to one of Jaki's law $k_{\mathrm{Jaki}} = 1\text{-}\sin j$. It is equal to 0.5 for j_0°. This model may be generalized to silos or oedometer tests with elastic walls.

The proposed model starts from the rheological laws of granular materials from triaxial tests, or shear box tests, which are now well established experimentally. We propose now a scheme which allows one to understand why Rowe's law of dilatancy is so powerful and robust. This is complementary to the demonstration of the Jacki law.

Symposium SP
Suspensions

Organizers: Ronald Phillips and Tony Ladd

Monday 9:45 Legislative SP1

NONLINEAR STRUCTURAL TIME RESPONSE OF A MAGNETIC SUSPENSION IN A TWO-DIMENSIONAL PULSED FIELD

A.S. Silva and D. Wirtz
Department of Chemical Engineering, The Johns Hopkins University, Baltimore, MD.

Video-microscopy, high-resolution particle tracking and time-resolved light scattering are used to investigate the remarkable non-linear motion of magnetic particles in a two-dimensional field. The use of two time-dependent pulsed crossed fields is shown to generate large aggregates of size and shape depending on the frequency and amplitude ratios of the two fields. In particular, we study the onset of an interfacial instability, where particles at the interface rotate in a direction opposite to that of the core of the domain. This instability is studied using models recently developed to study electrophoretic instabilities.

Monday 10:10 Legislative SP2

MECHANISMS CONTROLLING YIELD AND FLOW IN ER MATERIALS

Frank E. Filisko, Steve Henley, Greg Quist, Carl Aronson
Materials Science and Engineering and Macromolecular Science & Engineering, The University of Michigan, Ann Arbor, MI 48109

The rheological activity of ER materials(under field) is in the simplest case illustrated as a Bingham Body fluid (T=Tc + [etao][gamma dot]); but unlike a BB fluid, the critical stress Tc is a strong and reversible function of electric field. The solid or pre-yield mode occurs when the yield stress T<Tc(E), and the flow or post-yield behavior when TTc(E). Thus the apparent solid state is characterized by its maximum strength or Tc(E), whereas the flow regime by the apparent viscosity [etaap](E) = Tc(E)/[gammadot] ap + [etao], where [etao] is the constant slope dT/d[gammadot] independent of field. Thus both relevant parameters involve Tc(E) and understanding and controlling it are important. Tc(E) is of course related to the strength of interaction between particles but more correctly it is a measure of yield which can be drastically different than due to particle interactions alone. Specifically flow occurs not by uniform shear but by slippage of the activated fluid at the walls and/or along internal planes. Secondly, it is well known that for a given particulate system, the slope [etao] is completely determined by the viscosity of the matrix fluid. Therefore the T at any shear rate could be increased by simply using a higher viscosity fluid, however this leads to a less effective ER fluid. It does however tell us that the base viscosity of the fluid used does affect the difficulty by which the slipping planes slide over each other. Ideally this suggests that the dispersing liquid should have a very low ambient viscosity and a high viscosity at high field. In this paper we will discuss our studies understanding the yield mechanisms in ER fluids, how these can be hindered for increased strength, and how under shear the slope ho can also be varied by being a function of electric field.

Monday 10:35 Legislative SP3

ELECTROHYDRODYNAMIC INSTABILITIES IN SUSPENSIONS OF DNA, COLLOIDS AND CHARGED GELS IN HIGH ELECTRIC FIELDS

J.L. Viovy*, B. Ladoux*, S. Magnusdottir*, H. Isambert, and J.F. Léger*****
*Lab. PCC (UMR CNRS 168), Institut Curie, 11 Rue P. & M. Curie, F-75005 PARIS ; ** Physics Dpt, 532 Clark Hall, Cornell University, Ithaca, NY 14853 2501, USA ; ***LUDFC, Institut de Physique, 3 Rue de l'Université, F-67084 Strasbourg

It has been known form a long time that colloidal suspensions under AC or DC electric fields beyond a given threshold, may undergo rearrangements in "pearl neckless" strings. This is at the origin of important electrorheological properties. When the field is increased further, new and more complex instabilities are observed, which lead to spectacular recirculations, and the creation of chevron-like symmetry-broken aggregates. We discovered a few years ago, that a similar instability occurs in suspensions of large DNA molecules, and is responsible of the present limitations in the separation of large DNA by capillary electrophoresis. Until very recently, however, the origin of this instability was unclear. A theory recently developed in our group associates it with the development of space charges on distances much longer than the Deby length, due to spontaneous-occurring gradients in ion concentration. Two predictions of this theory will be discussed in the conference at the light of experiments recently performed in the laboratory. In particular, we will show that, in agreement with the theory: i/ the use of zwitterionic buffers is an efficient way to control electrohydrodynamic instabilities, and ii/ the instability does not require the presence of mobile dipoles, and can occur also at the surface of a fixed charged gel.

Monday 11:00 Legislative SP4

POLYMER SOLUTION DISPERSED ER ACTIVE SUSPENSIONS

Greg Quist, Frank E. Filisko
Materials Science & Engineering, The University of Michigan, Ann Arbor, MI 48109

ER materials are most commonly suspensions of dielectric particles in fluids, the activity being ascribed to interactions between particles with the fluid being passive, i.e. having no ER activity by itself. The rheological properties of these materials under the influence of an electric field often are modeled in a simplified manner as Bingham Body fluid behavior. Using this model, the critical yield stress can be attributed to the particulate phase while the slope of the flow curve dT/d[gammadot] is related to the viscosity of the fluid phase as well as other factors(e.g. interactions between the suspended particles). In this study the focus has been observing the properties of ER materials in flow when using an ER active polymer solution as the suspending fluid. Electrorheological characterization was performed on several systems, each comprising an ER active particulate phase suspended in a polymer solution. It was consistently found that the slope dT/d[gammadot] was greater than that expected by the superposition of the flow curves of the individual components(i.e. the particulate phase suspended in a non-ER active fluid and the polymer solution alone). Attempts to explain the synergistic nature of this increase involve the interaction between the solvated polymer molecules and the surface of the particles.

Monday 11:25 Legislative SP5

ON THE ROLE OF INTERPARTICLE GAP PROPERTIES IN ELECTRORHEOLOGICAL SUSPENSIONS

I. A. Shkel and D. J. Klingenberg
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This presentation discusses the effect of conductivity and permittivity on the electrorheological (ER) response of suspensions. We present an approximate analytical solution for a chain of particles in an ac electric field, which is valid for touching particles or particles with small separations. For large differences between the particle and continuous phase conductivities or permittivities, the electrostatic force on particle, and thus the magnitude of the ER effect, is dominated by the electric field near the interparticle gap. The electric field in the gap is proportional to α^2, where α is the ratio of magnitudes of the complex particle and liquid permittivities. Such a field distribution leads to a static yield stress proportional to α, and a log α-dependence of the suspension dielectric constant. Of particular importance is that the response is governed by the dielectric properties (permittivities and conductivities) within the interparticle gap. Thus the analytical solution may be applied for situations where the conductivity varies with field strength or chemical composition, provided that the values within the gap are known or can be extracted.

We compare our theoretical results with various experimental results. Permittivities are much less sensitive than conductivities to the electric field strength, as well as chemical composition. In this case, local permittivities will not differ from bulk values. The local conductivities, extracted from experimental data for yield stresses, agree well with suspension dielectric constant measurements over a wide range of frequencies. Our analytical results for yield stresses and suspension dielectric constants are in good agreement with experimental results for suspensions with different values of α.

Monday Afternoon

Symposium SL
Rheology of Solids

Organizers: Gregory B. McKenna, Robert Shay and Omar A. Hasan

Monday 1:30 Senate SL6

MONOTONICITY OF RESPONSE FOR NONLINEAR VISCOELASTICITY WITH A STRAIN CLOCK

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An important class of constitutive equations for nonlinear viscoelastic response utilizes the concept of a strain clock. The clock takes the form of a material time variable which increases faster than physical time, with a strain dependent rate of increase. Important consequences of the strain clock are that stress relaxation occurs faster as strain increases, and the stress may not increase with the strain in a monotonic fashion. In this work, we discuss the possibility that the strain clock may impose a general loss of monotonicity of response and that deformation histories may branch into multiple histories.

Monday 1:55 Senate SL7

THE USE OF GENERALIZED STRAIN MEASURES IN A THERMOVISCOELASTIC CONSTITUTIVE EQUATION FOR AMORPHOUS POLYMERS

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Using the framework of Rational Mechanics as developed by Coleman (Arch. Rat. Mechan. Anal., 1964), thermoviscoelastic constitutive equations for amorphous fluids and solids have recently been developed (Lustig, et al, J. Rheol., 1996), where relaxation occurs on a material timescale t*. During the development of these constitutive equations, the nonequilibrium Helmholtz free energy was expanded in a Frechet series in terms of the temperature and deformation histories, where the deformation was given in terms of right Cauchy-Green deformation tensor C for solids and the relative right Cauchy-Green deformation tensor Ct for fluids. Objectivity and material symmetry only require that the constitutive functionals depend upon C or Ct; however, the constitutive functionals could just as well depend upon any function of C or Ct. We have introduced generalized deformation tensors, which are arbitrary functions of C or Ct respectively, and then rederived the relevant constitutive equations. For situations where there is no rotation of the principal axes of deformation, the resulting constitutive equations are structurally similar, where there is only a change in the strain measure; however, for deformations that include rotation of the axes there are additional couplings between the various components in the stress constitutive equation. The predictions of the new constitutive equations have been compared with nonlinear viscoelastic data for an epoxy resin system, where predictions using the generalized deformations are better able to describe the experimental data. We believe that the constitutive equations reported in this communication using the generalized deformation tensors are the most general formulation consistent with the principles of Rational Thermodynamics for a rheologically simple material, where the viscoelastic relaxation occurs on a material timescale.

Monday 2:20 Senate SL8

ADIABATIC CREEP AND RECOVERY IN SHEAR

John M. Wiest
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All polymer processing operations involve changes in the temperature of the material, and these temperature changes can be large and occur rapidly. Furthermore, the constitutive behavior of polymeric materials depends in a complicated and not well-known way on the temperature and temperature history of the material. The role of the temperature and temperature history in the constitutive equation for the stress has been studied intermittently for many years, and we are beginning to gain a rudimentary understanding of it. However, much less is known about the constitutive behavior of the heat flux and the internal energy, although these may actually dominate the behavior of polymer processing operations. Here we present the predictions of several models for adiabatic creep and recovery experiments. We demonstrate that these experiments show potential for studying the non-equilibrium nature of the internal energy.

Monday 2:45 Senate SL9

VISCOELASTIC AND PHYSICAL AGING RESPONSES IN AMORPHOUS PEN FILMS

M.L. Cerrada and G.B. McKenna
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Characterization of the aging response of poly(ethylene naphthalate) (PEN) is of increasing interest as this material begins to see increasing commercial applications. Because PEN can be obtained in both amorphous and semi-crystalline (and oriented) forms, it is of interest to compare the aging response in both conditions. We have already carried out aging experiments in which the creep response of the semi-crystalline film material was characterized in the temperature range from ambient to just above the glass transition temperature. Here we will report results for the amorphous material in which we see that the large sub-glass beta transition evidences itself in such a way that at low temperatures and short aging times, one observes power law behavior and typical time-aging time superposition. However, as aging times get longer, a second mechanism becomes evident and time-aging time superposition is no longer valid. In addition, as the temperature increases one also sees evidence for two mechanisms and lack of superposability until at the highest temperatures examined we observed again a single relaxation mechanism and a return to data superposability.

Symposium BS
Rheology and Flow-Induced Structure of Blends and Solutions

Organizer: Jan van Egmond

Monday 3:35 Senate BS1

MICRORHEOLOGICAL MEASUREMENTS OF POLY(ACRYLIC ACID) GEL MODULI USING OPTICAL TWEEZERS

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*Dept. Chemical Engr., Princeton Univ., Princeton, NJ 08544 ; **Dept. Molecular Biology, Princeton University, Princeton, NJ 08544

The ability of infrared laser traps to apply controlled force on micron-sized probe particles is used in a study of the viscoelastic properties of soft polymeric materials such as poly(acrylic acid) gels. The loss and storage moduli of these materials can be determined over a greatly extended frequency range by the measurement of the mean square displacement of the probe particle by under the influence of fluctuating Brownian forces. As a model system we study soft poly(acrylic acid) gels near the gelation threshold and study the uniformity and/or heterogeneity of gel structure at the length scales of a micron. The mechanical properties are measured at several hundred locations in the gel by monitoring the response of probe particles introduced to the gel during polymerization. The use of the optical trap technique to measure rheological properties in the free oscillation mode by measuring the power spectrum of mean squared displacement will be compared with measurements using forced displacement of the particle in a trap with a known potential field.

Monday 4:00 Senate BS2

JUNCTION DYNAMICS AND RHEOLOGY OF MODEL WORMLIKE MICELLAR SOLUTIONS

Martin Kroger and Avinoam Ben-Shaul

The Hebrew University of Jerusalem, Department of Physical Chemistry and The Fritz Haber Research Center, IL-Jerusalem 91904, Israel

Recent molecular-level calculations suggest that, in equilibrium, branching of a living wormlike micelles in dilute solutions is, generally, energetically unfavorable [1]. Nevertheless micellar junction formation may be (entropically) favorable at higher concentrations due to excluded volume interactions and/or under nonequilibrium (flow) conditions. We study the dynamics and lifetime of junctions in wormlike micellar systems both theoretically and by nonequilibrium molecular dynamics simulations. The simulations will be performed using a modified FENE-C multibead model, which was originally introduced in [2,3] to investigate linear micelles in dilute and concentrated solutions. The model is extended to incorporate multifunctional beads. We present results for the dynamics and lifetime of junctions, the size distribution, the shear flow rheology, the flow-alignment and structure factors. We focus on the dependence of the rheological behavior on the density and stability of junctions and the total bead concentration.

[1] S. May, Y. Bohbot and A. Ben-Shaul, 'Molecular theory of bending elasticity and branching of cylindrical micelles', submitted 1997. [2] M. Kroger and R. Makhloufi, Phys. Rev. E 53 (1996) 2531. [3] W. Carl, R. Makhloufi and M. Kroger, J. Phys. France II, in press.

Monday 4:25 Senate BS3

INHOMOGENEOUS SHEAR FLOW OF WORMLIKE MICELLES

J.-F. Berret*, G. Porte*, J.L. Harden* and J.-P. Decruppe**

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Combining nonlinear rheology, flow birefringence and small-angle neutron scattering under shear, we have investigated semidilute and concentrated solutions of wormlike micelles. From their linear mechanical responses, these viscoelastic fluids are pure Maxwellian fluids. The stress relaxation function reads G(t) = Gexp(-t/t0), where G is the elastic modulus and t0 the relaxation time. When subjected to steady shear, wormlike micelles are found to undergo a transition toward an inhomogeneous state of flow. This transition manifests itself through a plateau in the shear stress versus shear rate behavior, for stresses ~ G and strain rates ~ 1/t0. In the plateau regime, flow birefringence measurements in the direction of the vorticity (using Couette flow) enables a direct visualisation of the two coexisting phases. One is strongly birefringent whereas the other exhibits a much weaker birefringence.

We propose a phenomenological explanation of these results in terms of an effective non-equilibrium potential that accounts for the free energy stored in a viscoelastic material under steady shear conditions. This model relies on two observations which present striking analogies with ordinary field-induced phase transitions in equilibrium systems : the robustness of the two-state banded-flow regime and the kinetics of the band formation under shear (metastability and spinodal decomposition).

Monday 4:50 Senate BS4

GELATION, SLIP, PHASE SEPARATION, AND COEXISTENCE IN SHEARED MICELLAR SOLUTIONS

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The formation of flow-induced structures in low-concentration worm-like micellar solutions is studied using simultaneous visualization and rheological methods in the same flow cell. The visualization measurements show growth of a new viscous shear-induced phase (SIP) which is closely correlated to the increase in the apparent viscosity. The shear-induced phase transition depends on whether the applied stress or the shear rate is held constant. When the shear stress is held constant, the system macroscopically phase separates into two coexisting phases with a single stable interface between them. By contrast, when the shear rate is held constant, the system still undergoes a phase transition, but the steady states are homogeneous and no coexistence is observed. This leads to different rheological behavior and unusual long-lived metastable states. The velocity profile in the gap was obtained during the transition and shows slip between the SIP and the flow cell surfaces. Above a certain shear rate, the SIP exhibits "fracture" or "shear banding" type instability, which is characterized by a stress plateau and multiple flow regimes as shown by the visualization images.

Symposium MT
Molecular Theories for Polymer Dynamics

Organizers: Ralph H. Colby and Michael Rubinstein

Monday 1:30 Executive MT6

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

Charles P. Lusignan* and Ralph H. Colby**

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

Monday 1:55 Executive MT7

DYNAMIC RHEOLOGY OF BRANCHED (AND UNBRANCHED) POLYMERS: INSPIRATION FROM THE STARS.

S. T. Milner* and T. C. B. McLeish**

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Recently, we have computed the relaxation spectrum of entangled star polymer melts using the concepts of arm retraction and "dynamic dilution" [1] -- the notion that more quickly relaxing portions of a melt are not effective in entangling slower relaxing portions of the same melt on the timescale of their relaxation. The result is a parameter-free theory for G"(w) that compares surprisingly well to dynamic rheology data over the entire frequency range up to the "glassy" region [2]. This success led us to consider two new applications of these ideas, which we shall present here:

1) Blends of star and monodisperse linear polymers, as a case where dynamic dilution is no longer valid, because of the abrupt relaxation of the linear chain fraction at their reptation time. In such a case, tube dilation by the dynamic dilution ansatz is replaced by a slower process, "constraint-release Rouse dilution". We compute G"(w) for star-linear blends for different star volume fractions, and without adjustable parameters obtain reasonable agreement with published data.

2) Rheology of monodisperse linear chains as a melt of "two-arm stars". This approach gives an simple analytical expression for the stress relaxation of linear chains that contains the effects of contour-length fluctuations, exhibits the effective dependence of zero-shear viscosity on the 3.4 power of chain length N over a broad range, and results in a -1/4 power law in G"(w) in the plateau region, in reasonable agreement with published data on large-N monodisperse linear melts.

[1] R. C. Ball and T. C. B. McLeish, Macromolecules 22, 1911 (1989).

[2] S. T. Milner and T. C. B. McLeish, Macromolecules 30, 2159 (1997).

Monday 2:20 Executive MT8

EVOLUTION OF THE RELAXATION PROCESSES DURING THE GEL FORMATION

D. Durand, T. Nicolai, F. Prochazka

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Polyoxypropylene (POP) triol cross-linked with diisocyanate is a good model system to study the relaxation processes over a very broad frequency range covering both the glass transition and the sol-gel transition dynamics. By varying the amount of diisocyanate, stable systems are formed at different stages of the gel formation. By varying the molar mass of POP the influence of the size of the precursor can be investigated. The glass transition is controlled by local segmental motion (so-called a-relaxation) and can be described by a stretched exponential. Cross-linking increases the glass transition temperature to an extent approximately proportional to the ratio isocyanate to alcohol groups: r=[NCO]/[OH], up till r=1. The influence is of course larger for smaller POP precursors. As one increases the amount of cross-linker self-similar aggregates are formed. The structure, size distribution and dynamics of these aggregates are well described by the percolation model for aggregates larger than about 8 precursor molecules. After the gel point we observe in addition to a gel modulus slow relaxation processes which have a power law frequency dependence. These relaxation processes which occur even in the fully grown gel (r=1) and are, as far as we are aware, observed in all gels are not expected by the standard model of polymeric gels.

Monday 2:45 Executive MT9

THEORY OF CHAIN BREAKAGE IN ULTRASONICALLY TREATED RUBBERS

Victor V. Yashin and Avraam I. Isayev

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Rubber treatment with high power ultrasound is a novel technology for recycling waste rubber. In numerous experiments with different types of rubbers, ultrasound was proved to be capable of breaking both polymer chains and chemical crosslinks. A model of the devulcanization process which had been proposed earlier was based on ultrasonic cavitation collapse of gas microbubbles existing in any real rubber. Comparison with experimental data revealed some limitations of this model. In particular, the cavitation model fails to describe the devulcanization process at ambient pressures higher than the acoustic one. Hence further understanding of the molecular mechanism of ultrasonic rubber devulcanization is required. An additional possible mechanism of molecular breakup in rubber network is dynamic fatigue taking place under high frequency mechanical loading. We propose a microscopic model of this fatigue by considering the dynamics of a polymer chain in cyclically loaded viscoelastic medium. Due to the condition of incomplete chain relaxation during repeated loading cycles, the residual stress accumulates in the chains reducing the activation barrier and therefore increasing the probability of chain breakage. The stochastic process of stress accumulation is described using a generalization of the Rouse model which includes the effect of medium relaxation.

Monday 3:35 Executive MT10

RHEOLOGY OF BREAKING AND HEALING OF BLOCK COPOLYMER GELS

A. Turc, W. Wedler, and H. H. Winter
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Block copolymers are known to form ordered structures when subjected to slow flow at intermediate strains. Larger strains and higher rates produce disorder. In this study, soft block copolymer gels are first ordered and then disordered by large strain. The main emphasis is on the recovery of the connected structure after disordering. The associated development of long range connectivity will be monitored by dynamic mechanical spectroscopy. Liquid-solid transitions express themselves in power law spectra at long times. Parameters are temperature history, strain magnitude, and strain rates.

Monday 4:00 Executive MT11

RHEOLOGY OF THE MISCIBLE POLYMER BLENDS POLYSTYRENE/POLY(VINYL METHYL ETHER) AND POLY(METHYL METHACRYLATE)/POLY(STYRENE-CO-ACRYLONITRILE)

Jai A. Pathak*, Ralph H. Colby*, George Floudas, Robert Jerome*** and Reimund Stadler******
*The Pennsylvania State University, University Park, PA ; **Foundation for Research and Technology (FORTH), Heraklion , Crete, Greece; ***University of Liege, Liege, Belgium; ****Universitaet Bayreuth, Bayreuth, Germany

The linear viscoelasticity of two miscible blends have been investigated using oscillatory shear, and compared to that of the pure components. The Flory interaction parameter of each blend is weakly negative. Blends of polystyrene and poly(vinyl methyl ether) exhibit strong dynamic asymmetry ($\Delta Tg = 130$ K), and we find that these blends show thermorheological complexity. In contrast, blends of poly(methyl methacrylate) and a random copolymer of styrene and acrylonitrile, whose glass transitions are closely matched ($\Delta Tg = 20$ K), are thermorheologically simple, in that their oscillatory response can be superposed with the empirical time-temperature superposition principle. These results support the theory of concentration fluctuation induced dynamic heterogeneities in miscible polymer blends.[1] While composition fluctuations are present in both types of blends, the fluctuations are not manifested dynamically in PMMA/SAN blends, because all compositions have roughly the same glass transition, and hence the same monomer friction.

1) Kumar, S. K., Colby R.H., Anastassiadis, S.H. and Fytas, G. *J. Chem. Phys.* 105, 3777 (**1996**).

Monday 4:25 Executive MT12

BULK AND INTERFACIAL CONTRIBUTIONS TO ADHESION OF PRESSURE SENSITIVE ADHESIVES

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Strong adhesive forces between a pressure sensitive adhesive (PSA) and a substrate are often obtained, even when the only direct bonds across the interface are relatively weak Van der Waals bonds. The viscoelastic dissipation of energy within the bulk of the adhesive is much larger than the energy required to break the direct adhesive bonds, and it is well-known that the rheological properties of a PSA must be appropriately tuned in order to optimize its performance. Interfacial properties play a very important role however, in that that they determine the amount of energy which will be dissipated by bulk deformation of the adhesive. The driving force for adhesive (interfacial) failure can be quantified in terms of an energy release rate, which is an experimentally accessible quantity. The relationship between the energy release rate and the rate of adhesive failure determines the stress to which the bulk of the adhesive will be subjected. The energy dissipation is a complicated non-linear function of this stress level, so that subtle changes in the interfacial properties give large changes in the overall adhesion energy. We have developed adhesion tests based on the contact of a transparent, spherical indenter with a thin adhesive layer. By simultaneously measuring the applied load, the resulting displacement, and the contact area between the adhesive and the indenter, we are able to monitor both the interfacial and bulk contributions to the adhesive properties. A transition to extensive fibrillation of commercially available PSA's has been observed. High values for the adhesion energy are obtained when this transition occurs prior to adhesive failure of the interface.

Monday 4:50 Executive MT13

MICROSCOPIC THEORY OF DIFFUSION AND RELAXATION IN DIBLOCK COPOLYMER MATERIALS

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A microscopic theory of diffusion of diblock copolymers above, near and below the order-disorder transition(ODT) has been developed based on polymer mode-coupling and equilibrium integral equation methods. A strong coupling of entanglement constraints, long wavelength concentration fluctuations, and local physical clustering is predicted which can strongly suppress translational motion. Novel, thermodynamic-state-dependent scaling laws for the self diffusion constant as a function of degree of polymerization are predicted. Near, and somewhat below, the ODT the self diffusion constant is reduced in a roughly exponential, thermally-activated manner. At low temperatures, where microdomains are almost pure ,a nearly temperature-independent reduction of relative diffusivity emerges which increases strongly with chain length. The theoretical predictions have been shown to be in good agreement with recent experiments on lamellae-forming polyolefin diblock melts. A theory for homopolymer and diblock tracer diffusion in copolymer matrices has also been developed and applied. Extensive model calculations reveal a rich dependence of translational slowing down on copolymer solution concentration, composition, block local friction constant asymmetry, and chain entanglement characteristics. Generalization of the theory to treat single chain conformational and stress relaxation has been initiated.

Symposium HT
Heterogeneous Systems

Organizers: Joe Goddard and Andrew M. Kraynik

Monday 1:30 Judicial HT6

QUASI-STATIC STATISTICAL MECHANICS AND PLASTICITY OF RIGID SPHERE ASSEMBLIES

J.D. Goddard, K. Ledniczky and A.K. Didwania

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Based on a recently developed numerical simulation [1] of the quasi-static mechanics of assemblies of nearly-rigid frictional spheres, we develop a statistical mechanical model for such systems. The model is based on the hypothesis that the mechanics is defined by a deterministic motion of the particles given by the mean kinematics ("mean-field" or "affine motion" assumption) plus a diffusion-like random motion resulting from stochastic micromechanical interactions. We evaluate both single particle and certain cluster diffusivities, showing that these appear to be relatively small in magnitude and leading to the conclusion that the mean-field model is surprisingly accurate.

1. J.D. Goddard and A.K. Didwania,"Theoretical Estimates and Computations of Yield and Dilatancy Surfaces in Sphere Assemblies", in the press, Quart. J. Mech. Appl. Math., 1997.

Monday 1:55 Judicial HT7

GRAIN ROTATION, CONVECTION AND DIFFUSION IN A 2-D EMBANKMENT UNDER QUASI STATIC CYCLIC DEFORMATION

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Recently, mechanics of granular matter is attracting much interest. Most of the works concern beds fluidized by vibrations where convection occurs, chute flows or avalanche. But quite interesting problems occur also in the so-called quasi-static regime for which the initial concepts of friction and dilatancy have been introduced. We demonstrate in this paper that convection and diffusion of grains can also be generated in quasi-statics when samples are submitted to slow cyclic horizontal strains. This result seems quite important since it has some consequence in two different kinds of problem:

i) as explained in the paper, this convection is mainly induced by solid friction which imposes that a grain at a given point is submitted to two different local motions (i.e. sliding directions) depending on the push or pull condition. This local motion has to be counterbalanced by a global motion to preserve global mass conservation after a push-pull cycle. We draw then a parallel with what occurs in horizontally vibrated samples where two convection rolls have been found [1]; this parallel is made possible by settling the problem in the granular material frame, which requires to introduce an inertia force which acts in a similar way to the vertical boundary condition. So the question of the importance of solid friction as a motor of the vibro-convection [2] in granular media is addressed definitely.

ii) The second possible application concerns soil mechanics: In this domain, specialists know how to characterize precisely dilatancy, cohesion and friction of granular materials and the mechanical behaviour of granular media under quasi-static conditions. The apparatus they use (triaxial test,...) can also be used to investigate cyclic quasi-static responses. Our diffusion-convection result demonstrates that the actual quasi-static mechanical behaviour is more complex than the simple cyclic behaviour.

Monday 2:20 Judicial HT8

IMPACT-WAVY PHENOMENA IN HETEROGENEOUS SYSTEMS

L. M. Hadjikov
Institute of Mechanics, BAS, Sofia, Bulgaria

Liquid-Solid heterogeneous systems, like electric or magnetic rheology systems, are considered. Different questions from thermohydrodynamics and acoustics of the specified systems, with the help of accepted models and joint mathematical analysis, are discussed: impact compression; transformation of the system from one state to another; possibility of existence of the specific structural forms; the influence of relaxation processes upon the kinematic movements of the heterogeneous systems; the structure of impact waves during the existence of the electric and magnetic fields or their absence.

Monday 2:45 Judicial HT9

STEADY RELIEF GENERATION AT A SAND-LIQUID INTERFACE DUE TO HORIZONTAL VIBRATION

A. Ivanova* **, P. Evesque*, V. Kozlov* **, D. Lyubimov*, B. Roux***
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It is well known that sand liquefaction may arise from horizontal vibrations; a vivid example of such a process is the liquefaction of water-saturated soil which occurs during earthquakes. In this paper, this liquefaction process has been used to study the form of the sand-liquid interfaces and the dynamics of a granular material. For instance, at large vibration intensity, we observe the spontaneous formation of a standing relief pattern, which consists of a series of hills and valleys, oriented perpendicularly to the axis of vibrations at the interface of a sand-alcohol mixture filling a cylindrical cell.

The experimental set-up consists in a hollow transparent short horizontal cylinder which can be submitted to horizontal vibrations of various amplitudes b ranging from 0 to 4cm (db=0.01cm) and various frequencies f w/2* ranging from 10 Hz to 40 Hz. Different transparent cavities of various diameters D (D= 2.11 cm, 2.97 cm and 4.04 cm) and equal lengths (2.0 cm) were used. They were filled with alcohol and quartz sand (bead size: 0.3 ±0.1mm).

Investigations of (i) the time dependence of the liquid-granular-medium interface, (ii) local motion of grains and (iii) the convective flows generated by the vibrator were performed using photography- and stroboscopy- techniques as well as direct visual observations. furthermore, 2-viscous-liquid experiment was also performed to study the differences. We highlight a few of these results here.

The observed relief pattern is composed of a series of hills and valleys oriented parallel to the cylinder axis and perpendicular to the axis of vibration when linear vibration is applied. This pattern arises from the vibration since stopping vibration renders it flat; furthermore, the pattern was quasi-steady, persisting for several periods of vibration.

Monday 3:35 Judicial HT10

PARTICLE INTERACTION TIME AND STRESS RELAXATION MECHANISM IN DENSE GRANULAR FLOWS

Duan Z. Zhang and Rick M. Rauenzahn
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In dense granular flows, multi-particles interactions dominate the stress in the system. The particle interaction time can be the same order as the time scale of the externally imposed mean flow gradient. In this talk, we use an averaged equation method to study multi-particle interactions in dense system from statistical principles. Under a simple assumption of cluster interaction we proved that in systems of high particle concentrations, the probability distribution of particle interaction time is exponential. This theoretical prediction is verified by direct numerical simulations. We studied the effect of the particle interaction time to the collisional stress by using our recently

developed evolution equation. It is found that interaction time is related to stress relaxation time. At high particle concentrations, plasticity of granular systems is observed numerically for small deformation rates.

Monday 4:00 Judicial HT11

COMPRESSIBLE FLOW OF GRANULAR MATERIALS

T. Astarita*, R. Ocone, and G. Astarita*****

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Elementary compressible flow problems in granular materials have been analysed recently (Ocone and Astarita, J. Rheology 37, 727, 1993). Even only moderately complex problems present subtle difficulties due to inelasticity of particle- particle collisions. The full unsteady state balances, momentum and energy need to be solved, and the techniques used in classical gas dynamics have to be appropriately modified. A steady solution has been found (Astarita, Ocone and Astarita, ibid., 41, 513, 1997) which, however, cannot furnish a complete explanation of what happens in the case of subsonic perturbations. To get a complete answer, a complete numerical analysis of the unsteady problem is needed. We present some results obtained from such an approach: standing compression and rarefaction waves and thermal relaxation tails of such waves are critically analysed. The analogies and the differences with "classical" gas dynamics results are discussed and the significance of such results for the analysis of classical problems is presented.

Symposium GN
General Session

Organizer: Robert L. Powell

Monday 4:25 Judicial GN1

REPRESENTING POLYOLEFIN MELT VISCOELASTICITY DATA WITH CARREAU-YASUDA MODELS: SOME INDUSTRIAL EXPERIENCE

Jay Janzen, David C. Rohlfing, and Michael J. Hicks

Phillips Petroleum Company Research Center, Bartlesville, Oklahoma 74004 USA

The Carreau-Yasuda (RCYS) expression for the deformation rate-dependent viscosity (or complex viscosity) of a polymer melt is a five-parameter model that, even after simplification leaving only three adjustable parameters, is capable of representing, with high precision, essentially all of the polyethylene linear viscoelasticity data routinely generated in the authors' laboratories. (That is, the data we rely on for purposes of product description, quality control, and processing performance prediction.) The set of parameter values obtained by nonlinear least-squares fitting of a CY model to results from a typical experimental determination of complex viscosity vs. frequency (or of viscosity vs. shear rate) is an efficient and compact encoding of virtually all the information in the data. The parameters are also physically interpretable. Such parameter sets have been observed to be highly discriminating descriptors that unambiguously reflect very subtle, but nonetheless systematic, differences among closely similar resins. For example, rheological changes in a series of polyethylene specimens originating as a single parent RfluffS and differing only in finishing extrusion treatments are easily discerned. We call attention to the utility of CY models in the contexts of several practical problems, including WLF time-temperature shifting, making decisions about when polymers are or are not significantly different, splicing data from dynamic and capillary rheometers, making reasonable extrapolations beyond experimentally accessible rate windows, assessing extensional characteristics of resins, modeling converging-flow situations such as in melt-flow plastometers, and realistically appraising rheological RbreadthS characteristics of various polymers.

Symposium SP
Suspensions

Organizers: Ronald Phillips and Tony Ladd

Monday 1:30 Legislative SP6

OPTICAL RHEOLOGY OF CHARGED DISC-LIKE COLLOIDAL PARTICLE GELS

V. Viassnoff, J.L. Harden, and D. Wirtz
Department of Chemical Engineering, Johns Hopkins University, Baltimore, MD.

We present rheological studies of aqueous suspensions of Laponite, a synthetic Hectorite clay composed of charged, monodisperse, disc-shaped particles, as a function of particle concentration and solution pH. Laponite suspensions form novel transparent colloidal gels at particle concentrations in the 1-2% range, depending on solution pH. These suspensions are shear-thinning and extremely sensitive to external perturbations. They also display anomalously long curing times, due to the slow dynamics of particle transport in a glassy suspension. We have employed diffusing wave spectroscopy (DWS), a non-invasive optical technique, to deduce the linear viscoelastic properties of these colloidal suspensions by monitoring the thermally-induced fluctuations of a dilute collection of added scattering particles using dynamic light scattering. The advantages of this technique over conventional mechanical rheometry are two-fold: (i) its superior sensitivity over many decades of frequency and (ii) the non-perturbative nature of the technique. The latter is particularly important since these colloidal suspensions are strongly affected by weak applied stresses. Using DWS, we have studied the complex modulus G* as a function of frequency in both the fluid and gel states. We were able to precisely identify the transition from fluid to gel by the emergence of an elastic plateau in G* with increasing concentration of clay particles. The onset of this transition is quite sharp, occurring near a mass concentration of 2% at pH=9.8. This transition concentration decreases rapidly with decreasing pH. We discuss the relationships between the microstructural and the rheological behavior of these colloidal gels and their dependence on preparation pH and curing time.

Monday 1:55 Legislative SP7

ON THE RELATIVE MOTION OF TWO SEDIMENTING SPHERES IN A VISCOELASTIC FLUID

Edwin Bot, Martien Hulsen, Ben van den Brule
Delft University of Technology, Laboratory for Aero and Hydrodynamics, Rotterdamseweg 145, 2628 AL Delft, The Netherlands

We will show experimental results on the motion of two spheres along the axis of a cylinder filled with a polyacrylamide in glucose and water solution. The spheres are released at a pre-set initial distance with zero initial velocity. The release mechanism is such that it causes minimum disturbance of the surrounding fluid. The results show that when the spheres are released close to each other they will separate and when released far apart they move towards each other. In both cases they move to the same, more or less stable, arrangement.

Monday 2:20 Legislative SP8

NONLINEAR RHEOLOGY OF A CONCENTRATED SPHERICAL SILICA SUSPENSION

Hiroshi Watanabe*, Ming-Long Yao, Kunihiro Osaki*, Toshiyuki Shikata***, and Yotaro Morishima*****
*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan; **Rheometric Scientific F. E., 2-19-6 Yanagibashi, Taito-ku, Tokyo 111, Japan; ***Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560, Japan

Nonlinear rheology was examined for a 50 wt% suspension of spherical silica particles (with radius of 40 nm) in a glycerol/ethylene glycol mixture. At a quiescent state the particles were isotropically dispersed in the medium, and their equilibrium Brownian motion resulted in the linear viscoelastic relaxation. The nonlinear relaxation modulus G of the suspension significantly decreased against large step strains and obeyed the time-strain separability at long

time scales, enabling us to determine the damping function h. Under flow, the steady/transient viscosities exhibited thinning and thickening at low and high shear rates. The thinning behavior was well described by a BKZ-type constitutive equation using the G and h data. On the other hand, this equation failed in describing the thickening behavior of the viscosities. These applicabilities of the BKZ equation were utilized to discuss the thinning and thickening mechanisms in relation to shear effects on the spatial distribution and motion of the suspended particles.

Monday 2:45 Legislative SP9

NON LINEAR VISCOELASTIC BEHAVIOR OF FUMED SILICA SUSPENSIONS

F. Yziquel, P.J. Carreau and P.A. Tanguy

Centre de Recherche Appliquée sur les polymères, CRASP, Department of Chemical Engineering, École polytechnique, Montréal, H3C 3A7, Canada

Suspensions of fumed silica exhibit a wide range of rheological properties depending on the nature and magnitude of the interparticles forces. In a non polar solvent, the particles interact between themselves through hydrogen bonding and can form a tri-dimensional network. The formation of microstructure is responsible for the non linear viscoelastic behavior of fumed silica suspensions, under small deformation flow. These non linear rheological properties were studied in small amplitude oscillatory experiments as a function of particle size, surface treatment of particles, suspending medium polarity and solids concentration. The non linear viscoelastic behavior is characterized by a non sinusoidal waveform of the signal response during oscillatory measurements. A structural network model based on the Marrucci et al. (1973) and the Coussot et al. (1993) models is proposed to predict the distorted signal responses.

Coussot P., Leonov A.I., Piau J.M.: Rheology of concentrated dispersed systems in a low molecular weight matrix, J. non Newt. Fluid Mech., 46, 94-114 (1993).

Marrucci G., Titomanlio G., Sarti G.C., Testing of a constitutive equation for entangled networks by elongational and shear data of polymer melts, Rheol. Acta, 12, 269-275 (1973).

Monday 3:35 Legislative SP10

RHEOLOGICAL BEHAVIOR OF SILICA-FILLED POLYMER MELTS: EFFECT OF INTERFACIAL ADHESION

D. P. Rucker and S. G. Bike

Chemical Engineering Department and Macromolecular Science and Engineering Program, The University of Michigan, Ann Arbor, MI 48109

Filled polymers are commonly used in applications ranging from product packaging to magnetic recording media, and prediction of rheological behavior is critical to their processibility. Most previous work has assumed that the effects of polymer-filler surface interactions on this behavior are insignificant. Our work indicates that this is not always the case.

In this study, octadecyltriethoxysilane was grafted to the surface of monodisperse colloidal silica (St^ber) in three concentrations, resulting in fillers of varying surface energy. Various volume fractions of the surface modified silica were then compounded into poly (methyl methacrylate) (PMMA) and polyethylene (PE), and the rheological behavior of the composites was investigated at typical processing temperatures. The materials were studied in both dynamic and steady-shear experiments, and the observed behavior correlated to the work of adhesion between the filler and polymer as determined by contact angle measurements.

Dynamic experiments showed that the resistance to flow of the material was inversely related to the work of adhesion between polymer and filler. This trend was found to be true within the linear viscoelastic region for all filler volume fractions over all frequencies tested. Furthermore, the shape of the graphs indicate that the mechanisms of energy storage and dissipation change only slightly with filler volume fraction when there is strong adhesion between the two components. This is not the case when there is poor adhesion; large (3 orders of magnitude) changes in the storage moduli result from changes in the filler volume between 3 and 33%, indicating that the mechanism of energy storage changes, especially at low frequencies. Constant stress experiments showed that the time required for filled PMMA to reach steady-state behavior is very long, on the order of one hour. The steady state viscosities determined from

Monday 4:00 Legislative SP11

EXPLOITING SURFACE CHEMISTRY AND RHEOLOGY TO PRODUCE HIGH DENSITY LOW VISCOSITY LIQUIDS

P.J. Scales, T.W. Healy and D.V. Boger
School of Chemistry and Department of Chemical Engineering and Advanced Mineral Products Research Centre, The University of Melbourne, Parkville Victoria 3052, Australia

The paper demonstrates how a knowledge of colloidal chemistry and particulate fluid rheology can be exploited to produce extremely high density low viscosity fluids. These materials produced as a dense media separation device are now a commercial reality.

Monday 4:25 Legislative SP12

EFFECTS OF GRADUAL DESTABILIZATION IN POLYMERICALLY STABILIZED SUSPENSIONS

J. Mewis and G. Ourieva
Department of Chemical Engineering, K.U. Leuven, de Croylaan 46, B-3001, Belgium

Polymerically stabilized colloidal PMMA suspensions have been gradually made unstable by changing the suspending medium. Temperature changes have been used for more subtle variations in degree of stabilization. In this manner weakly flocculated systems can be produced, the flocs of which can be eliminated by shearing. Viscosity measurements on dilute systems at different temperatures are used to assess the applicability of the sticky sphere model and the square well model. In more concentrated systems the zero shear Newtonian plateau is used to characterize the degree of flocculation. Application of scaling principles to the experimental results was not completely satisfactory. Dynamic moduli were used to generate a phase diagram, which also provides means to characterize the particle interaction forces. Finally, SANS data are used to provide additional information about the structure.

Monday 4:50 Legislative SP13

USING CREEP MEASUREMENTS TO PREDICT THE PHYSICAL STABILITY OF A BETA-CYFLUTHRIN SUSPENSION CONCENTRATE

Horace Barnett and Gerald Otis
Bayer Corporation, Agriculture Division, Formulation Development, Kansas City, MO 64120

The rheology of a beta-Cyfluthrin 125 Suspension Concentrate with a d(50)=2 micron particle size distribution was compared to one with a d(50)= 7 micron particle size distribution. The recipes for both products were identical. Rheological measurements taken in the creep mode indicated the d(50) = 2 micron particle size distribution showed a viscoelastic behavior, whereas the d(50)=7 micron particle size distribution a resistance viscoelasticity. Creep experiments, the d(50) = 7 micron particle size distribution showed a resistance elasticity. This resistance to elasticity, along with the pseudo plastic and viscoelastic properties of the blank system (No beta-Cyfluthrin) enable the d(50) = 7 micron particle size distribution to show the same amount of syneresis as the d(50) = 2 microns particle size distribution after being stored for eight weeks at 50sC.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Governor's Ballroom PL2

OPTICAL RHEOMETRY OF COMPLEX LIQUIDS AND INTERFACES

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

Optical probes of structure and dynamics can offer a powerful, complementary means of elucidating the mechanisms responsible for the nonlinear rheology of complex liquids. This is especially true of materials characterized by a range of length scales, such as polymer blends, emulsions, liquid crystals, and systems undergoing flow-induced structural transitions (crystallization, for example). This lecture offers an overview of techniques in optical rheometry that can be used to provide in situ measurements of complex liquids and interfaces subject to flow. Applications of polarimetry (birefringence and dichroism), small angle light scattering, and Raman scattering will be presented, along with techniques such as Brewster angle microscopy that can be used to follow the morphology of deforming interfaces. The use of these methods will be motivated by the following examples: 1. Applications of the stress optical rule. Two problems making use of the stress optical rule will be reviewed: uncoupling the component stress contributions in compatible polymer blends and spatially resolved measurements of stress distributions in complex flows. 2. Flow induced structural transitions. The use of scattering techniques to follow flow-induced structural transitions is motivated through their use in studies of the growth of concentration fluctuations in polymer solutions and surfactants. 3. Spectroscopic methods. Infrared dichroism and Raman scattering are both vibrational spectroscopies with the capability of isolating the separate components of mixtures. These methods are applied to problems involving polydispersity in polymer melts and the orientation of individual components in block copolymers. 4. Interfacial rheology. Optical methods can be designed with sufficient sensitivity to reveal the response of monolayers residing at fluid-fluid interfaces subject to flow. Experiments examining the behavior of both small molecule and polymer monolayers will be discussed.

Symposium FI
Melt Flow Instabilities and Wall Slip

Organizers: Shi-Qing Wang and John M. Dealy

Tuesday 9:45 Senate FI1

MELT FLOW INSTABILITIES OF POLYETHYLENE ON THE MULTIPASS RHEOMETER

M. Ranganathan, M.R. Mackley and P.H.J. Spitteler
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In this paper, we are concentrating on a particular type of melt flow instability in the extrusion of polyethylene, characterised by the occurrence of periodic fluctuations in the pressure of the system. A High Density PolyEthylene

(HDPE) was studied on the recently developed Multipass Rheometer (MPR). The MPR is a two piston capillary rheometer, with pistons entering into barrels on either side of the capillary, alternately moving the test material to make multiple passes through the capillary.

A number of experiments were done of a range of shear rates (i.e. piston velocities) to generate the complete flow curve of HDPE. Along this curve, we can distinguish four distinct flow regimes. Regime 1 at low shear rates constitutes the stable flow regime, where the pressure drop across the capillary builds up with time to a steady value. After this comes the second flow regime, where the pressure drop shows fluctuations in time and can hence be regarded as unstable flow. At even higher shear rates (regime 3), the pressure drop rises to show a single overshoot before it reaches a steady value. After this comes regime 4 (at very high shear rates) where the overshoot disappears and the pressure drop reaches a steady value with time.

A model has been developed by us for the flow of polyethylene through the MPR. In this model, we take the mass balance across the barrel and the capillary system and also express the change in the density of the system in terms of the pressure changes in the barrel by using the compressibility of the melt. This gives us a differential equation for the pressure drop across the capillary and this equation can be analytically solved using boundary conditions derived from the flow curve of HDPE to give the change in pressure drop with time. This model has been successful in predicting the pressure drop versus time profile in all the four regimes and also identifies the important variables governing the flow dynamics of polyethylene.

Tuesday 10:10 Senate FI2

EXTRUDATE SWELL SIMULATIONS-EFFECT OF WALL SLIP

K..J. Ang, I. Manas-Zloczower and S.Q. Wang
Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

Extrudate swell (commonly referred to as die swell) is a phenomenon of both practical and theoretical importance. The extrudate swell problem can not be solved analytically due to the presence of a free surface. Numerical methods such as the Finite Element Method (FEM) have to be used to solve the problem. In this study, we have successfully simulated the extrudate swell for both Newtonian and polymeric fluids by using a Fluid Dynamics Analysis Package -FIDAP, a package based on the Finite Element Method. We used different conditions at the die wall, namely, non-slip boundary conditions and slip boundary conditions. A mesh density refinement and analysis were performed to probe the effect of mesh density on convergence behavior and simulation results. Comparison of simulation results and experimental data proved satisfactory. Wall slip has a significant impact on extrudate swell and alleviates the stress singularity level of the problem.

Tuesday 10:35 Senate FI3

DEFORMATION IN CONVERGING FLOW WITH STICK OR SLIP BOUNDARY CONDITIONS

Charles E. Chaffey
Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, ON, Canada M5S 3E5

Two-dimensional flow in a truncated wedge-shaped region has been studied with different constitutive equations and boundary conditions, in order to model the deformation in polymer processing operations such as die-drawing and rolling. The analysis in the literature for Newtonian creeping flow uses a factorable stream function proportional to the nth power of the radial distance from the virtual wedge apex. Constant flux between stationary walls requires $n = 0$. Stick or slip boundary conditions give a force component on the walls respectively inward or outward, and rotational or irrotational flow. In die-drawing of polypropylene, a deformation 99.6% irrotational and 0.4% rotational approximated observations (Chaffey, Taraiya and Ward, Polymer Engineering and Science, accepted 1997). The rolling process is modeled when the walls slide with constant velocity like moving belts; when the fluid sticks to them, $n = 1$, and the downstream tension is less than that for die-drawing. If the tangential wall stress is constant, $n = 2$. However, if the tangential stress is proportional to the slip velocity at the walls, the stream function cannot be factored. Alternatively, the ideal plastic constitutive law has been used in the literature to analyze rolling. The increase in velocity from inlet to outlet can now only be accommodated in an incompressible material if it slips

at the wall, except at one neutral point. Without downstream tension, this neutral point approaches the outlet with decreasing coefficient of friction at the wall; when it reaches the outlet, flow ceases. Rolling of low friction polymers requires downstream tension. Thus these processing models differ greatly for different slipping boundary conditions.

Tuesday 11:00 Senate FI4

EXTRUDATE SWELL DUE TO STRESS BUILDUP AT DIE EXIT AND INFLUENCE OF WALL SLIP [1]

X. Yang and S.Q.Wang

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

We have carried out a experimental investigation on the difficult problem of extrudate swell of polymer melts from capillary extrusion. The focus of the present work is to elucidate a major contribution from the die exit region that has not previously been quantified. By studying a group of different polymers including the previously studied HDPE resins [2], we show that the stress build-up at the die exit due to the boundary discontinuity is partially responsible for the experimentally observed extrudate swell. In this paper we establish a rather accurate and reliable method to measure the initial extrudate swell in either capillary or slit dies. Using dies of bare aluminum walls and Dynamar-coated walls, we illustrate the influence of wall slip on the measured extrudate swell and reveal the true difficulty in predicting extrudate swell on the basis of bulk flow behavior of polymer melts. The results are used to provide additional explanation for our recently proposed molecular mechanism for sharkskin phenomenon [3].

1. X. Yang and S.Q. Wang, manuscript in preparation for publication. 2. S.Q. Wang and P.A. Drda, Macromolecules, 29, 2627, 4115 (1996). 3. S.Q. Wang, P.A. Drda and Y.W. Inn, J. Rheol., 40, 875 (1996).

Tuesday 11:25 Senate FI5

ENTRANCE PRESSURE OSCILLATIONS IN THE CAPILLARY FLOW OF BRANCHED POLYETHYLENE MELTS.

L. de Vargas*, J. Pérez-González*, L. Pérez-Trejo*, O. Manero*

*Departamento de Física, Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, C. P. 07300, Apdo. Postal 75-685, México D. F., MEXICO.; **IIM-UNAM, C. P. 04510, Apdo. Postal 70-360, México D. F., MEXICO

The capillary flows of branched polyethylene melts were studied in this work. The experiments were carried out at constant speed extrusion with an Instron capillary rheometer. It was found that extrudate distortions were accompanied by pressure oscillations made up of at least two components of different frequency and amplitude. Such oscillations were identified with different bulk defects appearing on the extrudates in a longitudinal direction with respect to the flow. Experiments performed with different capillary geometries provided information on the origin of the pressure fluctuations, with the main cause being the elongational flow in the capillary entrance.

Symposium MT
Molecular Theories for Polymer Dynamics

Organizers: Ralph H. Colby and Michael Rubinstein

Tuesday 9:45 Executive MT14

POLYELECTROLYTE SOLUTION VISCOSITY

Ralph H. Colby*, David C Boris, Wendy E. Krause* and Julia S. Tan****
*Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802; **Eastman Kodak Company, Rochester, NY 14650

We have measured the shear rate dependence of viscosity for aqueous solutions of two polyelectrolytes as functions of polyelectrolyte concentration and salt concentration (NaCl). The polyelectrolytes are the sodium salts of polystyrene sulfonate and poly(2-acrylamido-2-methylpropane sulfonate). The uncharged portions of these polymers have very different affinities for water. We compare the zero shear rate viscosities and longest relaxation times (determined from the onset of shear thinning) for these two polyelectrolytes. There appear to be several features that are universal for all polyelectrolytes that are based on inherently flexible chains. However, the effect of the uncharged polymer's affinity for water is also demonstrated clearly in our rheology data.

Tuesday 10:10 Executive MT15

THE DYNAMICS AND RHEOLOGY OF DILUTE POLYELECTROLYTE SOLUTIONS

N.C. Andrews, A. J. McHugh and J. D. Schieber
*Department of Chemical Engineering, University of Illinois, Urbana, IL 61801 ; **Department of Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616

The conformational and rheological dynamics of flexible and semi-flexible polyelectrolyte macromolecules undergoing shear and extensional flow are modeled using Non-Equilibrium Brownian Dynamics (NEBD) and Configuration Biased Monte Carlo simulations (CBMC). The mathematical model utilizes a discretized version of the Kratky-Porod wormlike (or persistent) chain as the building block, generalized to include flow. This discrete chain contains beads which are charged and interact through a screened Debye-Huckel potential, and which intramolecularly interact through stretching and bending forces. The diffusion (or Fokker-Planck) equation for the probability density of the positions of the beads of the chain is converted to a Stochastic Differential Equation (SDE) from which the simulation algorithm for the NEBD is obtained. The CBMC is used in the initial chain generation and in determining steady-state properties in elongational flows. Various conformational and rheological quantities such as the stress and birefringence are monitored, under both steady-state and transient conditions, with the primary independent variable being the salt concentration (parameterized through the Debye length) and the flexibility parameter which is the bending constant of the chain. It is found that this model is able to describe qualitatively many of the experimentally observed features in such systems.

Tuesday 10:35 Executive MT16

STRUCTURE AND RHEOLOGY OF DILUTE SOLUTIONS OF ROD-LIKE POLYELECTROLYTES

Shing Bor Chen* and Donald L. Koch**
*Department of Chemical Engineering, National University of Singapore, Singapore 119260;
**School of Chemical Engineering, Cornell University, Ithaca, NY 14853

Elongated colloidal particles such as tobacco mosaic virus and stiff charged polymers such as peptides may be modeled as high aspect ratio charged Brownian cylinders. We consider the orientation distribution and rheological properties of a dilute solution of Brownian, charged rods. The shear flow distorts the counterion cloud surrounding each polyelectrolyte, leading to an electroviscous stress that enhances the viscosity and normal stress differences of the solution. In addition, the deformed double layer leads to a torque that modifies the orientation distribution of the rods. We determine the leading order electroviscous effects on the structure and rheology of the solution for small

Hartmann number over the entire range of rotary Peclet numbers. At very high Peclet numbers, the electrical torque can lead to a fixed orientation of the fiber near the flow direction of the simple shear flow.

Tuesday 11:00 Executive MT17

BOUND STATE OF TWO POLYELECTROLYTE MOLECULES

S. Obukhov*, N. Lee* and M. Rubinstein**

*Department of Physics, University of Florida, Gainesville FL 32611 ; **University of North Carolina, Chemistry Department, Chapel Hill, NC 27599

We found a metastable entangled state of two polyelectrolyte molecules. Both molecules are charged with the charge of the same sign and are repulsive, but they are wrapped around each other in such a way that small local perturbations only increase electrostatic energy. Using Monte Carlo simulation we estimate the energy barrier separating this configuration from disentangled ones. The energy of entangled states is lowered in the concentrated solutions of polyelectrolytes due to presence of counterions. We argue that these new states can bring new insight on the role of entanglements in the rheology of polyelectrolyte solutions.

Tuesday 11:25 Executive MT18

SIMULATION OF POLYELECTROLYTE DYNAMICS

Mark J. Stevens

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Our basic understanding of polyelectrolytes has been rather poor. Molecular dynamics simulations have recently revealed a new picture of polyelectrolyte structure (J. Chem. Phys. **103**, 1669 (1995)). For flexible polyelectrolytes in the dilute limit the chains are significantly extended in comparison with neutral polymers, but are not rodlike. Furthermore, the chains contract with increasing density *below* the overlap density. In this talk the consequences of the new picture of polyelectrolyte structure on dynamics will be discussed. Direct examination of polyelectrolyte dynamics from molecular dynamics simulations will also be presented.

These simulations have been performed as a function of chain length, chain density and salt density. The chains are treated as bead-springs. Two types of simulations have been performed. One type explicitly treats all solvent ions; the other type uses the Debye-Hueckel potential to implicitly treat the solvent ions.

Symposium SL
Rheology of Solids

Organizers: Gregory B. McKenna, Robert Shay and Omar A. Hasan

Tuesday 9:45 Judicial SL10

CHARACTERIZING THE FREQUENCY, TEMPERATURE, AND PLASTICIZER EFFECTS ON THE DYNAMIC MODULI OF CROSSLINKED POLYMERS USING THE TUBE-JUNCTION MODEL

Philip P. Simon and Harry J. Ploehn

Swearingen Engineering Center, Dept. of Chemical Engineering, University of South Carolina, Columbia, SC 29208

The tube-junction (TJ) model for the viscoelasticity of crosslinked polymers describes a crosslinked chain as being confined in a series of affinely deformable tubes separated by frictional junctions. The viscoelastic response of the polymer can be calculated by modeling the dynamics of the strands of the chain in each sub-tube in response to the applied load. The model gives the first equation to our knowledge that can characterize the isochronal temperature sweep profile of the storage and loss moduli. The model can also predict the isothermal frequency sweeps for a resin of a given isochronal temperature profile. Thus, this model connects the time and temperature dependence of the moduli.

The temperature and plasticizer dependence enters the model primarily through the free volume dependence of the frictional coefficient at the junctions. The Kelley-Bueche free volume model has successfully modeled the decrease in *dilatational* glass transition with increase in water content in epoxy resins. We have incorporated this information to characterize the decrease in the *viscoelastic* glass transition temperature at a given frequency for increasing water content. In this paper, we show the various capabilities of the TJ model. We also comment upon its use in estimating the very long-term or very short-term response of the material without the use of time-temperature-plasticizer superpositioning.

Tuesday 10:10 Judicial SL11

THE RHEOLOGY OF POLYSTYRENE NANOPARTICLES

P.G Santangelo and C.M. Roland
Chemistry Division, Code 6126, Naval Research Laboratory, Washington, DC 20375

Rheological Properties of polystyrene nanometer-sized particles with varying degrees of crosslinking will be presented. The materials (the radii fall between 6 nm and 13 nm) have low polydispersity with molecular weights in the range of 40 K to 3000 K g/mole. These polystyrene nanoparticles display a number of interesting properties. In some respects, the nanogels exhibit behavior associated with linear, entangled chains.

Tuesday 10:35 Judicial SL12

VISCOELASTIC RESPONSE OF POLYURETHANE ELASTOMERS

V. Rouiller and G.B. McKenna
Polymers Division, NIST, Gaithersburg, MD 20899

We have undertaken the task of developing a model for prediction of the long term response of polyurethane elastomeric foams. As part of the project it is essential to establish the nonlinear thermoviscoelastic response of the neat resin for incorporation into any subsequent model for the mechanical response of the foam. As a result, we are implementing a BKZ viscoelastic model in which the kernel function is assumed to be a time dependent Valanis-Landel Function in which both time-temperature superposition and time-strain separability are assumed. The goal is to be able to predict the multiple step (load-unload) creep response from the stress relaxation experiments performed at strains up to 40% and temperatures from approximately Tg + 30 to Tg + 80 K and times at least one decade shorter than the time of the creep experiments. It is our observation that the slow relaxation behavior of the polyurethane elastomers makes reliable descriptions of the material response and, therefore, predictions of long term performance, very problematic. The sample-to-sample variability, while being only of the order of +/- 5% in stress relaxation measurements makes errors in, e.g., the temperature shift factors appear very large, reaching perhaps one order of magnitude. However, the task of actual predictability, in some sense becomes easier because errors in the predicted deformation depend far more on the "elastic" component of the response than on the time dependent component. The model validity, the creep predictions and the impact of the statistical variability of the material response on any conclusions or accelerated testing strategies will be discussed.

Tuesday 11:00 Judicial SL13

PLANE DEFORMATION IN AN INCOMPRESSIBLENEO-HOOKEAN MATERIAL

Eric Varley and Alparslan Oztekin
Department of Mechanical Engineering and Mechanics Lehigh University Bethlehem, PA 18015

Exact solutions to the equations governing the deformations of neo-Hookean materials are used to describe the response of a slab of material that is contained between infinite parallel plates. These plates can move in any manner consistent with them remaining parallel: they can be sheared, rotated and the distance between them can vary. For such deformations of neo-Hookean materials, material planes that are initially parallel to the bounding planes remain so. Here only static problems are described with an emphasis on the effect of the dependence of the material parameter on temperature.

Tuesday 11:25 Judicial SL14

MESOSCALE MODELING OF BIMODAL ELASTOMER NETWORKS

P. von Lockette and E.M. Arruda
Department of Mechanical Engineering and Applied Mechanics, University of Michigan, Ann Arbor, MI 48109-2125

The authors develop physically-based network models for the prediction of stress and optical responses of bimodal elastomer networks. The models evolve from a mesoscale representation of a 'bimodal chain' and the enforcement of novel force equilibrium and geometric compatibility constraints on the chain's constituents. The constraint equations provide the basis for long chain, short chain synergy in the mechanical and optic responses of the network--something heavily evidenced in the literature. The bimodal chains are then arranged in a network representation to simulate the fully three-dimensional interaction of a complete network of multiple chains. Efficacy of the model depends heavily on the topology of its representation of the bimodal chain. To this end, computer simulations of an equilibrated network of archetypical freely-jointed chains are examined for various concentrations of the constituents.

Symposium SP
Suspensions

Organizers: Ronald Phillips and Tony Ladd

Tuesday 9:45 Legislative SP14

AN ANALYSIS OF CONSTITUTIVE EQUATIONS FOR SHEAR-INDUCED MIGRATION

D. T. Leighton
Department of Chemical Engineering, University of Notre Dame, Notre Dame, IN 46556

Two constitutive equations for shear-induced particle migration in concentrated suspensions of non-colloidal spheres, the diffusive flux model proposed by Phillips, et al (1992) and the suspension balance model proposed by Nott and Brady (1994), are examined. Predictions arising from these approaches are compared for a model system: the high Peclet number limit of a dilute hard sphere colloidal suspension for which migration fluxes and rheology may be determined exactly. The constitutive equations are shown to be identical in this model system for plane Poiseuille flow. Further, the model system is used to demonstrate that the diffusive flux model is incomplete for more general shear flows, leading to qualitatively incorrect predictions in curved geometries such as parallel-plate flow (Chow, et al., 1994) and quantitative errors for unidirectional quadratic shear flows such as tube Poiseuille flow. In contrast, the suspension balance model correctly predicts the migration flux for the dilute model system in all these geometries. Application of the suspension balance model to published experimental data at high concentrations, however, demonstrates that while qualitatively correct, it is not capable of simultaneously describing migration in all geometries quantitatively. The difficulty is shown to lie with averaging assumptions that are invalid at high concentrations. The analysis suggests how an improved constitutive equation for general viscometric flows may be developed.

Tuesday 10:10 Legislative SP15

LDV MEASUREMENTS OF PARTICLE VELOCITY FLUCTUATIONS IN A CONCENTRATED SUSPENSION

Nina Shapley, Robert C. Armstrong and Robert A. Brown
Department of Chemical Engineering, M.I.T., Cambridge, MA 02139

Recent statistical continuum models of suspensions of neutrally buoyant, non-Brownian, non-colloidal, solid spheres in Newtonian fluids suggest that the particles migrate in response to gradients in "suspension temperature," defined as the average kinetic energy contained in the particle velocity fluctuations. These models have not yet been compared systematically with experimental data.

These models assume isotropic particle velocity fluctuations, since the "suspension temperature" is given as a scalar. However, highly anisotropic particle velocity fluctuations have been observed in granular chute flows and settling suspensions, which suggests that a "suspension temperature" tensor would be more realistic.

We have designed experiments to quantify the anisotropy of particle velocity fluctuations in a highly concentrated suspension under homogeneous shear flow, by using laser Doppler velocimetry (LDV) to measure the tangential, radial, and axial velocity fluctuations of particles in a narrow-gap concentric cylinder Couette device, enclosed in a rectangular bath containing a refractive index-matched fluid. We have demonstrated the feasibility of measuring the mean velocity and standard deviation in the three directions.

In order to distinguish the translational velocity fluctuations from other terms which contribute to the velocity standard deviation, such as LDV noise, optical noise, and particle rotation, we will run Couette flow for each average shear rate (ranging from 1 to 29 s^{-1}) over a range of average particle concentrations (0.1% to 55% solid volume fraction).

Tuesday 10:35 Legislative SP16

PARTICLE MIGRATION IN TUBE FLOW OF SUSPENSION

Chongyoup Kim*, M.-S. Han*, and S.-K. Kim*,M.-C. Kim# and S.-C. Lee#
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In this research, we investigated the migration of particles in the tube flow of suspension for a wide range of particle loading and particle Reynolds number(Re_p) using a magnetic resonance imaging (MRI) technique. The suspension consisted of nearly monodisperse polymethylmethacrylate spheres in a density matched Newtonian fluid. The volume fraction of solid was 0.05 - 0.4. Both the velocity and concentration distributions were measured under the fully developed condition. It has been found that, when particle loading is small(< 0.1) and Re_p is not small(> 0.4), the particles move toward the position at a distance of 0.5 R(tube radius) from the tube axis and the velocity profile is parabolic. When particle loading is not small (> 0.2) and Re_p is small(< 0.5), particles move toward the center of tube and the velocity profile is severely blunted. Between these two extreme cases, particle migration is dependent on Re_p. When Re_p is small the particles move toward the tube axis regardless of particle loading. When particle loading is 0.2 - 0.3 and Re_p > 0.5 particles stay both at the center and at the middle of the tube axis and tube wall. To explain the experimental observations a mathematical model will be presented taking into account both the fluid inertia and hydrodynamic interaction.

Tuesday 11:00 Legislative SP17

CONDITIONALLY AVERAGED HYDRODYNAMIC INTERACTION FUNCTIONS IN CONCENTRATED SUSPENSIONS

Robert A. Lionberger
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We have calculated the conditionally averaged hydrodynamic interaction functions between a pair of spherical particles in a concentrated suspension. These functions characterize the matrix relating the forces on a pair of particles to their velocity. In a concentrated suspension, because of many-particle interactions, the interactions between a pair of particles depend on the configuration of all other particles in the suspension. For theoretical calculations of the properties of suspensions it is of interest to find the pair interaction averaged over the positions of all the other particles.

To determine this average we first distribute the particles according an equilibrium distribution and evaluate the many-body hydrodynamic interactions according to the Stokesian Dynamics simulation method of Brady. For each pair of particles the apparent pair mobility for their separation is computed. This averaging is then repeated over many configurations. For monodisperse suspensions, the calculations cover a volume fraction range of 0.0 to 0.5. We have also performed similar calculations for several bimodal mixtures.

At large separations particles behave as if they are in an effective medium with a viscosity dependent on the overall volume fraction of the suspension. From the simulation results, we construct an empirical approximation for these functions based on the three-particle distribution functions. The hydrodynamic interaction functions are important for their use in statistical theories of suspensions and colloids. Examples of applications include calculation of the viscosity, the high frequency modulus, and the rate of flocculation in concentrated colloidal suspensions.

Tuesday 11:25 Legislative SP18

COLLOIDAL SURFACE CHARGE DETERMINATION IN CONCENTRATED DISPERSIONS THROUGH RHEOLOGICAL MEASUREMENT

J. Bergenholtz*, N. Willenbacher, and N.J. Wagner*****

*Univ. Konstanz, Dept. Physics, Konstanz Germany ; ** BASF AG, Ludwigshafen Germany ; and *** Center for Molecular and Engineering Thermodynamics, Univ. of Delaware, Dept. of Chemical Engineering, Newark DE 19716

Measurements of the high-frequency elastic shear modulus on concentrated liquid dispersions of polymer colloids as a function of colloid composition, concentration of colloid and added electrolyte, pH, and colloid size have been performed through the use of a commercial surface torsional resonator. A new theoretical analysis enables use of a concentration series of measurements to extract the intercolloidal potential. For the well-characterized dispersions investigated here, the colloidal surface charge is directly extracted for concentrated dispersions. These rheological measurements, which are currently the only method suitable for concentrated liquid dispersions, are compared to other methods of surface charge determination, such as titration and electrophoretic mobility measurements. In addition to the shear modulus the torsional resonator yields the high-frequency viscosity. The values for the high-frequency viscosity are compared to theory and simulation.

Tuesday Afternoon

Symposium FI
Melt Flow Instabilities and Wall Slip

Organizers: Shi-Qing Wang and John M. Dealy

Tuesday 1:30 Senate FI6

THE USE OF FLOW BIREFRINGENCE TO ASSESS SLIP IN THE FLOW OF LLDPE

D.G. Baird* and R.H. Moynihan**
*Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061; **Phillips Petroleum Company, Bartlesville, OK, 74004

The origin of "sharkskin" melt fracture observed for LLDPE is believed to be associated with slip at the exit corner of a die. In order to more fully understand the role of slip in the flow stability of LLDPE a fluoroelastomer (Dynamar, 3M) was dissolved in acetone and then applied to various places in a die(the entry corners, exit corners, and along one side of the die). The die was designed with glass windows in order to allow the use of flow birefringence to analyze the stress fields in the various regions. With the application of the flouroelastomer (FE) to the entry corners it appeared that the stresses in the entry region were reduced, but there was no sign of unstable flow down field from the entry corners. With the application of the FE to the exit corners it was again observed that the stress field at the die exit was altered, but it was not clear that slip was occurring. For this reason the FE was applied to only one side of the die over a length of five times the die height from the exit. The stress was distinctly reduced in the region coated with FE as determined by lower order fringes replacing the higher order fringes associated with higher stresses. The slip velocity was estimated using computations and the PTT model to match the stress patterns. Under no conditions when slip was present was an instability observed suggesting that it is the combination of slip and stick which leads to sharkskin.

Tuesday 1:55 Senate FI7

STUDIES ON SHARKSKIN MELT FRACTURE ON EXTRUSION OF POLYBUTADIENE

Y. W. Inn, D. E. Packard, R. J. Fisher and M. T. Shaw
Department of Chemical Engineering and Polymer Program, Institute of Material Science, University of Connecticut, Storrs, CT 06269-3136

The sharkskin phenomenon refers to small and regular surface distortions which can occur on extrusion of some polymer melts such as linear low-density polyethylene (LLDPE) at stresses above a critical value. Poly(dimethyl siloxane) (PDMS) and polybutadiene (PB) are also known to exhibit sharkskin. The sharkskin melt fracture of LLDPE and its peculiar flow properties have received particular attention over forty years because of its economic importance and scientific interest. However, in spite of this vast effort, there still remain questions concerning the spatial origin and mechanism of sharkskin melt fracture. In this paper we study the extrusion of PB, which exhibits similar flow properties and sharkskin behavior to LLDPE, but has the advantage of larger distortions. By using a video camera with close-up lenses focused on the exit of die, we observed in *profile* the development of sharkskin, which has provided valuable hints about the mechanism. Low angle light scattering, particle tracing and a die-wall removal experiment were used to observe flow disturbances in the die land.

Tuesday 2:20 Senate FI8

A MECHANICAL INTERPRETATION OF THE SHARKSKIN DEFECT

C. Venet and B. Vergnes***

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To go further within the comprehension of initiating mechanisms of sharkskin defect in linear polyethylenes, we carried out a numerical study of flow conditions in an axisymmetric die. Based on the finite element method, the software we used computes the flow of a viscoelastic fluid in the reservoir, the convergent, the die land and the free surface of the swelling extrudate. The constitutive equation is a multimode Phan Tien-Tanner model with five relaxation times, deduced from rheological measurements. To avoid problems due to the stress singularity at the die corner, simulation results are exploited along peripheral streamlines, close to the free surface. The information we are looking for are the tangential stresses and deformations supported by the molten polymer flowing along a streamline.

We put in evidence the existence of a small traction zone located at the periphery of the free surface of the extrudate, close to the die exit. Along the peripheral streamlines, tangential stress becomes positive within a small area, whereas along the symmetry axis, it increases monotonously within a compressive zone in the die land and in the swelling section. With an increase of flow rate, the dimensions and the intensity of the peripheral tensile area are growing up. Whatever the flow rate, the depth of this zone remains limited, and of the order of magnitude of sharkskin amplitude. If we assume a critical value of tensile stress, our numerical results can support the interpretation given by Cogswell about a rupture of the extrudate skin. On the other hand, whereas differences on sharkskin amplitude and periodicity are relevant between a long die and an orifice die, no dependence with die length is found neither on the area nor on the intensity of the traction zone. So tangential stress can not be the unique factor able to explain the morphology of the surface defect. The elongational deformation experienced by the polymer before the die exit seems to be also implied in the mechanism of sharkskin formation.

Tuesday 2:45 Senate FI9

EXPERIMENTAL INVESTIGATION OF MOLECULAR AND SPATIAL ORIGINS OF SHARKSKIN PHENOMENON IN LINEAR POLYETHYLENE EXTRUSION [1]

N. Plucktaveesak, J. Barone and S.Q. Wang

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

The goal of this project is to explore the molecular origins of sharkskin roughening of extrudates of polyethylene. Using a linear low density polyethylene (LLDPE) synthesized with a butene comonomer from BP Chemicals, we show that the periodicity of the sharkskin can be directly correlated with the molecular relaxation time of the polymer, in support of a previous study [2]. We find once again that the sharkskin period increases with decreasing temperature, just as the molecular relaxation time does. This is further elucidated by lowering the temperature of the die exit wall. The period of the sharkskin is shown to increase when the exit wall is cooled. This effect convincingly refutes the Cogswell type continuum mechanic interpretation of sharkskin phenomenon. Thus we illustrate that sharkskin spatially originates from a local molecular instability at the exit melt/wall interphase corresponding to oscillation between entanglement and disentanglement states involving the adsorbed and unbound chains. The proposed molecular mechanism also satisfactorily describes the influence of molecular weight distribution on the sharkskin characteristics.

1. N. Plucktaveesak, J. Barone and S.Q. Wang, manuscript in preparation for publication. 2. S.Q. Wang, P.A. Drda and Y.W. Inn, J. Rheol., 40, 875 (1996).

Symposium MX
Rheology and Mixing

Organizers: Deepak Doraiswamy and Ica Manas-Zloczower

Tuesday 3:35 Senate MX1

THE EFFECT OF SHEAR THINNING FLUIDS ON MIXING IN MECHANICALLY AGITATED TANKS

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The mechanically agitated tank is a work horse of the process industries. It is used for blending and dispersing of many complex fluids. The rheology of the fluids can strongly affect the blending behavior of such vessels in terms of mixing time and stagnation. Relations have been developed between certain rheologically properties and the fluid dynamics generated by the mixing devices. These relations will be reviewed and discussed. With these relations and the appropriate rheology it is possible to design and rate mixing equipment to give the performance required.

Tuesday 4:00 Senate MX2

3D MODELLING OF BOGER FLUID FLOWS IN HELICAL RIBBON MIXERS

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A 3D numerical investigation of the mixing flows of Boger fluids in an helical ribbon mixer is presented. The purpose of the study is to assess whether a simple second-order fluid rheological equation of state is sufficient to account for the extra power consumption observed in viscoelastic mixing as compared to inelastic one. A second objective is to evaluate the flow pattern and effective shear rate modifications induced by the presence of normal stresses. The model is based on a Galerkine-Uzawa finite element based solution of the equations of change in the vessel. The non-linearities associated with the second-order term are dealt with using an extension of the augmented Lagrangian method introduced in the 80s to treat shear-rate explicit non-linear rheological complexities.

Tuesday 4:25 Senate MX3

VISCOSITY MODEL FOR POLYDISPERSE POLYMERS

D. Nichetti and I. Manas-Zloczower
Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

The rheological behavior of polymer melts is profoundly influenced by the molecular weight and molecular weight distribution. It is well recognized that the relationship between viscosity and shear rate is sensitive to the polydispersity and they play a critical role in the polymer processability. We have developed a theoretical model relating the flow behavior of a polymer melt to its molecular weight distribution. The non-Newtonian behavior of a polymer melt is considered to be the consequence of gradual transition of high molecular weight fractions to the rubbery state. For a monodisperse polymer the flow behavior remains Newtonian up to the critical shear stress . At shear stress in excess to the critical value, the polymer shows a shear-thinning behavior. We assume the critical shear stress, to depend on the chain length for each polymer homologous series. This model provides a master curve, which gives realistic predictions of flow behavior for monodisperse systems. The model has been also extended to predict flow behavior for systems with broader molecular weight distribution. When a logarithmic-normal distribution function was used to characterize molecular weight distribution, we found an analytical solution for the relationship between shear viscosity, polydispersity index and weight average molecular weight. Our model has been applied to develop single screw extruder characteristic curves for polymers with the same weight average molecular weight but different polydispersity. We found a linear relationship between the flow rate and the polydispersity index.

Tuesday 4:50 Senate MX4

AGGLOMERATION AND MIGRATION EFFECTS IN PIPE FLOW OF PARTICULATE SUSPENSIONS

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The steady shear flow of well-dispersed, uniformly-sized, non-colloidal spheres suspended in a Newtonian liquid has been extensively examined in the technical literature. Unless such a suspension is stabilized by steric or electrostatic means, shear-induced collisions may lead to particle agglomeration and/or particle migration. Such effects might, for example, manifest themselves in the form of transients during rheological measurements.

In our earlier work, the phenomenon of flow-induced agglomeration was examined using a transparent cone-and-plate system to shear a model suspension containing 0.05 to 0.4% glass spheres in an aqueous corn syrup with added surfactant. There was a rapid increase in the average particulate size at short times followed by a leveling off at long times. In the present work, both particle agglomeration and migration were considered in the spatially non-homogeneous, but technologically important, situation of flow through a pipe. Tubes of different lengths and diameters were employed. Results were obtained as a function of composition, average shear rate and residence time, and these were consistent with the cone-and-plate data. A simple ordering analysis is presented to explain the observations and to delineate conditions favoring either particle agglomeration or particle migration.

Symposium MT
Molecular Theories for Polymer Dynamics

Organizers: Ralph H. Colby and Michael Rubinstein

Tuesday 1:30 Executive MT19

SCALING THEORY OF THE SOLUTIONS OF ASSOCIATIVE POLYELECTROLYTES.

Andrey V. Dobrynin and Michael Rubinstein

Department of Chemistry, University of North Carolina, Chapel Hill, NC, 27599-3290

The existence of 'tunable' interactions in solutions of associative polymers provides a convenient control of the physical properties of these polymers. This feature alone makes associative polymers extremely valuable for a number of industrial applications ranging from rheology modifiers for coating to flocculents for waste-water treatment. We have developed a scaling theory of the solution of charged associative polymers consisting of a polyelectrolyte backbone bearing the hydrophobic side chains. In the aqueous solutions the hydrophobes associate forming aggregates. At concentration below the overlap concentration, these associations are predominantly intramolecular. At higher polymer concentrations, intermolecular associations become more probable leading to the formation of the reversible network. This change from intra- to intermolecular associations is reflected in the unusually high concentration dependence of the zero shear viscosity. The effect of the added salt on the rheological properties of the solutions is also discussed.

Tuesday 1:55 Executive MT20

DRIFT AND DEFORMATION OF HETEROGENEOUSLY CHARGED CHAINS IN ELECTRIC FIELDS

A. Ajdari*, D. Long*, A. Dobrynin, and M. Rubinstein****

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We consider the motion and deformation of charged chains under DC electric fields in two limiting regimes: very low and very high ionic strength. The first regime is quite easily dealt with through the classical Zimm model. To describe the second regime, a proper understanding of the hydrodynamic flow generated by the electric drag on the counter-ions is needed. This results in very different effects: for example, 1) the mobility of homogeneously charged chains is length independent, 2) a chain neutral on average can be set into motion, 3) the mobility of a circular chain can change sign when it is cut into a linear chain. An analytical description is proposed for any charge distribution through a linear response analysis. Strong deformation in high electric fields is also discussed for some specific examples.

Tuesday 2:20 Executive MT21

BROWNIAN DYNAMICS SIMULATIONS OF DNA MOLECULES IN EXTENSIONAL FLOW

R.G. Larson

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Brownian dynamics simulations for the worm-like chain model are performed to complement and supplement recent single-molecule DNA experiments in extensional flow fields performed by Perkins, Smith, and Chu. The elasticity and frictional drag properties of DNA has been measured, and so the parameters of the simulations can be chosen to match those of the experiments to allow a detailed comparison between predicted and measured stretching behavior. In agreement with the DNA experiments, the Brownian dynamics simulations show highly heterogeneous unraveling behavior, with some molecules unraveling in "dumbbell" or "yo-yo" type configurations, others unraveling from "folded" configurations, and still others unraveling relatively uniformly. The percentage of "folded" configurations increases as the Deborah number begins to greatly exceed unity, and a comparison is made between the predictions of the Brownian dynamics simulations and those of a simple one-dimensional "kink dynamics" simulation at high Deborah number. The heterogeneity in unraveling characteristics results from Brownian fluctuations, which produce different initial configurations at the onset of stretching and different interactions of the configuration with the flow after flow starts. The degree each of these two sources of heterogeneity contributes to the total is assessed by performing simulations with identical starting configurations and different random-force histories during stretching, and simulations with different initial configurations but identical random-force histories. It is found that the unraveling of "folded" configurations is especially sensitive to the Brownian-force history. Numerous aspects of the unraveling behavior are poorly, or not at all, described by simple dumbbell models.

Tuesday 2:45 Executive MT22

STRUCTURE AND DYNAMICS OF CONCENTRATED PASTES

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We shall discuss dynamical properties of concentrated solutions of soft colloidal particles. The particles are micro-networks of crosslinked polyelectrolytes, whose swelling can be controlled by the pH. The effective volume fraction of the swollen particles is a key parameter to characterise their structure and their dynamical properties. When the effective volume fraction is smaller than the volume fraction at maximum packing, the suspensions behave like viscous solutions. However, in contrast to hard sphere suspensions, volume fractions higher than the maximum packing can be achieved by osmotic de-swelling of the particles; the suspensions now look like highly concentrated pastes. The dynamics of such pastes shows universal features independently of microscopic parameters such as polymer concentration, amount of crosslinker, ionic strength. There exists a yield stress above which the pastes reach a stationary macroscopic flow regime after a short period of time. Below the yield stress, the strain slowly

increases but the macroscopic shear rate never reaches a stationary value even over very large time periods. The yield stress depends on the local interactions between the particles and scales very well with the elastic modulus at equilibrium. The corresponding strain at which the paste first flows is constant and, strikingly, is as large as 0.1. In the macroscopic flow regime, the variations of the stress versus the shear rate can be described by a single master curve. We propose a microscopic interpretation of this behaviour.

Tuesday 3:35 Executive MT23

DYNAMIC PROPERTIES OF SEMIDILUTE SOLUTIONS AT THE THETA POINT

M. Adam*, B. Farago*, D. Lairez and E. Raspaud****

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At the theta point, thermodynamic binary interactions vanish but topological interactions remain due to the impossibility for entangled polymers to cross each other. Two lengths play a role [1]: the correlation length ξ_θ of concentration fluctuations (~1/C) and the diameter (A) of the tube within which polymers move by reptation ($\sim C^{-2/3}$). This model accounts for rheological results obtained in polystyrene dissolved in theta and in good solvent [2].

At a length scale smaller than ξ_θ, the diffusion coefficient is sensitive to the distance between binary contacts (Neutron Spin Echo experiments [3], for C between 0.02 g/cm^3 and 0.1 g/cm^3). The characteristic time of internal mode relaxation ($\sim q^3$) is linked to local viscosity, η_{loc}, temperature and monomer concentration dependent (in good solvent η_{loc}/η_s=1, app.). At a given concentration, the variation with temperature of η_{loc}/η_s, and of the macroscopic viscosity, η_m/η_s, are identical.

Working in a concentration range ($C < 0.015$ g/cm^3), where $\eta_{loc}/\eta_s = 1$ (app.), the η_m/η_s of entangled semidilute theta solutions increases with temperature, as predicted theoretically.

1) M. Rubinstein, R.H. Colby *Macromolecules* **23**, 2753 (1990).

2) M. Adam, M. Delsanti *J. Phys. (Paris)* **45**, 1513 (1984).

3) M. Adam, D. Lairez, E. Raspaud, B. Farago *Phys. Rev. Lett.* **77**, 3673 (1996).

Tuesday 4:00 Executive MT24

COMPARISON OF DIELECTRIC AND VISCOELASTIC BEHAVIOR OF POLYISOPRENE SOLUTIONS: COHERENCE IN SUBCHAIN MOTION

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For polyisoprenes (PI) having dipoles parallel along their contour, global chain motion induces both viscoelastic and dielectric relaxation. This motion is differently reflected in viscoelastic and dielectric quantities, the former detecting orientational anisotropy of subchains (or segments) at respective times while the latter detecting orientational correlation of the subchains at two separate times. This difference enables us to experimentally examine coherence of subchain motion in each chain at short time scales: For two extreme cases of perfectly coherent and incoherent subchain motion, the viscoelastic moduli are differently calculated from dielectric data. On the basis of this background, the moduli calculated for respective cases were compared with the viscoelastic data for solutions of a PI (M = 50K) of various concentrations. The comparison revealed that the subchain motion is incoherent for unentangled chains but a limited degree of coherence emerges for entangled chains. These findings were utilized to reexamine conventional interpretation for viscoelastic changes with concentration in terms of the Zimm/Rouse/reptation dynamics.

Tuesday 4:25 Executive MT25

VISCOELASTICITY AND DIFFUSION IN CONCENTRATED POLYMER SOLUTIONS

Tim Lodge*, Hui Tao*, and Ernst von Meerwall**
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The concentration and molecular weight dependencies of the viscosity, dynamic moduli, and self-diffusion of homopolymers in concentrated solutions are not yet fully understood. For example, the diffusivity in the melt generally appears to follow the reptation scaling with molecular weight, but in some solutions even stronger exponents (e.g. -3) are reported; furthermore, there are no diffusion data between concentrations of 40% and the melt. We report measurements of diffusion, viscosity, and dynamic moduli for a series of hydrogenated polybutadienes, at concentrations ranging from 20% up to the melt, as functions of molecular weight and temperature. The results are compared with various theoretical predictions.

Tuesday 4:50 Executive MT26

DYNAMICS OF COIL-GLOBULE COLLAPSE TRANSITION: THEORETICAL CONJECTURES AND EXPERIMENTAL SITUATION

Alexander Yu. Grosberg
Room 13-2009, Department of Physics, MIT, Cambridge, MA 02139

Dynamics of a single polymer chain collapse is of fundamental importance both because it is one of the simplest non-trivial models in polymer dynamics and because of its relevance to protein folding and other studies in molecular biology. In the present talk we plan to review the theoretical models developed so far to describe this transition, including sausage, necklace, crumpled globule, plum pudding and others. We then plan to discuss recent experimental findings and compare them with theoretical predictions. We shall also consider computer simulation data. Finally, we plan to discuss related questions that emerge in the current studies of heteropolymer freezing and protein folding. Although many questions in the field remain open and final understanding remains to be achieved, the critical comparison of the existing works seems both timely and instructive.

Symposium FM
Non-Newtonian Fluid Mechanics

Organizers: Gary L. Leal and Frank Baaijens

Tuesday 1:30 Judicial FM1

TRANSIENT EXTENSIONAL FLOW AND TACK CHARACTERISTICS OF A TERPOLYMER ADHESIVE.

Jim Ferguson*, John F. Forsyth* and Nick Granville**
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Recent work has suggested that transient extensional viscosity measurements made at a constant temperature, using different techniques, fall on a unique 3D surface when plotted against strain and time of extension. In order to test this hypothesis a series of experiments have been carried out in which a terpolymer of acrylic acid, n-butyl acrylate and 2-ethyl hexyl acrylate has been extended in a sequence of different rates. This has shown that although the extensional viscosity of the terpolymer deviates instantaneously to a point above or below the 3D surface when rate of extension is changed, it then relaxes back to the original surface as extension proceeds at the new rate. This would indicate that the surface is one of "minimum energy".

Studies on the adhesion of the terpolymer during extension have shown that the mode of failure of the adhesive bond is related to the strain hardening behaviour of the terpolymer. At low strain rates, fibrils form between the adhesive and the surface to which it is attached. At high strain rates, this does not happen.

Strain hardening during extension has been related to the formation of temporary crystalline structure in elastomeric polymers as strain increases. The influence of this on the terpolymer under investigation will be discussed.

Tuesday 1:55 Judicial FM2

THE RHEOLOGY OF FIBER SPINNING

Manfred H. Wagner and Anke Bernnat
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Melt spinning is a prototypical example of many polymer processes: The polymer melt is first subjected to simple shear flow, which is followed by uniaxial extension under constant force. The analysis of this complicated deformation history is simplified by the existence of Rheotens Super- and Grandmastercurves /1,2/. These allow a direct and straightforward description of material behaviour in the fiber spinning process, and a simplified determination of an effective elongational viscosity under the action of a constant draw-down force. For a broad range of operating conditions, spinning behaviour of a LDPE melt was investigated. Along the spinline, two different deformation regimes were found: below a critical strain, deformation occurs at (approximately) constant strain rate, while above this threshold, deformation can be described by a purely viscous power-law model.

/1/ M.H. Wagner, V. Schulze and A. Goettfert, Polym. Eng. Sci. 36(1996) 925-935

/2/ M.H. Wagner, B. Collignon and J. Verbeke, Rheol. Acta 35(1996) 117-126

Tuesday 2:20 Judicial FM3

BROWNIAN DYNAMICS SIMULATIONS OF POLYMERS IN SOLVENTS OF VARYING QUALITY: STARTUP AND RELAXATION IN EXTENSIONAL FLOW

Thomas C. B. Kwan and Eric S. G. Shaqfeh
Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025

The effects of solvent quality on the equilibrium properties of polymers have been well-established. On the other hand, the non-equilibrium dynamics of polymers in solvents of different quality have received relatively little attention. We present a study of the transient extensional behavior of polymers modeled as bead-rod chains in solvents of different qualities. Lennard-Jones potentials are introduced to describe the interactions between different segments of a polymer, and by adjusting the depth of the potential well, solutions of varying solvent quality can be simulated. Adding this new polymer interaction force to the original Brownian dynamics approach of Doyle et al., we perform simulations of bead-rod chains in uniaxial extensional flow. The simulations are performed over a wide range of strain, Weissenberg number and over a range of second virial coefficient describing the solvent interactions. Dynamics in both good and poor solvents are simulated. The chains are simulated as they evolve from an initially coiled state to full extension and finally, through stress relaxation following cessation of the flow. We observe a highly solvent-quality dependent stress growth and relaxation, where, in particular the coil-stretch transition in poor solvents is postponed to larger strains and strain rates when compared to theta and good solvent conditions. Universal scalings (for arbitrary numbers of Kuhn steps) are presented to describe the dependence of the coil-stretch transition on solvent quality. Furthermore, there exists a stress-birefringence hysteresis that is solvent-quality dependent with larger hysteresis predicted for poorer solvents. These observations are discussed, and comparisons to recent experimental measurements of stress growth by Solomon & Muller are made.

Tuesday 2:45 Judicial FM4

FLUID DYNAMICS OF WEAKLY STRAIN-HARDENING FLUIDS IN FILAMENT STRETCHING

Minwu Yao*, Stephen H. Spiegelberg, Gareth H. McKinley****
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Numerical simulations with dumbbell models, and video-imaging of experiments with Boger fluids, have shown that the kinematics in Filament Stretching Rheometers are nonhomogeneous at short times and small strains, but become increasingly homogeneous as the tensile stress in the fluid grows and the fluid column becomes increasingly axially

uniform. The assumption of one-dimensional homogeneous kinematics is then appropriate, and independent measurements of the total force and the birefringence can be used as sensitive probes of the evolution in configurational microstructure and stress during uniaxial elongation and also following cessation of stretching. Less extensive comparisons between experimental data and numerical simulations have been performed for semi-dilute or concentrated polymer solutions. Such materials typically exhibit shear-thinning viscometric material properties and less pronounced strain-hardening in extension. In this case the need for direct comparison between experiments and numerical simulations is more pressing since the kinematics in the device never become spatially or temporally homogeneous [1]. In the present work, we use time-dependent finite-element numerical simulations with the Giesekus model to show that even if the fluid exhibits some strain-hardening, this can be insufficient to stabilize the contraction in the filament radius as the sample is exponentially elongated. Viscoelastic effects result in a rate of thinning that is enhanced beyond that of a non-strain-hardening Newtonian filament and the fluid thread is predicted to break in a finite time. This qualitative difference compared to Oldroyd-B-like fluids can be understood in terms of a modified Considère analysis commonly employed for describing necking in tensile tests of solid polymer samples. Comparison with experimental measurements for a concentrated solution of 2 wt% polystyrene show that the transient elongational viscosity can still be accurately extracted from the device by careful measurement of the temp

Tuesday 3:35 Judicial FM5

FAST CHANNEL FLOWS OF POLYISOBUTYLENES

V.B. Birman*, A.I. Leonov* and J. Padovan**

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A large multi-purpose set up with air cylinder was built up for quantitative visualization of fast flows of polymers. The channels with circular (f=0.406"), square (0.39"X0.39") and rectangular (0.39"X0.78") cross-sections had either transparent windows or were made of transparent materials. The flows of two polyisobutylenes, low molecular weight (57,000), PIB-1, and high molecular weight (800,000), PIB-2, were studied under constant pressure, Po, at 25 and 70C wall (and initial polymer) temperatures, respectively.

The following effects were observed for fast flows of PIB-1: (i) a significant (up to 90C) increase in surface extrudate temperature; (ii) at Po= 5,000 psi, rotations of chaotically dispersed air bubbles as well as rotations of a long air bubble set in the center of piston chamber, accompanied by rotations of PIB-1 extrudates. At Po < 100 psi, all air bubbles remained in the center of channel.

Two haze spirals accompanied by spiral shapes of extrudates, were detected in fast rectangular channel flows of PIB-2. They disappeared in a couple of minutes after flow was stopped.

For both PIB-1 and PIB-2, the centers of flow rotations in circular and square channels coincided with the channel centerline. Two centers of rotation were observed in the rectangular channel.

Tuesday 4:00 Judicial FM6

DYNAMICS OF A CYLINDRICAL VISCOELASTIC DROP IN PERIODIC ARRAYS OF CYLINDERS

D. Backes and K. Jayaraman

Department of Chemical Engineering, Michigan State University, E. Lansing, Michigan, 48824

The mobilization and breakup of a cylindrical viscoelastic drop with varying length has been investigated in flow transverse to a spatially periodic square array of cylinders with a porosity of 0.5. Capillary numbers based on the radius of the drop range from .005 to .05 and the viscosity ratio is of order one. The array of cylindrical acrylic rods with a diameter of 0.476 cm was fit in an aluminum flow cell with transparent windows for observation of the bubble movement. The drop is neutrally buoyant and the continuous liquid phase is a chloroparaffin oil that is refractive index matched with the glass rods making up the array. A criterion for mobilization of the viscoelastic drop in the periodic array has been derived and tested with the experiments. The relative velocity of the viscoelastic drop has been compared with that of a Newtonian drop at corresponding capillary numbers.

Tuesday 4:25 Judicial FM7

ENTRY FLOW AND CONSTITUTIVE MODELLING FOR FLUID S1

J.A. Byars, R.J. Binnington and D.V. Boger

Department of Chemical Engineering, Advanced Mineral Products Research Centre, The University of Melbourne, Parkville Victoria 3052, Australia

Experimental observations of the flow through an axisymmetric 4 to 1 contraction for the shear thinning test fluid S1 are presented. In order to provide the basis for comparison with numerical simulations of the flow in the viscoelastic spectrum, the non linear parameters for the three constitutive models are also presented based on the rheological characterisation of the fluid by Ooi and Sridhar (J. Non-Newtonian Fluid Mech., 52 (1994), 121-125). The results of flow visualisation experiments are presented for the flow of S1 through the 4 to 1 axisymmetric contraction, with either an abrupt entry or a rounded re-entry corner. Dimensionless vortex size increases with increasing Weissenberg number for each geometry, with a larger vortex observed for the abrupt entry for identical flow conditions. No elastic lip vortex or flow instability was observed for Weissenberg numbers less than or equal to 5. Data provided for this well characterised fluid provide an ideal set of information to test current numerical simulation procedures.

Tuesday 4:50 Judicial FM8

SURFACE INSTABILITIES DURING EXTRUSION OF LINEAR LOW DENSITY POLYETHYLENE

M.R. Mackley*, R.P.G. Rutgers* and D.G. Gilbert**

*Department of Chemical Engineering, University of Cambridge, Cambridge CB2 3RA, UK;
**BP Chemicals S.N.C., Centre de Recherche, 13117 Lavera, France

This study concerns the extrusion behaviour of a film blowing grade of linear low density polyethylene. LLDPE shows a variety of instabilities with increasing production rate. The purpose of this study is the understanding of the mechanism underlying the onset and development of the first instability to occur with increasing flow rate, which affects only the surface of the extrudate.

The onset and progress of the surface distortion is studied as a function of process conditions, die geometry and polymer blend composition, using a Betol 20 mm extruder, equipped with an abrupt entry slit die allowing rheo-optical measurements. We show the qualitative characteristics of the surface distortion obtained via scanning electron microscopy and quantitative surface roughness data obtained through stylus surface profile measurements. In a processing window of 160 to 200 degrees Celsius, the severity of the instability for LLDPE increases with increasing exit stress level. Under these conditions pure LDPE does not show the instability, but blends of the two materials show significantly more severe extrudate distortions than pure LLDPE.

Using flow induced birefringence measurements the stress fields in the die can be studied in detail, simultaneously to monitoring the extrudate appearance. Polyflow simulations allow further in-depth investigation of the stress concentrations and local velocities of the fluid in the exit region. Large velocity gradients, deformations and stresses are found near the exit, confined to the surface region. For the individual materials, the relationship between critical elongational stresses obtained from Rheotens experiments and the local exit stresses at onset of surface extrudate instability is investigated.

Symposium SP
Suspensions

Organizers: Ronald Phillips and Tony Ladd

Tuesday 1:30 Legislative SP19

FLOW OF RIGID PARTICLES IN VISCOELASTIC MEDIA

J. Azaiez
Chemical Engineering Department, Laval University, Quebec G1K 7P4. CANADA.

The present study is part of an ongoing investigation of the rheological properties of particle suspensions. A basic understanding of the rheology of filled polymers and an accurate modeling of the filler-matrix interactions is in fact of great scientific interest and has important practical applications. We use the kinetic theory of elastic dumbbells for the polymer melt, and continuum theory for the suspension rheology to derive a model that incorporates the major concepts of fiber-polymer interactions as well as those related to the viscoelastic nature of the matrix. The new model introduces new phenomenological constants that depend on the properties of the fibers, and whose expressions can be related to formulations already existing in the literature. We discuss results for the steady state shear flow, and examine the variations of the steady-shear viscosity and first normal stress difference with the fiber aspect ratio, volume fraction, and particle-particle interaction coefficient. Comparisons with existing experimental measurements show the great potential of the new model to accurately predict the qualitative behavior of the flow of fibers in a polymer melt in the case of simple flows. We conduct experimental measurements for a suspension of glass fibers in a polypropylene melt and show that, when compared with existing models, the new one leads to better qualitative and quantitative agreements with the experiments.

Tuesday 1:55 Legislative SP20

ORIENTATIONAL DRIFT OF A FIBER SUSPENDED IN A POLYMER SOLUTION SUBJECT TO OSCILLATORY SHEAR FLOW

Oliver G. Harlen* and Donald L. Koch**
*Department of Applied Mathematical Studies, University of Leeds, Leeds LS2 9JT, UK;
**School of Chemical Engineering, Cornell University, Ithaca, NY 14853

Small amplitude oscillatory shear flow of a fiber suspended in a dilute polymer solution is considered. Averaged over a cycle of the shear flow, the nonlinear elasticity produces a mean angular velocity of the fiber proportional to the square of the amplitude of the shear flow. Over many cycles this produces a slow drift in the orientation of the fiber towards alignment with the flow direction, an orientation that minimizes the fiber's effect on the rheology. The flow-orientation of a fiber in small amplitude oscillatory shear may be contrasted with the vorticity orientation predicted previously for steady shear.

Tuesday 2:20 Legislative SP21

DYNAMICS OF ISOLATED FLEXIBLE FIBERS AND FIBER SUSPENSIONS

C. F. Schmid, P. Skjetne, M. D. Graham, and D. J. Klingenberg
Department of Chemical Engineering and Rheology Research Center, University of Wisconsin, Madison, WI 53706

Suspensions of flexible fibers are encountered in many industrial applications, from papermaking to fiber-filled composites manufacturing. Describing the flow behavior of these suspensions is complicated by shear induced deformation and entanglement of the constituent fibers. We have developed two simple mechanical models for a flexible fiber, and employ both in particle-level simulations to study the flow behavior isolated particles and concentrated suspensions. Flexibility is controlled by two model parameters; a bending constant and a twisting constant, which are directly related to the Young's modulus and shear modulus, respectively, of the fiber material.

Studies of individual fibers show increased deviation from rigid Jeffery orbits with increasing fiber flexibility, and demonstrate qualitative agreement with the experimental observations of Forgacs and Mason [O. Forgacs, S. Mason, J. Coll. Sci., vol. 14, (1959) p. 473]. Studies of the stability of flexible and permanently-deformed fiber orbits are presented, and results are compared to the experiments of Arlov, et al., [A. Arlov, O. Forgacs, S. Mason, J. Coll. Sci., vol. 14, (1959) p. 457]. Simulations show rigid straight fibers to orbit periodically, rigid deformed fibers to orbit quasiperiodically, and flexible fibers to drift to preferred orbits. Mechanisms of orbital drift are proposed.

Results for the flow of suspensions of flexible and permanently-deformed fibers are also presented. The influence of fiber properties (*e.g.*, aspect ratio, modulus, and permanent deformations) on entanglement behavior are discussed.

Tuesday 2:45 Legislative SP22

DYNAMIC OSCILLATIONS OF A FILLED COMPOUND UNDER CURE REACTION

R. Ding and A.I. Leonov
Department of Polymer Engineering, The University of Akron, Akron, OH 44325-0301

Cure kinetics and rheological behavior of a carbon black filled SBR compound under dynamic tests were studied using Rheometrics and Mechanical Energy Resolver instruments. Using a kinetic approach based on a cure reaction scheme, the whole cure kinetics curve has been described at isothermal and non-isothermal conditions. The gel point was determined according to a characteristic point on the cure kinetics curve. Samples with different degree of cure were then studied in oscillatory simple shear experiments. The relaxation spectrum for the uncured sample was found in the small amplitude region, where due to the filler-polymer interactions, the rheological behavior was still nonlinear. The dependencies of relaxation parameters on the degree of cure were established before and after gelation. When such dependencies are incorporated into a nonlinear constitutive equation, it enables to continuously describe the rheological behavior of the reactive compound from the uncured till fully cured state.

Symposium BS
Rheology and Flow-Induced Structure of Blends and Solutions

Organizer: Jan van Egmond

Tuesday 3:35 Legislative BS5

RHEO-OPTICAL INVESTIGATIONS OF VISCOELASTIC MICELLAR SOLUTIONS

E. K. Wheeler, P. Fischer, G. G. Fuller
Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025

Both optical and mechanical techniques are used to investigate aqueous surfactant solutions of cetylpyridinium chloride and sodium salicylate during different flow geometries. We report the effect of varying the surfactant to salt ratio on both the viscoelastic properties of the solution and the micellar structure. An in depth study of an equimolar solution of this system shows evidence of a shear induced structure (SIS) that results in a flow instability. Shear induced structures have been observed before in the strong flow regime (Rehage and coworkers, 1986) and are characterized by an increase in turbidity. Not only do we see this initial increase in turbidity but as the shear rate is increased we see rings of alternating turbid and clear solution indicating that the flow is capable of both forming and destroying these structures. Visualization in a Taylor-Couette flow cell again shows bands of clear and turbid solution. Similar bands have been observed for Boger fluids seeded with mica flakes that exhibit elastic instabilities. Other similarities to experimental results for instabilities are present. Based on the experimental results we propose that a SIS causes instabilities in the flow to arise. However, comparing critical parameters of the experimental solution to stability analyses in the literature for Giesekus fluids shows that the instability is not purely elastic. Clearly, there is a strong coupling between the flow instability and the structural changes of the solution that must be taken into account before a stability analysis can be performed.

Tuesday 4:00 Legislative BS6

FLOW AND STRUCTURE OF ASSOCIATING HYDROPHOBICALLY MODIFIED POLYMERS AND ROD-LIKE SURFACTANT MICELLES

S. Panmai*, R.K. Prud'homme*, and D. Peiffer**

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The rheology of interacting hydrophobically modified hydroxyethylcellulose (HMHEC) and surfactants, sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) is presented. With the addition of SDS, the viscosity of the HMHEC solutions first increases, due to the polymer/surfactant hydrophobic networking associations, and then decreases, due to the solubilization of each hydrophobe by a single micelle and the breakdown of the network. HMHEC interacts less strongly with CTAB. We note the importance of the hydrophobic length on the HMP/surfactant interactions: the C16-HMHEC interacts much more strongly with both SDS and CTAB than the C12-HMHEC does. Unlike interactions with spherical CTAB micelles, the interactions between HMHEC and rod-like CTAB micelles, show a monotonic increase in the viscosity with CTAB concentration. The relatively faster increase in the micellar length compensates for the increase in the micellar concentration at higher CTAB concentrations and maintains the hydrophobic interactions. Neutron scattering under shear was conducted on the solutions. Under shear the rodlike micelle solutions show the strong alignment of the micelles. In contrast , the rodlike micelle/HMHEC solutions show essentially no alignment in shear. The implications of these results for modeling these association fluids will be presented.

Tuesday 4:25 Legislative BS7

ANOMALOUS STRESS IN PHASE SEPARATING POLYMER SOLUTIONS

J. W. van Egmond

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

A constitutive model is developed for flow-induced concentration fluctuation enhancement in polymer systems. This anomalous stress can be of the same order of magnitude as the viscoelastic stress supported by polymer molecules in the system. We also investigate the rheology of a near critical, single phase solution where noise and coupling of the order parameter with viscoelastic stress is important. When such fluids are subjected to flow fields, concentration fluctuations undergo an anisotropic enhancement due to a coupling between the stress and mesoscopic structure of the solution. Depending on the strength of this stress-structure coupling, the excess stress due to anisotropic concentration fluctuations can either increase or decrease the overall stress thus leading to shear-thickening or shear-thinning behavior.

Tuesday 4:50 Legislative BS8

MECHANISMS FOR STRESS RELAXATION IN IMMISCIBLE POLYMER BLENDS

P. Moldenaers and I. Vinckier

Department of Chemical Engineering, K.U. Leuven, B 3001 Leuven, Belgium

In immiscible polymer blends, the stress relaxation at long times is governed by the microstructural changes that occur during relaxation. This is most pronounced for the normal stress relaxation. By applying suitable shear histories to droplet/matrix systems, various initial structures can be generated. Slightly deformed droplets relax by regaining their spherical shape after cessation of flow. Fibrillar structures can relax by either break-up caused by Rayleigh instabilities or by end-pinching. It is shown that these various mechanisms can be identified by means of the shapes of the corresponding relaxation curves. The Doi-Ohta scaling relations can be applied to the experimental results but none of the existing models describes the stress relaxation resulting from highly stretched droplets. However, by combining the Tomotika theory with the approach of Doi-Ohta, the shape of the stress relaxation curves for a fibrillar structure can be predicted.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Governor's Ballroom PL3

"RHEO NMR": RHEOLOGICAL INSIGHTS BY MEANS OF NMR MICROSCOPY

Paul T. Callaghan
Department of Physics, Massey University, Palmerston North, New Zealand

The term "Rheo-NMR" was first coined by Samulski and co-workers who measured NMR spectroscopic parameters for polymer melts under shear. Subsequently we reported a different, but complementary, approach in which velocity profiles and local self-diffusion coefficients were imaged for a semi-dilute polymer solution exhibiting non-Newtonian flow in a capillary.

An overview of the NMR Microscopy method will be given, along with examples of flow measurement in different geometries, including capillary flow, cylindrical Couette flow (with examples of Taylor vortex motion), cone-and-plate flow and both twin-jet and four-roll-mill extensional flow. The work presented will focus on studies of non-linear viscosity in complex fluids, including entangled polymer random coils, rigid rod polymer solutions, wormlike surfactants and a range of food materials. These imaging studies have proven effective over a range of phenomena including apparent slip, the "spurt effect", shear banding, fracture, yield stress phenomena and polymer demixing. One intriguing outcome of this work has been the demonstration of non-uniform shear within the gap of a small-angle cone-and-plate rheometer.

A combination of NMR imaging and NMR spectroscopy has led to the possibility of investigating the molecular origins of non-Newtonian rheological properties, thus marrying the original Rheo-NMR approaches. Some preliminary results for polymer melts and wormlike surfactants will be presented.

Symposium FI
Melt Flow Instabilities and Wall Slip

Organizers: Shi-Qing Wang and John M. Dealy

Wednesday 9:45 Senate FI10

DYNAMIC WALL SLIP OF MOLTEN POLYETHYLENE ON FLUOROPOLYMER SURFACES

J. M. Dealy and R. S. Jeyaseelan
Chemical Engineering, McGill University ; 3610 University St., Montreal, Canada, Qc H3A 2B2

Creep experiments were conducted on molten polyethylene in simple shear between two clean steel walls, and between a clean steel and a fluoropolymer-coated wall. Assuming that the melt did not slip on steel, the data were used to determine the slip displacement at the polyethylene-fluoropolymer interface, as a function of time.

We found a large variation in slip displacement when experiments were repeated using different samples. Furthermore, successive experiments on the same sample usually resulted in a higher steady state slip velocity. We hypothesize that this is due to a partially irreversible breakdown of adsorption during each experiment. The large scatter in the slip displacement data measured for different samples could be due to nonuniform wetting of the fluoropolymer wall when the sample is squeezed between the two walls prior to the experiment. The surface roughness of the fluoropolymer coating may also be an important factor in these experiments, and causes an increase in the scatter of the steady state slip velocity data. The experiments also reveal that when the slip displacement is sufficiently large, the sample progressively loses contact with the fluoropolymer surface by a peeling mechanism.

The dynamic slip displacement data show that a large fraction of the steady state slip velocity is reached as soon as the shear stress is imposed on the sample. A reasonable representation of the data was obtained using a separable BKZ constitutive equation (Wagner model) in conjunction with a dynamic wall slip model proposed by Black and Graham (for molten polymers on clean steel surfaces, 1996), which we have modified to incorporate static slip and nonuniform wetting.

Wednesday 10:10 Senate FI11

VISCOELASTIC INSTABILITY OF FLOW WITH SLIP

William B. Black and Michael D. Graham

Dept. of Chemical Engineering and Rheology Research Center, University of Wisconsin-Madison, Madison WI 53706-1691

Slip between flowing molten polymer and metal die surface is the most commonly cited reason for extrusion instabilities such as sharkskin. Nevertheless, the underlying instability mechanisms are not known. Most phenomenological models of slip in polymer melt flows relate the slip velocity to the shear stress. Unless they allow slip velocity to decrease with increasing shear stress, such models always lead to a flow that is stable with respect to two-dimensional perturbations. We discuss here a monotone increasing slip model in which both shear and normal stresses arise. Analysis of viscoelastic plane Couette flow (upper convected Maxwell and Phan-Thien Tanner models), with this slip model as a boundary condition, predicts instability with respect to short-wavelength, boundary-localized fluctuations at Weissenberg numbers greater than about 10, suggesting that slip can lead to instability in viscoelastic shear flow. The analysis predicts stability in the no-slip limit, as it should for consistency with previous results, and also predicts that instability will not occur if the fluid is Newtonian, or if the slip coefficient (extrapolation length) is sufficiently large. The destabilizing fluctuations travel with the slip velocity, so short waves, which are the most unstable, have high frequency. The instability mechanism involves a coupling of steady state stresses with perturbation velocity gradients that is absent in the no-slip case.

Wednesday 10:35 Senate FI12

COMPARISON OF SLIP AND NO-SLIP SPURT MODELS WITH EXPERIMENTS

C.F.J. den Doelder*, R.J. Koopmans*, J. Molenaar, and A.A.F. van de Ven****

*Dow Benelux N.V., P.O. Box 48, 4530 AA Terneuzen, The Netherlands; **Department of Mathematics and Computing Science, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

The spurt phenomenon occurring during flow rate imposed extrusion has been described on a global level with a coupled system of equations relating pressure to flow rate, see [1]. This so-called relaxation-oscillation model makes use of a non-monotonic F-function that was introduced heuristically in [1]. In the present study, we have derived this function ab-initio via the laws of conservation of mass in the barrel (compressible flow) and of momentum in the die (incompressible axisymmetric shear flow). We have compared three models. Model A: Newtonian flow with a slip die wall boundary condition. Model B: the Johnson-Segalman-Oldroyd (JSO) constitutive model with a no-slip boundary condition. Model C: two concentric Newtonian flow regions with different viscosities and a no-slip boundary condition.

We found that Model A and Model C are capable of generating spurt oscillations in qualitative agreement with experiments, whereas Model B is not. From a mathematical point of view, the existing controversy between slip and no-slip supporters needs not be relevant.

In order to obtain quantitative agreement with experiments, we replaced the simple Newtonian constitutive equations of Model A with models involving shear thinning. We found excellent agreement between the experimental flow curve characteristics and the model predictions, with only a few fit parameters in the slip law.

[1] Molenaar and Koopmans, Modeling polymer melt-flow instabilities, J.Rheol. 38(1) 99-109.

Wednesday 11:00 Senate FI13

WALL SLIP IN POLYMER MELTS: A PSEUDO-CHEMICAL MODEL.

Davide A. Hill
Department of Chemical Engineering, University of Notre Dame du Lac, Notre Dame, IN 46556

Reiterating on available, chemical-type theories for slip in polymer melts, we model the process of exchange of bridging sites between a polymer and a solid surface. Kinetic-rate equations, describing surface coverage by bridging sub-chains, are derived and analyzed to evaluate the stability of adhesive contact and slip characteristics of the viscoelastic liquid. The model displays the following features: 1) At less than 100% equilibrium (no flow) coverage the polymer slips at all stresses. 2) At small stresses the slip velocity is linear in shear stress and proportional to a function of the work of adhesion; also, the slip parameter b (the slip extrapolation length scale) takes on the same form as that proposed by de Gennes. 3) At higher stresses the slip velocity assumes a strong non-linear dependence (nearly of the power-law type in some ranges) on stress. 4) A catastrophic loss of adhesion finally occurs at a maximum, critical stress that depends on the work of adhesion. Predicted adhesion free energies for polyethylene on steel, assuming a recoverable shear of order unity at the onset spurt flow, fall within realistic ranges.

Wednesday 11:25 Senate FI14

MATERIAL INTABILITIES AND INTERNAL DISCONTINUITIES

David S. Malkus
Engineering Physics Department and Rheology Research Center, University of Wisconsin, Madison, WI 53706

Over recent years, many investigators have proposed a relationship between wall-slip or apparent slip-like phenomena and large-scale polymer flow instabilities, e.g. wavy extrudate distortion, persistent oscillations, and melt fracture. My colleagues and I have proposed that very similar behavior may be attributed to bulk rather than surface phenomena. We have used the Johnson-Segalman model as a prototypical model of material behavior that can reproduce the large-scale flow instabilities with remarkable qualitative correspondence to the observations. An inescapable conclusion of this modeling is that the flow instabilities are often associated with the dynamics of internal -- rather than wall -- discontinuities. The correspondence between slip-like instabilities and bulk, or 'material' instabilities occurs only in flows in which regions of higher stress are confined to regions close to the walls. This talk will explore how these internal discontinuities arise in computation and analysis, and how they might be inferred or observed in experiment.

Symposium MT
Molecular Theories for Polymer Dynamics

Organizers: Ralph H. Colby and Michael Rubinstein

Wednesday 9:45 Executive MT27

THE ROLE OF THE ORIENTATION TENSOR IN THE NONLINEAR VISCOELASTICITY OF FLEXIBLE POLYMERS

Manfred H. Wagner
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The stress-strain relations for extensional deformation of linear and branched polymer melts as well as of (crosslinked) rubbers are discussed in terms of the orientation tensor. It is shown that orientation and network strand extension are decoupled, and that the relative tube diameter and its inverse, the molecular stress function f, can be extracted directly from the experimental data, if the effect of network orientation is accounted for by the orientation tensor (Wagner and Geiger, Macromol. Theory Simul. 6 (1997) in press). The tension of the average network strand increases with increasing deformation. This is caused by an increasing restriction of lateral movement of polymer chains due to tube deformation. At small strains, the square of the molecular stress function is found to be linear in the average stretch for melts as well as for rubbers, which corresponds to a constant tube volume. At large strains, melts show maximum molecular tension, depending on the degree of long-chain branching, while rubbers show maximum extensibility. An analysis of new experimental data supporting these statements is presented.

Wednesday 10:10 Executive MT28

PATH DEPENDENCE OF THE VISCOSITY-TEMPERATURE RELATIONSHIP IN POLYMER MELTS: FRAGILITY AND TIME-PRESSURE-TEMPERATURE EQUIVALENCE

D.M. Colucci* and G.B. McKenna**

*Exxon Chemical Company, Baytown Polymer Center, Baytown, TX 77520; **Polymers Division, NIST, Gaithersburg, MD 20899

The viscosity-temperature relationship of polymer melts and other glass forming systems is often observed to follow a strong non-Arrhenius type behavior. In polymers it is common to present the viscosity-temperature data as log viscosity vs. T. In addition, it is observed that the polymer behavior under high pressures can be readily described using time-temperature-pressure superposition (TTPS). In the area of inorganic and small molecule glasses, on the other hand, it is more common to present the viscosity-temperature data in a so-called Angell plot as log viscosity vs. Tg/T which results in a normalized Arrhenius representation. In the Angell plot, deviations of behavior from Arrhenius behavior (i.e., curvature in the plot) are interpreted in terms of the fragility of the liquid. The fragility concept arises as a sense of the liquid showing glass-like Arrhenius behavior (strong) or very large deviations (fragile) from the glassy temperature dependence of viscosity. We have observed that polymers can exhibit a range of behaviors from strong to fragile depending, apparently, upon chemical structure. In addition, we find that representation of the viscosity-temperature data at constant volume (isochorically) results in a different fragility than does the representation as viscosity-temperature isobars. The isochoric liquid appears stronger than does the isobaric liquid for the same glass formation volume, temperature and pressure. This result, if one takes the fragility classification literally, suggests that the isochoric liquid differs less from the isochoric glass than the isobaric liquid does from the isobaric glass. We have data for polycarbonate that shows that the isochoric liquid and glass compressibilities are nearly the same while the isobaric compressibilities show significant differences. Here we address the meaning of these observations and how the conventional polymer community representation of data in terms of TTPS principles can account for the fragility observations.

Wednesday 10:35 Executive MT29

DOI-EDWARDS THEORY WITH PARTIAL STRAND EXTENSION

Vijay Mhetar and L.A. Archer

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

We previously proposed a scaling argument which shows that linear polymer molecules in entangled melts and solutions retract only by a fraction of their deformed lengths. Specifically, if a polymer molecule with initial contour length L_0 is suddenly deformed by an amount λ, its contour length after retraction is found to be $L_0\ \lambda^{1/2}$, not L_0. In this paper we study the implications of this partial strand extension (PSE) idea on reptation dynamics. It is shown, for example, that PSE removes predictions of constitutive instabilities from the Doi-Edwards theory and yields steady shear viscosities consistent with Cox-Merz rule. PSE also introduces a strain-dependent reptation time and revives old issues about time-strain separability in entangled polymers. This last part of the study is facilitated by new polymer melt data from tests designed to eliminate slip at the walls.

Wednesday 11:00 Executive MT30

EXAMINATION OF THE TUBE MODEL IN HIGHLY NONLINEAR TRANSIENT FLOWS

D.W. Mead and M.K. Lyon

Department of Mechanical Engineering and Applied Mechanics, University of Michigan, Ann Arbor, MI 48109

Although the Doi-Edwards tube and reptation model correctly predicts the linear viscoelastic behavior of monodisperse systems of linear flexible polymers, it does very poorly in the non-linear regime. Specifically, in

"simple" shear flow the model predicts an asymptotic viscosity that scales with the shear rate to the -3/2 power. The fundamental cause of this excessive shear thinning is over-orientation of the chain segments in the direction of flow. Incorporation of segmental stretching into the model does not improve this shear thinning behavior, because the fundamental problem lies in over-orientation. Thus, counter-intuitively, in order to obtain less severe shear thinning, an additional orientational relaxation mechanism must be introduced rather than an additional stress generation mechanism such as segmental stretch. Marrucci has recently suggested that an orientational relaxation mechanism driven by the convection of chains away from one another must necessarily be involved. We build on this idea of a convective relaxation process by incorporating an empirical orientational relaxation mechanism into the Doi-Edwards model with segmental stretch. We examine predictions of this new model in transient and steady simple shear, planar flows and uniaxial extension.

Wednesday 11:25 Executive MT31

DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTIONS FROM COMPLETE LINEAR VISCOELASTIC RHEOLOGICAL DATA

T.J. Van Dyke and D.W. Mead
Department of Mechanical Engineering and Applied Mechanics, The University of Michigan, Ann Arbor, Michigan 48109

The status of rheological methods of determining the molecular weight distribution has evolved tremendously since Tuminello introduced the first viable method in 1985. This work investigates inverting the double reptation and weight average mixing rules to determine the MWD for systems of linear flexible polymers when a complete dynamic moduli data set exists. In order to apply mixing rules for MWD determination, the contribution to the dynamic moduli from the glassy modes must be subtracted off as it contains no information on the MWD. We illustrate a viable, automated means of accomplishing this subtraction based on the Rouse model. For the double reptation mixing rule, we present a novel numerical inversion methods based on moments of the MWD. The moments are determined by taking the Mellin transform of the double reptation mixing rule. Employing moments in the numerical scheme greatly improves the accuracy of the inversion. Numerical methods to invert the empirical weight average mixing rule are also described and evaluated. A principal advantage of the weight average method is that it involves direct conversion of the dynamic moduli to MWD thereby avoiding the clumsy determination of the relaxation modulus necessary with the double reptation scheme; however, the weight average method can be seen to be less accurate in capturing the dynamic moduli. The above models and methods are applied to a variety of commercial and model systems of linear flexible polymers and quantitatively evaluated.

Symposium FM
Non-Newtonian Fluid Mechanics

Organizers: Gary L. Leal and Frank Baaijens

Wednesday 9:45 Judicial FM9

MEASUREMENT OF VISCOELASTICITY FOR POLYMER SOLUTIONS IN POROUS MEDIA

Nancy M. Henderson and George B. Thurston
Rheology Laboratory, Department of Mechanical Engineering; The University of Texas at Austin; Austin, TX 78712

Measurements of viscoelasticy in flow through porous media show that the properties of polymer solutions of the type used in enhanced oil recovery exhibit major differences from those measured in bulk. The rheometer used (Vilastic Scientific Inc.) can excite oscillatory flow in porous media as well as in small and large tubes, and also can produce fundamental pressure-to-flow relations. For porous media, a complex Darcy's law provides a permeability which in turn is related to an equivalent bundle of cylindrical tubes. This permits determination of an effective complex viscosity and rigidity of the polymer solutions in porous media.

Measurements were performed over a wide range of frequencies and rates of flow. Data show major differences between the behavior of stiff molecules (xanthan gum) and flexible chains (polyacrylamide and polyethylene oxide). Xanthan gum exhibits shear thinning both in bulk and in porous media. Above a critical shear rate, polyacrylamide and polyethylene oxide show viscoelastic dilatant behavior, which may be due to a coil-stretch transition in the chain configuration.

Wednesday 10:10 Judicial FM10

SELF-SIMILAR FLOWS OF OLDROYD FLUIDS

Alparslan Oztekin and Eric Varley
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Exact solutions of the equations governing flows of an Oldroyd fluid are used to describe several technically important self-similar flows. The analyses include the effects of inertia, the dependence of the material parameters on temperature, viscous dissipation and thermal conduction. These solutions generalize those describing Blasius-Heimens flows at a forward stagnation point: they are applicable when local, rather than global, conditions control the flow.

As illustrations, the general solutions are used to describe stagnation point flows when the incident stream is at normal and at oblique incidence to the surface.

Wednesday 10:35 Judicial FM11

A NEW CLOSURE APPROXIMATION FOR THE FENE DUMBBELL KINETIC THEORY OF DILUTE POLYMERIC SOLUTIONS

G. Lielens, P. Halin, I. Jaumain, R. Keunings and V. Legat
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In the present paper, we address the closure problem for the most elementary non-linear kinetic model of a dilute polymer solution, known as the Warner Finitely Extensible Non-Linear Elastic (FENE) dumbbell model. In view of the closure problem, the FENE theory cannot be translated into an equivalent macroscopic constitutive equation for the polymer contribution to the stress tensor. In the first part of the paper, we demonstrate by means of stochastic simulations that the classical consistent pre-averaging approximation due to Peterlin (leading the FENE-P constitutive equation) can have a significant impact on the rheological response of the model, both qualitatively and quantitatively. We also show that an algebraic closure based on the second moment of the distribution function only is in general unable to accurately predict the behavior of FENE dumbbells. This is especially true in time dependent flows wherein the FENE theory gives rise to hysteretic stress evolution. In the second part of the paper, we present a new fourth-order closure approximation that is in markedly improved agreement with the FENE theory. This is demonstrated in a number of flow problems, including transient elongation.

Wednesday 11:00 Judicial FM12

STRESS BOUNDARY LAYERS IN VISCOELASTIC FLUIDS

Michael Renardy and Thomas Hagen
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Viscoelastic fluids, in particular the upper convected Maxwell fluid, develop pronounced stress boundary layers in high Weissenberg number shear flows with variable shear rate. Such boundary layers have been observed in numerical simulations of a number of flows, e.g. flow past a sphere and flow between eccentric cylinders. They also play a role in the reentrant corner problem. The lecture discusses the asymptotic analysis of such boundary layers and gives a comparison between different constitutive models. Specifically, it is shown that the thickness of the boundary layer scales like Ω^{-1} for the upper convected Maxwell model, $\Omega^{-1/3}$ for the PTT model and $\Omega^{-1/2}$ for the Giesekus model. Hence boundary layers with the latter two models are expected to be much less pronounced, which is in agreement with numerical observations.

Wednesday 11:25 Judicial FM13

A THERMOVISCOELASTIC CONSTITUTIVE MODEL FOR DESCRIBING THE MELT FLOW AND SOLIDIFICATION FOR AMORPHOUS POLYMERS

P. Shirkhande and J. M. Caruthers
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In polymer manufacturing operations the polymer is processed in the melt, cooled into the solid state, and then deformed as a solid, where the deformation history in the melt and the thermal history during solidification can strongly influence the mechanical response in the resulting solid. Although there are numerous constitutive equations that have been developed for melt rheology and for deformation of solids, in order to model the overall manufacturing operation a single constitutive equation is needed that can describe the nonlinear mechanical behavior in the melt, the effect of thermal and deformation history on the solidification process, and three-dimensional nonlinear deformation in the solid. A thermoviscoelastic constitutive equation has recently been developed (Lustig, *et al., J. Rheology*, 1996) that can accurately describe both the solidification process and the nonlinear mechanical behavior including yield in the solid state for amorphous polymers. This communication will report on the predictions of this thermoviscoelastic constitutive equation for steady and unsteady deformations in the melt. The constitutive equation only has one nonlinear parameter which defines the order of a generalized strain measure, where the other material functions are the linear viscoelastic properties that have all been determined via independent experiments. For steady shear flow the constitutive equation predicts a shear thinning viscosity and normal stress and for transient shear deformations the constitutive model predicts overshoot in stress growth, nonlinear stress relaxation, etc., where the predictions are in agreement with experimental data. The predictions of the constitutive equation for uniaxial and biaxial elongational viscosity will be reported and compared with experimental data. For large deformations the thermoviscoelastic constitutive equation is structurally similar to a rate dependent constitutive equation, where the relaxation times depend upon the configurational entropy.

Symposium BS
Rheology and Flow-Induced Structure of Blends and Solutions

Organizer: Jan van Egmond

Wednesday 9:45 Legislative BS9

STUDY OF FLOW-INDUCED STRUCTURAL CHANGES AND PHASE BEHAVIOR OF POLYMER BLENDS

Zhengyu Hong*, Montgomery T. Shawand Robert A. Weiss****
*Institute of Material Science and **Department of Chemical Engineering, U-136, University of Connecticut, Storrs, CT 06269

It has been controversial whether the flow-induced miscibility of polymer blends is due to thermodynamic effects or hydrodynamic effects. To elucidate the origin of the phenomena more clearly, we investigated the structural changes of phase domains in polymer blends under the influence of flow. Near-critical blends of poly(styrene-co-acrylonitrile) / poly(methyl methacrylate) which exhibit LCST type of phase behavior, have been studied. A reason for choosing this system was the proximity of the LCST to the Tg, thus allowing the sample to be quenched. A rheo-SALS (small angle light scattering) setup was used for probing the time-dependent structural evolution during shear. Quenched samples were examined with TEM and light microscopy to compare with the two-dimensional light scattering results. The blends were also subjected to pressure-driven flows and drag flows at very high stresses, and their morphologies similarly studied. Ascribing flow-induced phenomena to hydrodynamic effects will be discussed in terms of droplet breakup theory.

Wednesday 10:10 Legislative BS10

DEFORMATION OF INTERFACIALLY MODIFIED POLYMER DROPS

Leon Levitt* and Christopher W. Macosko**

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The influence of diblock copolymers (BCP) and interfacial reaction on polymer drop deformation inside a molten polymer matrix was studied by means of a parallel plate counter-rotating visualization apparatus with transparent disks (1). Copolymers were blended into PP, PS, and PE homopolymers which were used to form the drops. The addition of BCP significantly increases the amount of area that a deformed drop generates. This is important for decreasing the permeability of sheets and blow molded articles (2). Interfacial imidation reaction was also shown to be very effective in improving area generation in simple shear flow. Polymers with terminal amine groups (PMMA, PS and PA6) were coupled with random co-polymers containing maleic anhydride (PS-MA and PE-g-MA) which formed a branched graft copolymer at the interface. Reactive pairs produce at least twice as much area as non-reactive pairs. Crosslinking reaction at the drop and matrix interface immobilized the interface and no deformation was observed. 1. L. Levitt, C.W. Macosko, and S.D. Pearson, Polym. Eng. Sci., 36, 1647 (1996). 2. P.M. Subramanian, Polym. Eng. Sci., 25, 483 (1985).

Wednesday 10:35 Legislative BS11

RHEOLOGY AND DISPERSED PHASE MORPHOLOGY IN IMMISCIBLE BLENDS CONTAINING A LIQUID-CRYSTALLINE POLYMER

W.A. Kernick and N.J. Wagner

Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering, University of Delaware, Newark, DE 19716

The morphology of immiscible polymer blends is strongly coupled to the blend rheology, a consideration important in technological applications involving the processing of such polymer blends. Most scientific and theoretical investigations have focused on blend components with similar rheological properties. In this work we specifically examine the importance of *rheological contrast* on the rheology and morphology of immiscible polymer blends by using a liquid-crystalline polymer (LCP) as the dispersed phase. A new application of small angle neutron scattering enables the study of the morphology of micron-sized droplets of a LCP dispersed in a normal thermoplastic matrix under flow. The LCP inclusions are observed to be micron-sized spheres at rest, but deform into refined spheres, elongated ellipsoids, and sometimes fibers under shear flow. These phenomena, especially the onset of fiber formation, can be understood by considering the rheological contrast between components. The quantitative results are compared with current theoretical predictions to determine the importance of the LCP component rheology on the blend rheology and microstructure. Uniaxial elongation and recovery experiments are also to be presented for a thermotropic/thermoplastic blend. The importance of shear versus elongational flow on the blend morphology, as well as the rheological properties, is to be discussed.

Wednesday 11:00 Legislative BS12

VISCOELASTICITY AND FLOW BIREFRINGENCE OF BLOCK COPOLYMER SOLUTIONS IN THE FLUCTUATION REGIME

Timothy P. Lodge and Xiaoling Jin

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The oscillatory flow birefringence and viscoelastic properties of solutions of styrene-isoprene block copolymers have been examined, as functions of temperature and concentration. Emphasis is placed on the "fluctuation regime", i.e. in the disordered state but close to the order-disorder transition. The onset of fluctuation effects is clearly visible in the low frequency shear moduli, and results in a large form contribution to the birefringence. These results are in qualitative agreement with the predictions of Fredrickson, Larson, and Helfand, but the effects are considerably larger than anticipated by theory. The flow birefringence properties in the absence of fluctuation effects are also interesting, owing to the opposite signs of the stress-optic coefficients for the two blocks. These results are reasonably well described by the Rouse model, using a self-consistent set of parameter values.

Wednesday 11:25 Legislative BS13

A SPECTROSCOPIC STUDY OF FLOW INDUCED CONFORMATIONAL CHANGES IN POLY-L-LYSINE

Aravind Immaneni and Anthony J. McHugh
Department of Chemical Engineering, University of Illinois, Urbana, IL 61801

The effect of shear-flow, temperature and pH on secondary structure, conformational states, and phase stability of macromolecules with charged side groups is investigated using the techniques of modulated polarimetry and Laser Raman spectroscopy. Poly-L-lysine (PLL), a polypeptide which undergoes a helix-coil-β-sheet conformational transition, under varying conditions of temperature and pH, is used to understand the effect of shear-flow on the conformational stability of the macromolecule. Raman spectroscopy distinguishes effectively between the three conformations, through noticeable changes in the amide-I band. Evidence for flow-induced formation of β-sheet conformation at low temperatures and high pH is presented.

Wednesday Afternoon

Symposium FI
Melt Flow Instabilities and Wall Slip

Organizers: Shi-Qing Wang and John M. Dealy

Wednesday 1:30 Senate FI15

EFFECT OF MOLECULAR MASS ON THE WALL SLIP BEHAVIOUR OF MONODISPERSE POLYSTRYENE

Eric M. Weisser, Yoosup Park and Michael E. Mackay
Department of Chemical Engineering, University of Queensland, St Lucia Queensland, Australia

The parallel plate, torsional geometry was used to characterise the slip behaviour of four different molecular mass monodisperse polystryene (MDPS). The parallel plate technique has the advantage of being able to accurately measure behaviour at low stress levels, below what is usually available from either capillary or slit-die rheometry. We have also been able to perform measurements at high stress levels by utilising small gaps thereby reducing the familiar edge fracture phenomenon. The three molecular masses that were above the critical molecular mass for MDPS all showed slip at stress levels below the *critical stress* level of approximately 0.1 MPa. The slip velocity was a smooth function of the shear stress and does not appear to be double valued for the shear rates examined. The shear stress - shear rate behaviour of these three molecular mass polystryenes did asymptote towards the same constant value with increasing shear rate. The rate of approach increased with increasing molecular mass. For the MDPS below the critical molecular mass, neither a *critical stress* for slip to occur, nor the appearance of a stress asymptote, were observed. However, significant slip was observed at all shear rates examined.

Discussion will also be given for a second monodisperse polymer, polybutadiene, aimed at confirming the slip behaviour as a function of molecular mass observed with the MDPS.

Wednesday 1:55 Senate FI16

A HIGH PRESSURE SLIDING PLATE RHEOMETER AND ITS USE TO STUDY THE WALL SLIP AND RHEOLOGY OF AN ELASTOMER

F. Koran and J.M. Dealy
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A novel high-pressure rheometer has been developed to investigate the effect of pressure on the rheology and wall slip of polymer melts. The sliding plate fixtures are enclosed in a pressure vessel capable of operation at pressures of 10000 psi and 200°C. The sample is subjected to simple shear flow, and the resulting shear stress is measured locally using a shear stress transducer. This design eliminates flow inhomogeneities that occur in high-pressure capillary and slit rheometers. The effect of pressure on the viscosity and wall slip of a melt has been determined. The effect of a Teflon(TM) wall coating on the wall slip of polyisobutylene was also studied. Under atmospheric conditions, visual observations demonstrate that PIB samples undergo minimal shear deformation and nearly total slip at the wall. Increasing the pressure above 5000 psi decreases the wall slip significantly. The results for the Teflon(TM) interface suggest that both cohesive and adhesive wall slip can occur.

Wednesday 2:20 Senate FI17

WALL SLIP BEHAVIOR IN CAPILLARY FLOW: AN EXPLANATION FOR ABSENCE OF STICK-SLIP TRANSITION AND FLOW OSCILLATION IN VARIOUS POLYMER MELTS [1]

X. Yang and S.Q. Wang
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

We generalize our previous knowledge [2] of melt/wall interfacial slip behavior of linear polyethylenes (LPE) by studying capillary flow rheology of a representative group of other polymer melts including polystyrene (PS), polypropylene (PP), and low density polyethylene (LDPE). Like LPE, these melts appear to adsorb strongly on bare aluminum die walls. Unlike LPE melts, none of PS, PP and LDPE exhibits a measurable stick-slip transition. Nevertheless, these polymers do display some level of interfacial wall slip when the die wall is coated with a fluorocarbon elastomer (Dynamar). The magnitude of the wall slip diminishes at high stresses, as the effective degree of chain entanglement decreases due to chain deformation. Thus, these new results reveal the adverse effect of shear thinning on wall slip and explain why these polymers do not undergo melt flow instabilities such as flow oscillation and sharkskin-like extrudate distortions.

1. X. Yang and S.Q. Wang, manuscript in preparation for publication. 2. S.Q. Wang and P.A. Drda, Macromolecules, 29, 2627, 4115(1996)

Wednesday 2:45 Senate FI18

SLIP IN ENTANGLED POLYMER MELTS

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Department of Chemical Engineering, Texas A & M University, College Station, TX 77843

Wall-slip of a series of narrow molecular weight distribution polybutadienes (67,000 < M.W. < 247,000) was studied using a plane-Couette shear flow cell capable of measuring slip velocity and wall shear stress simultaneously. We find weak slip at low shear stresses, a stick-slip type of instability at intermediate stresses followed by macroscopic slip at high stresses. The experimental observations are compared with a scaling model proposed to describe polymer slip on weakly grafted surfaces.

Wednesday 3:35 Senate FI19

'FRACTURE' PHENOMENA IN SHEARING FLOW OF VISCOUS LIQUIDS

R.G. Larson*, L.A. Archer, and D. Ternet*****
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In startup of steady shearing flow of two viscous unentangled liquids, namely unentangled polystyrene and alpha-D-glucose, the shear stress catastrophically collapses if the shear rate is raised above a value corresponding to a critical initial shear stress of around 0.1-0.3 MPa. The time-dependence of the shear stress during this process is similar for the two liquids, but visualization of samples in situ and after quenching reveals significant differences. For alpha-D-glucose, the stress collapse evidently results from debonding of the sample from the rheometer tool, while in polystyrene, holes open up within the sample, similar to that occurring in cavitation. Similarities are pointed out between these phenomena and observations of "lubrication failure" reported in the tribology literature.

Wednesday 4:00 Senate FI20

EXTRUSION INSTABILITIES DRIVEN BY FLOW-INDUCED PHASE TRANSITIONS

M. Cloitre*, L. Leibler*, B. Ernst**

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Recently, we have observed and studied jet instabilities in polymer-like systems undergoing a flow-induced phase transition. The system under study consists of surfactants dissolved in water, which aggregate into wormlike micelles. The dynamical properties of these solutions exhibit strong analogies with those of flexible polymers ; this makes them very attractive to study highly non-linear situations. The extrusion of wormlike micelles is accompanied by most of the phenomena encountered during the extrusion of polymer melts : die-swell, delayed die-swell, and instabilities.

We shall focus on extrusion instabilities. One of the most interesting results is that the onset of instabilities coincides exactly with the appearance of a remarkable structuration of the flow associated with a flow-induced phase transition of wormlike micelles, above a critical flow rate. Birefringence observations reveal that a new phase appears near the capillary wall where the shear rate is the higher. This new phase is less viscous that the central visco-elastic core and acts as a lubricating layer. At this critical shear rate, the stress-flow rate curve reaches a plateau. After showing the sequence of instabilities which are observed when the shear rate is increased, we shall discuss two different mechanisms which can lead to hydrodynamic instabilities. To conclude, we shall discuss some possible connections with extrusion instabilities in polymers.

Wednesday 4:25 Senate FI21

WALL SLIP OF SHEAR THICKENING GUAR:BORATE POLYMER GELS

S. Subramanian and R.K. Prud'homme

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Gels formed by crosslinking dilute guar polysaccharide gels with borate ions create fluids with unique rheological behavior. At low rates of strain they are linear viscoelastic fluids displaying a single Maxwell fluid modulus and relaxation time. At higher rates of deformation they shear thicken. In the shear thickening state they slip at solid boundaries. Measurements of flow in Couette geometries and capillary geometries have been conducted. The relationship between these measurements and older measurements by Kraynik and Schowalter who used these fluids as model fluids in their study the slip of polymer melts will be presented. For these fluids slip is shown to occur when either a Weissenberg number is greater than one or the Deborah number is greater than one.

Wednesday 4:50 Senate FI22

RHEOLOGY AND EXTRUSION PROPERITES OF THE NATURAL RUBBER COMPOUNDS

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The rheological properties of raw natural rubber and natural rubber compounds are investigated before and after extrusion process. The raw natural rubber used in experiments has been masticated. From these masticated raw natural rubbers the compounds with carbon black have been prepared. The fifteen samples have been prepared by Box-Hunter statistical scheme, where concentration of two special process additives and time of mastication have been varied. The concentrations of the two special process additives have been changed, additive A from 0 to 4 phr and additive S from 0 to 5 phr. The time of mastication varies from 0 seconds to 240 seconds. Three types of measurement's procedure have been used for rheological characterisation of the samples. The shear steady state measurements on capillary rheometer, GOTTFERT Rheograph 2001 with the capillary of 10 mm in length and 1 mm in diameter at 100YC. Oscillation measurements have been made by RPA 2000 (Rubber Process Analyser 2000). The RPA 2000 operates under shear oscillatory condition. The third type of the experiments used in simple extension measurements made on universal testing machine Instron 1185. The natural rubber compounds have been extruded on laboratory extruder with Garvey type die. Results of the measurements are analysed by empirical models, which provide the yield stress at all natural rubber compounds and raw natural rubber. The special process additives that are added into compounds decrease the viscosity and have the function of softeners. The softeners increase free volume in the compounds. The free volume enables segments of the chains to change the position in the system and thus causes orientation of chains in the direction of flow. The extrusion process is analysed by rheological measurement before and after extrusion. The effect of the two special additives and time of mastication on extrusion process are studied for natural rubber compounds with carbon black.

Symposium LC
Liquid Crystals: Structure and Rheology

Organizers: Davide A. Hill and Lynn Walker

Wednesday 1:30 Executive LC1

FLOW-INDUCED STRUCTURES FORMING DURING THE SHEAR RELAXATION OF LIQUID CRYSTALLINE POLYMERS

P. Harrison and P. Navard

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The band texture which occurs following the cessation of flow in most liquid crystalline polymers is an intriguing phenomenon. We look once more at its properties, in particular its resistance to shear deformation. The idea is to shear the liquid crystalline polymer while the band texture is present and to determine whether this flow destroys the texture. In addition, another goal is to measure the viscosity of the liquid crystalline polymer during the existence of the band texture. Both lyotropic and thermotropic liquid crystalline polymers will be used in this study.

Wednesday 1:55 Executive LC2

TEXTURE AND LIGHT SCATTERING FROM NEMATIC SOLUTIONS OF A RODLIKE POLYMER DURING CREEP AND RECOVERY

S. Vijaykumar, G. C. Berry and Z. Tan

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Textural patterns and small-angle light scattering (SALS) during shear deformation in a parallel-plate torsional rheometer under constant torque (creep) and following removal of the torque (recovery).will be discussed for nematic solutions rodlike polymers. Results will be presented for solutions of poly(1,4-phenylene-2,6-benzobisthiazole), PBZT, complemented by a more limited study of solutions of poly(1,4-phenylene terephthalamide), PPTA. Behavior will be discussed for samples in a defect-free state prior to creep or filled with defects of various scales (including line defects). Three regimes of flow behavior are observed: (1) For recently small deformations (including very slow flows for a long time), the sample is turbid, with a diffuse scattering pattern; (2) For a certain intermediate range of deformation and deformation rate, the scattering pattern develops lobes orthogonal to the flow direction, and the texture may reveal striations in flow along the flow direction; and (3) For some cases, under high deformation and deformation rate, the sample appears to be texture free, with little observable SALS, but does not exhibit the birefringence expected for a well-aligned monodomain. The possibility will be discussed that differences in the Frank curvature elasticities for splay and twist distortions for the PBZT reported elsewhere for nematic solutions may play a role in textural patterns observed during creep and recovery for certain ranges of L and concentration.

Wednesday 2:20 Executive LC3

CONOSCOPIC OBSERVATIONS OF SHEAR INDUCED ROTATIONS IN NEMATICS

David Boudreau, Richard Stein, Peter Lillya, and H. Henning Winter

University of Massachusetts, Amherst, MA 01003

Monodomains of liquid crystalline nematics were prepared between two parallel plates to study the effect of initial molecular orientation on shear. The director was initially aligned in the shear plane with a variation of alignment

angle ranging from parallel with the shear direction, to parallel with the vorticity direction. The change in orientation upon shear was measured by conoscopy which was able to follow both the rotation in the shear plane (ϕ) and the rotation out of the shear plane (θ). The most recent experiments have focused on low molecular weight nematics such as 5-CB and MBBA. Experiments with thermotropic polymers are in progress.

Wednesday 2:45 Executive LC4

TIME-TEMPERATURE AND TIME-CONCENTRATION SHIFT FACTORS FOR A SEMI-FLEXIBLE LIQUID CRYSTAL POLYMER

J.J. Magda*, C.-M. Huang*, and R.G. Larson**

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It is generally believed that liquid crystal polymers do not obey time-temperature equivalency. However, here we show that time-temperature shift factors, based on steady flow measurements, provide meaningful probes of viscoelastic time scales in liquid crystalline hydroxypropyl cellulose. Surprisingly, at fixed polymer concentration, time-temperature shift factors based on the Region II viscosity value and on the location of the inflection point in the N1 flow curve are essentially identical. Furthermore, by looking at the temperature and concentration dependence of the shift factor, one can identify changes taking place in the nematic state which are too subtle to be seen via DSC measurements.

Wednesday 3:35 Executive LC5

MESOSCOPIC MODELS FOR LIQUID CRYSTALLINE POLYMERS

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The model of Larson and Doi [J. Rheol. 35, 539 (1991)] is discussed in detail, and we focus on a discrepancy regarding the Leslie-Ericksen torque balance, which requires an additional molecular field term. It is shown where the additional terms appear in the resulting equations for the mesoscopic stress tensor and the order parameter tensor. We suggest some criteria for the construction of mesoscopic (textured) models, and a specific two-dimensional example based on the Leslie-Ericksen theory is presented in the form of a mesoscopic Smoluchowski equation. It is shown that the second moment of the equation corresponds formally to the structure of the Larson-Doi theory, and it is further demonstrated how a judicious choice for the form of the molecular field will produce the texture term originally suggested by Larson and Doi.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC073-76SF00098.

Wednesday 4:00 Executive LC6

CLOSURE APPROXIMATIONS FOR THE DOI THEORY IN SIMULATING COMPLEX FLOWS OF LCPS

Jimmy Feng, Charu V. Chaubal and L. Gary Leal

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In simulating the flow behavior of liquid crystalline polymers, direct solution for the molecular orientation distribution function in the Doi theory is cumbersome. An alternative is to reduce the Doi theory, by using a closure approximation, to a theory about the second moment of the orientation distribution function. A number of closure models have been proposed in the literature. The work to be presented studies the performance of closure approximations in homogeneous and unsteady non-homogeneous flows. The objective is to identify one or more closure models that are best suited for numerical computations of complex flows. By using finite element computations, we compare the predictions of (1) the quadratic closure; (2) the quadratic closure with finite molecular aspect ratios; (3) the Hinch-Leal closure and (4) a newly proposed closure based on the Bingham distribution function. The main difference among various models is in the prediction of director tumbling in near-

shear flows. The choice of closure models becomes less significant in non-homogeneous flows containing regions of rotational, shear and extensional flows.

Wednesday 4:25 Executive LC7

GENERALIZED MODELING OF NEMATIC LIQUID CRYSTALLINE FLOWS

Tomohiro Tsuji and Alejandro D. Rey
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Flow modeling of liquid crystalline materials is performed using a theory that takes into account short range and long range order elasticity, and viscous flow effects. The present theory is shown to be fully compatible with the well-known Leslie-Ericksen and Doi theories, and thus fills the parametric gap where these classical theories are inapplicable. Predictions for simple shear flow are presented in the form of a rheological phase diagram, span by the ratio of short to long range elastic forces and the Ericksen number. The rheological phase diagram is divided into four regions corresponding to the flow orienting the planar flow-orienting modes in the presence of fixed planar orientation at the bounding surfaces. The director modes in the four regions are: (i) elastic-driven steady state, (ii) tumbling-wagging mixed mode, (iii) wagging state, and (iv) flow-driven steady state. The transitions between the four regimes are characterized mathematically, as well as in terms of the basic physical mechanisms. Finally the mechanism that allows tumbling director modes in the presence of fixed director orientation at the bounding surfaces during shear flow is identified by direct observation of the solutions to the presented model. Thus the apparent contradiction of director rotation in the presence of static boundary orientation is clearly resolved by a model that includes the classical theories of liquid crystals.

Wednesday 4:50 Executive LC8

MOLECULAR ORIENTATION IN CERTAIN NONLINEAR FLOWS OF LIQUID CRYSTAL POLYMERS

Qi Wang
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We study the molecular orientational patterns in Poiseuille flow and Couette flows of liquid crystal polymers using a Doi type kinetic theory formulated by Bhave et al. with certain closure approximations. We focus on the orientational patterns of the steady states across the channel of the flow fields as well as the variation of the major director in the flow. Stability of the steady states will be commented as well.

Symposium FM
Non-Newtonian Fluid Mechanics

Organizers: Gary L. Leal and Frank Baaijens

Wednesday 1:30 Judicial FM14

RELAXATION AND EXTENSION OF DILUTE POLYMER SOLUTIONS IN A FOUR-ROLL MILL WITH ABRUPT CHANGES IN THE ROLLER SPEED

Jimmy Feng and L. Gary Leal
Department of Chemical Engineering, University of California, Santa Barbara, CA 93106

The reaction of polymer solutions to abrupt changes of the strain-rate in an extension-dominated flow is manifest of the behavior of the polymer chains. In our laboratory systematic experiments on sudden changes of flow are being carried out using two-roll and four-roll mills. Because of the coupling between fluid flow and polymer stretching, a sudden change of roller speed generates a rather complex flow history at the stagnation point where flow birefringence is measured. The objective of the numerical simulations to be presented is to complement and elucidate the experimental measurements. We use the Chilcott-Rallison model to represent Boger fluids, and solve the coupled equations for fluid flow and polymer stretching using a finite element method. Results show that when

the roller speed is suddenly changed, the strain-rate at the stagnation point undergoes an overshoot and an undershoot before approaching the steady state. The polymer stretching (or birefringence) may also have undershoots and overshoots. Away from the stagnation point, the velocity and strain-rate oscillates during the transient. In particular, the polymer solution exhibits considerable recoil after the rollers are suddenly stopped.

Wednesday 1:55 Judicial FM15

A NUMERICAL SCHEME FOR SOLVING VISCOELASTIC FLOW PROBLEMS

S. Acharya*, J. Padovan and A. I. Leonov***

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A general purpose stable and convergent algorithm for the solution of viscoelastic flows is developed. Specific application of this code is demonstrated for a standard benchmark problem, the four-to-one abrupt 2D steady, inertialess and axisymmetric contraction flow. The behavior of the viscoelastic material, polyisobutylene (PIB) is approximated by a stable nonlinear multimode constitutive equation. A Finite-Element method is utilized to solve the set of continuity and momentum equations along with a Galerkin solver for the set of evolution equations. The finite element discretization has 6 noded triangular elements for the velocities (2 for each space directions) and 3 noded triangular elements for the pressure. The evolution equation is solved using two different methods. One employs a semi-implicit iterative method and another involves a Newton-Raphson type method. The two schemes are compared for their numerical stability, convergence and the limiting Deborah number. A dynamic storage is used to exploit the sparse matrices involved in the discrete formulation. Also, a scaling approach is utilized to extend the calculations to multiple modes. This reduces the number of computations corresponding to the multimodal constitutive equation. The results are compared with experimental observations for flow of PIB through a die with a rectangular cross section.

Wednesday 2:20 Judicial FM16

COMPUTATIONAL MODELING OF VISCOELASTIC DRIVEN LID CAVITY FLOWS

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In this study we have used convergent and highly accurate adaptive DEVSS/hp-Galerkin and DEVSS/hp-SUPG finite element techniques to model the effect of fluid elasticity on the flow kinematics and the stress distribution in driven lid cavity flows. Specifically, we have used asymptotic techniques to investigate the nature of the stress singularity near the intersection of the moving and stationary walls. In addition a number of simulations in cavities of various aspect ratios using the Oldroyd-B, Chilcott-Rallison and FENE-P constitutive models have been conducted. In these simulations we have used a number of boundary conditions in the vicinity of the points where the moving and stationary walls intersect (i.e., no-slip, small leakage, and slip based on the magnitude of the stress tensor or an assumed slip velocity) to make the stress field square integrable as well as investigating the influence of various boundary conditions on the stress distribution near this intersection. The effect of shear thinning of viscosity and first and second normal stresses on the flow structure is also examined by utilizing the multimode Giesekus constitutive equation. In turn, the computed results are compared with existing experimental results to check their accuracy as well as determining the required constitutive complexity for obtaining a quantitative comparison between experimental and computational results.

Wednesday 2:45 Judicial FM17

NUMERICAL AND EXPERIMENTAL ASSESSMENT OF VISCOELASTIC FLOWS OF POLYMER SOLUTIONS AND MELTS

Frank P.T. Baaijens, Jeroen F.M. Schoonen, Gerrit W.M. Peters and Han E.H. Meijer

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The numerical and experimental assessment of viscoelastic flows remains a challenging research area, requiring state-of-the-art numerical methods and experimental techniques. In particular the performance of numerical methods

has improved significantly over the past decade, and a number of different numerical techniques developed at various research groups generate reproducible results for a variety of benchmark problems. In this presentation, critical research issues of the numerical analysis of viscoelastic flows are reviewed and recent progress to resolve these are addressed. As a result of the improved performance of numerical methods, confrontation of numerical and experimental results becomes feasible, and the performance of various constitutive models in complex flows may be addressed. In this study, the two and three dimensional flow of polymer solutions and melts around a confined cylinder, planar contraction and opposed jets device is investigated. The inability of existing constitutive models (i.e. PTT and Giesekus) to fully predict the experimentally observed stress distribution, in particular during elongational flows, is demonstrated. Based on these results a new class of constitutive models is proposed that does capture the complicated stress fields in complex flows.

Wednesday 3:35 Judicial FM18

THE MOTION OF SMALL PARTICLES IN VISCOELASTIC BOGER FLUIDS

H. Binous and R. J. Phillips
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We are performing dynamic simulations of particle motion in bounded and unbounded viscoelastic fluids. The viscoelastic nature of the fluid is incorporated by direct calculation of hydrodynamic interactions between the particles and Finite-Extension- Nonlinear-Elastic (FENE) dumbbells, and hence the simulations include three-dimensional and time-dependent effects. The rheology of the suspension of dumbbells without suspended particles is similar to that predicted by the Chilcott- Rallison model, and allows direct comparison with experiments performed in constant- viscosity, elastic (i.e., Boger) fluids. Simulations of the sedimentation of one sphere show an initial decrease in the drag coefficient followed by a strong increase as the Deborah number increases. A transition to time-periodic behavior is also apparent at high enough Deborah numbers. Results for the motion of two spheres and non-spherical particles show interesting deviations from the corresponding low- Reynolds-number Newtonian case: two sedimenting spheres move together or apart depending on the initial configuration, and non-spherical particles rotate so that the particle velocity is in the direction of the major axis. To examine wall effects, we have extended the method by using the method of images to obtain the no-slip boundary condition on planar surfaces. Spheres falling near vertical walls are shown to move toward the wall and exhibit anomalous rotation, and a sphere suspended in a pressure driven flow through a channel moves away from the wall and towards the channel center. The above simulation results are in good qualitative agreement with experimental observations that have been reported in the literature, and provide valuable insight into the effect of elasticity on particle motion in viscoelastic fluids.

Wednesday 4:00 Judicial FM19

EFFECT OF THE RHEOLOGY ON POLYMER-INDUCED DRAG REDUCTION

R.Sureshkumar*, Costas D. Dimitropoulos and Antony N. Beris****
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This work provides a theoretical demonstration of the polymer-induced drag reduction phenomenon through direct numerical simulations of a fully turbulent viscoelastic channel flow, using, for the first time, an independently evaluated rheological model (FENE-P). A preliminary account of this work has appeared in Phys. Fluids, vol.9, 743 (1997).

The simulations have shown a significant reduction in the streamwise vorticity implying the inhibition of the quasi-streamwise ``roll'' vortices near the wall which are important in the production and sustenance of turbulence. In particular, the presence of viscoelasticity results in a reduction of the streamwise vorticity generated by the vortex stretching mechanism. This has further been connected with the capability of the polymer chains to extend in response to transient (local) extensional flow fields generated within the flow domain.

An analysis of further simulation results in the light of modifying the rheological properties of the FENE-P dumbbell model by employing various parameter values, has indicated that the onset of drag reduction depends primarily on the Weissenberg number. On the other hand, an increase in the extensibility of the model was found to lead to a significant increase in the ultimate drag reduction achieved at higher Weissenberg numbers.

Wednesday 4:25 Judicial FM20

FLOW SIMULATIONS USING A SINGLE VECTOR APPROXIMATION TO REPTATION MODELS WITH CHAIN STRETCH

Johan Remmelgas and L. Gary Leal
Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106

Recent studies of viscoelastic flow by numerical simulations have focused largely on constitutive models derived from FENE dumbbell based models. These models are suitable primarily for dilute polymer solutions, such as Boger fluids. Among their properties is a strong tendency to undergo strain-rate hardening, i.e. an increase in the solution viscosity with increasing strain rate for any strong flow (which for 2D flows means that the rate of strain exceeds the vorticity). The strain-rate hardening of these models results in a decrease in the extensional strength of the flow due to large polymeric stresses, in qualitative agreement with experiments on dilute, **as well as** entangled polymer solutions. Models describing entangled polymer systems, on the other hand, show strain-rate softening due to chain orientation at intermediate strain rates, with strain-rate hardening occurring only at strain rates large enough that the Weissenberg number based upon the Rouse time exceeds unity. Since the models describing entangled polymer solutions exhibit strain-rate softening at intermediate shear rates, it is not clear that they can accurately predict the decreased extensional strength of the flow observed experimentally for entangled polymer solutions. The present paper focuses on a numerical study of the viscoelastic flow in a two-roll mill using a constitutive equation based upon a vector approximation to recently developed reptation models that include chain stretching. The constitutive equation employed exhibits strain-rate softening at intermediate strain rates and strain-rate hardening at large strain rates, and the paper thus aims to understand the behavior of entangled polymeric solutions in a nontrivial fluid mechanics context. In particular, the role played by the strain-rate thinning behavior at intermediate shear rates versus the strain-rate hardening at large shear rates will be addressed.

Wednesday 4:50 Judicial FM21

SIMULATIONS OF FLOWS OF POLYMER MELTS BY AN UNSTRUCTURED CONTROL VOLUME METHOD

R. I. Tanner, X. Huang, N. Phan-Thien
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An unstructured control volume method is implemented for the Upper-Convected Maxwell (UCM) and the Phan-Thien-Tanner (PTT) models. The code is validated in simple flows, where analytical solutions are available. We simulate the complex flow of polyisobutylene solutions in a channel past a right circular cylinder symmetrically placed. A good comparison with the experimental results of Dhahir and Walters (1989) and Baaijens et al. (1995) is obtained. The key features of the method are the unstructured mesh, which is lacking in standard control volume methods, and a self-consistent false diffusion and boundary stresses integration techniques, which allow stable solutions to be obtained at high Weissenberg numbers.

Symposium BS
Rheology and Flow-Induced Structure of Blends and Solutions

Organizer: Jan van Egmond

Wednesday 1:30 Legislative BS14

VISCOELASTIC JETS OF POLYMER SOLUTION DISCHARGING FROM A CAPILLARY

R. Y-C. Liang, A. Oztekin, and S. Neti
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Viscoelastic jets of Boger fluid discharging from a vertical, circular, long capillary are studied photographically. Detailed structure of the interface has been analyzed using digital image analysis. The instantaneous free surface has been reconstructed allowing quantitative study of the evolution and dynamics of the free surface.

The profiles of the jet vary strongly with flow rate (Deborah number, De). At small values of De, necking of the jet similar to that of Newtonian jets is observed, while at larger Deborah numbers the jet exhibits die-swell. Near the exit, the radius of the jet increases monotonically with Deborah number.

At low flow rates, the surface of the jet is smooth, while the free surface is distorted as a result of instabilities at higher values of De. The instabilities manifest themselves into a uniformly spaced structure around the free surface of the jet. These are observed as vertical stripes laid along the jet. The critical value of De for the onset of the instability is measured, and the spatial structure of the surface distortion is determined quantitatively from gray scale information of images. The number of stripes is measured to be about 30 around the free surface near the exit, and is a weak function of De. At very high Deborah numbers, the flow becomes time dependent near the capillary exit, and the number of stripes at a given axial location varies with time.

Wednesday 1:55 Legislative BS15

GEL-INHIBITOR ASSISTED DISSOLUTION PROPERTIES OF THE ELECTRICALLY CONDUCTIVE POLYMER POLYANILINE

Dali Yang, Hsing-Lin Wang and Benjamin R. Mattes
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Progress towards realizing the commercial potential of polyaniline has been slow to develop since it is notoriously difficult to process into useful geometries by conventional engineering methods. Polyaniline solutions prepared even at dilute concentrations (< 5% w/w) always tend to form gels in very short time. This problem becomes more pronounced at the practical concentrations required for solid fiber spinning (> 20% w/w). We have discovered that the between polymer chain interactions can be minimized by adding a certain class of secondary amine compounds, e.g., 2-methyl-aziridine, to concentrated dispersions of emeraldine base (EB) in N-methyl-2-pyrrolidinone (NMP). We call these additives gel inhibitors (GI) since they serve to sequester the imine nitrogens from further interaction with the next nearest neighboring secondary amine of the polymer repeat unit. This interaction greatly prolongs the functional life of the solution. Gelation and stability studies of highly concentrated high molecular weight EB/NMP/GI (15-20wt%) solutions were investigated by viscosity measurements. Depending on the GI/EB/NMP volume ratios selected for study, long gelation times (up to 40 hours) were obtained. This achievement permits the formation of high quality fibers at an industrially meaningful scale. We have determined equilibrium state conditions for selected EB/NMP/GI solutions. We conclude that gel-inhibitors exert their beneficial effects by competing with the 3between chain² hydrogen bonding molecular interaction sites. Additionally, such systems were studied in the dilute regime by measuring the intrinsic viscosity of solutions as a function of varying EB/NMP/GI volume ratios. It was found that intrinsic viscosity, and thus, the interaction between solvated polymer chains decreases with increasing GI/EB volume ratios. We describe this anomalous solution behavior in terms of enhanced Hansen solubility parameters which may be manipulated to approach theta conditions for the polymer.

Wednesday 2:20 Legislative BS16

THE EFFECT OF CONCENTRATION, TEMPERATURE AND MOLECULAR WEIGHT ON THE DYNAMICS OF RIGID-ROD MOLECULES IN SEMI-DILUTE SOLUTIONS

Aravind Immaneni and Anthony J. McHugh
Department of Chemical Engineering, University of Illinois, Urbana, IL 61801

The dynamics of rigid-rod like molecules are studied using rheo-optical techniques. Measurements of flow birefringence as a function of shear rate, are utilized to understand the scaling behavior of rotational diffusivity with respect to concentration and temperature. The concentration scaling exponent increases with increasing concentration, and the scaling laws are valid in narrow concentration windows. The Doi-Edwards (DE) scaling law $D_r \sim c^{-2}$, holds at very high concentrations ($cL^3 > 150$). The concentration scaling exponent decreases dramatically with increasing temperature at concentrations, $cL^2d < 1$. Scaling of rotational diffusivity, with respect to temperature and solvent viscosity in the semi-dilute regime, does not follow the predictions of DE theory (and related caging ideas). On the contrary, a model proposed by Fixman was found to explain both the temperature and concentration dependence of the rotational diffusivity.

Wednesday 2:45 Legislative BS17

OPTICAL RHEOLOGY OF WORMLIKE MICELLES

Karl Rufener, John van Zanten, and Denis Wirtz
Chemical Engineering Department, Johns Hopkins University, Baltimore, MD.

Wormlike micelles provide a unique model system made of living polymers, which dynamically break and recombine at various rates. There is a large body of work that has focused in extracting the different time scales associated with this complex self-assembling system using mechanical rheometry. But at high frequencies there is a lack of experimental data due to various system and instrument limitations. Moreover, it has been shown that small strains can dramatically affect the structural and associated rheological properties of these systems. We have used a non-invasive optical technique, diffusing wave spectroscopy (DWS) to probe the many time scales which describe the diffusive motion as well as the breaking and recombination rates of wormlike micelle systems. In order to compare our optical measurements with more published rheological measurements, we use the model semi-dilute solution of water / cetyltrimethylammonium bromide (CTAB) / Sodium Salicylate (NaSal) mixed with a small concentration of optical probes. The non-invasive nature of the DWS combined with its ability to extract high frequency rheological data from autocorrelation function measurements allows for a stringent test of current dynamic theories that describe living polymer systems. At higher frequencies not reachable by mechanical measurements, the micelle breaking and reformation time scales are easily probed using DWS. The water-CTAB-NaSal micelles are probed at various salt concentrations along with a limited pH range, and low end frequency results are compared directly with mechanical rheological data.

Symposium NP
Novel Polymer Systems

Organizers: Michael Mackay and Anthony J. McHugh

Wednesday 3:35 Legislative NP1

PARTICLE-TRACKING MICRORHEOLOGY OF A CONCENTRATED DNA SOLUTION IN THE PRESENCE OF TOPOISOMERASE TYPE II

Denis Wirtz and Thomas G. Mason
Chemical Engineering Department, Johns Hopkins University, Baltimore, MD.

During the anaphase of the cell cycle, spindles pull daughter chromosomes apart. The force necessary to execute this task would be much too large in the absence of enzymes called topoisomerase type II. These enzymes catalyze the dynamic cutting and recombination of the double stranded DNA and effectively render the DNA molecule "phantom-like" (able to cross itself). The presence of these enzymes allows the DNA molecule to relax both by reptation and constraint release. Current rheometers require large volumes of samples to reach their level of sensitivity and shear fragile DNA solutions. We study the enhanced relaxation of DNA molecules in solution in the presence of topoisomerase type II by using a novel high-resolution video-microscopy technique, which avoids the limitation of mechanical rheometers. This technique consists in monitoring the thermally excited motion of a single small bead imbedded in the DNA solution. From the measured mean-square displacement, we extract both loss and elastic moduli of the DNA solution. Both the mean-square displacement and the crossover frequency at which loss and elastic moduli are equal are shown to increase with topoisomerase concentration, which is the signature of enhanced relaxation due to the elimination of topological constraints by the enzyme. This study answers some fundamental issues in polymer physics since the constraint release mechanism of relaxation is enhanced with respect to the reptation mechanism of relaxation.

Wednesday 4:00 Legislative NP2

RHEO-OPTICAL STUDY OF ELASTOMERIC POLYPROPYLENE

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Elastomeric homopolymer polypropylene (EHPP) synthesized from an unbridged metallocene catalyst is studied via mechanical rheometry, visible polarimetry, and infrared dichroism. The elastomeric nature of EHPP is presumed to arise from a multiblock structure of isotactic (iPP) and atactic (aPP) polypropylene blocks. At lower temperatures stereoregular blocks of iPP are able to crystallize while stereoirregular blocks of aPP remain amorphous. Connectivity inherent in a block structure allows iPP crystallites to be tethered together by aPP segments. The rheological role of connectivity is studied by comparing the flow behavior of EHPP with that of iPP/aPP homopolymer blends possessing the same isotacticity as EHPP. Small amplitude (0.5% strain), oscillatory mechanical measurements on crystallized samples (T=25°C) show that the polymer chain length between constraints is shorter for EHPP than for the homopolymer blends. Large amplitude (100% strain), step-shear experiments carried out on crystallized samples show that EHPP does not completely relax from an applied strain and that a cross-linked network has formed. Imperfections in the network structure are revealed by optical experiments that show a fast, partial relaxation of the applied strain. In addition, double step-strain experiments leave irreversible anisotropies in the elastomeric material. In contrast, crystallized homopolymer blend samples are able to completely relax after the application of a step-shear. As EHPP is heated above T_{melt} (~140°C), evidence of a rheological network disappears and the sample behaves like the polymer blends with a terminal relaxation time that scales with the molecular weight of the species.

Wednesday 4:25 Legislative NP3

CARBON-BLACK NETWORK CREATION IN POLYMERS: NEW RESULTS

V.Bouda* and J.Mikesova**

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The dynamical modulus, electrical conductivity of alternating current (AC), and permittivity of carbon-black (CB) - filled low density polyethylene (LDPE) was measured as function of time at a temperature higher than the melting temperature of matrix polymer. At a characteristic time (delay time t°), as a result of the agglomeration of CB particles, the network of CB particles were formed and a percolation-like transition was observed; i.e. the modulus and AC conductivity suddenly increased and the permittivity suddenly decreased. The delay time t° increases with the weight percent of CB. It was also found that t° increases as the temperature of annealing decreases. The delay time t° decreases with an external alternating electrical field. The experimental values of t° were compared to the calculated values using a model in which we suggest there are three types of CB particles in the matrix polymer after the mixing process: the CB particles which contribute to the conductive networks, the reversible disintegrated CB particles, and the irreversible disintegrating CB particles. The delay time t° is interpreted as a relaxation of potential energy of electrostatic repulsion forces between the reversible disintegrated CB particles.

Wednesday 4:50 Legislative NP4

RHEOLOGY OF DENDRITIC POLYMERS

M.E. Mackay*, P.J. Farrington, C.J. Hawker*** and J.M.J. Frechet******
*Department of Chemical Engineering, The University of Queensland 4072, Australia;
**Nanyang Technological University, Singapore; ***IBM Almaden Laboratory, U.S.A.;
****Department of Chemistry, University of California, Berkeley, U.S.A.

Dendritic polymers have an unique structure which has great promise for a variety of applications. In this presentation a brief overview of the structure and properties of dendritic polymers is first given. It is found the glass transition temperature as a function of molecular mass is described by a simple relation regardless of end group type. The end group does, however, influence the absolute magnitude of the glass transition temperature.

The melt rheological properties were measured in steady and dynamic shear for dendrimers based on Poly(benzyl-ether). Interestingly, the terminal melt viscosity can be adequately described by free volume theory. It is shown that, perhaps, this theory is too robust and dendrimers may not follow this type of theory. The dynamic shear properties are compared to the Rouse model modified for a polymer melt. This theory also seems to describe these rheological properties.

Thursday Morning

Symposium BL
Biological Systems

Organizer: Charles Shoemaker

Thursday 8:05 Senate BL1

MAGNETIC TRAPPING AND MICROMANIPULATION OF BIOLOGICAL MACROMOLECULES

Charbel Haber and Denis Wirtz
Chemical Engineering Department, Johns Hopkins University, Baltimore, MD.

A magnetic manipulator is designed to control the position and velocity of a superparamagnetic microsphere. The magnetic bead is attached to a single DNA macromolecule, allowing for the characterization of its transport properties. Transport properties of macromolecules are generally measured by techniques that yield ensemble averages with no direct information on the local conformation of the probed molecules. Our new technique measures instead the transport properties of an individual polymer. DNA molecules, connected to magnetic beads via biotin-streptavidin link, are labeled with fluorescent dyes. The solution containing the end-tethered DNA is loaded onto a microscope cell and subjected to a magnetic field gradient. The migration of DNA is visualized using an inverted microscope equipped with an image-intensified video camera. The resulting recorded images are processed and analyzed. The measured steady-state velocity is plotted against the magnetic force yielding the friction coefficient of an individual DNA molecule. The effects of DNA length, the pH and ionic strength of the medium, as well as the transport of DNA in confined geometries will be discussed. This novel and versatile technique provides a powerful tool to study numerous and diverse problems in the physics of macromolecules.

Thursday 8:30 Senate BL2

MICRORHEOLOGY OF THE CELL

S. Yamada*, S.C. Kuo, and D. Wirtz***
*Chemical Engineering Department, Johns Hopkins University, Baltimore, MD. ; **Biomedical Engineering Department, Johns Hopkins University, Baltimore, MD.

This paper will present the first direct measurement of the rheological properties of the cytoskeleton of a living cell. Under external stimulus, such as an electric field or a shear flow, a cell changes its shape and motility. By monitoring the thermally-excited motion of microorganelles within the cell using a quadrant-detection technique, we monitor their mean-square displacement with nm spatial resolution and ns time resolution. From these measurements, we extract the local elastic and loss moduli at different positions within the cell simultaneously. Using optical tweezers which manipulate a protein-coated polystyrene sphere, we create an external mechanical stimulus to the cellular membrane, which creates a cascade of spatially-dependent and time-dependent rheological changes within the subcellular cytoskeleton. This paper will also discuss our application of this novel technique to probe subcellular changes during cell motion on a substrate as monitored at both the leading edge and the trailing edge of the cell.

Thursday 8:55 Senate BL3

OSCILLATORY PRESSURE-TO-FLOW RELATIONS AND VISCOELASTICITY OF HUMAN BLOOD IN TUBES AND IN POROUS MEDIA

George B. Thurston
Rheology Laboratory, Department of Mechanical Engineering ; The University of Texas at Austin; Austin, TX 78712

Blood flowing in the human circulation encounters a variety of vessel sizes and complex geometries. While the red blood cell dominates the rheological properties, these properties differ in vessels that are large compared to the dimensions of the red blood cell from those in small vessels. In addition, red cell aggregation tendency and deformability play pivotal roles in blood rheology. The complex vascular geometry of the smaller vessels can be approximated by a porous medium in that the plenum approaches the dimensions of the red cell and the blood is subjected to both shear and extensional stress. Oscillatory pressure-to-flow measurements in a large tube and in a porous medium show significant differences in viscoelastic properties. These in turn are related to cell aggregation and deformation. In the small spaces of porous media, cell aggregation effects are diminished and cell deformability effects become more evident. It is only through the viscoelastic properties that the combined effects of aggregation and deformability can be seen.

Thursday 9:20 Senate BL4

A FRACTAL ANALYSIS OF THE ERYTHROCYTE SEDIMENTATION RATE

Lawrence C. Cerny and Elaine R. Cerny
Cernyland of Utica, 6849 Barbara Drive, Huber Hts., OH 45424-3467

The use of fractal geometry and scaling techniques has been quite effective in modeling biological systems and processes. These methods are applicable because of the vast range of sizes spanning many orders of magnitude. The biological fluid, blood, fits into this category since it contains a wide spectrum of sizes in its components such as water, salts, proteins and red cells. Several years ago, a model system for the erythrocyte sedimentation rate (ESR) using "cheerios" to represent the red cells introduced the fractal dimension for this process (Biorheology 25, 85-04, 1988). In this presentation, an attempt is made to determine the fractal geometry for blood in clinical situations. The systems to be discussed include tube geometry, temperature, blood disorders and cell concentration. Model systems using fixed cells serve as a database because there are no cell-cell interactions. The results will be compared with a semi-empirical approach which has been useful to represent the ESR (Biorheology 14, 43-49, 1977).

Symposium MX
Rheology and Mixing

Organizers: Deepak Doraiswamy and Ica Manas-Zloczower

Thursday 10:10 Senate MX5

STRUCTURE AND CHOSEN MECHANICAL PROPERTIES OF POLYMER BLEND FIBRES

A. Wlochowicz and M. Linek
Technical University of Lodz, Branch in Bielsko-Biala, Poland

The content of admixture in the mass of material is one of the most important factors, deciding about aggregation form of dispersed phase. In the case when the content of admixture is high, about 10-90%, both component blends occur as homogeneous bundle of microfibrils. Such kind of structure can be quantitatively characterized based on Takayanagi's series-parallel models. Using these models the statistical relative content in the cross-section and along the fibre axis of the dispersed phase can be determined. The Takayanagi's models in opposite to others classical rheological model, can be used for any uniaxial deformation including breaking deformation. Moreover, this model can be used in the same time for characterization of the semi-crystalline component. The model parameters and stress characteristic of component allow us to simulate the effect of quantitative content of blends on breaking stress

and breaking elongation. The model parameters can be determined based on the measure of sound speed in one-component fibres. The experimental data for PMMA-PS, PP-PS, and PE-PS are presented.

Thursday 10:35 Senate MX6

POLYMER MIGRATION BASED ON THE TWO FLUID MIXTURE THEORY

P.N. Kaloni

Department of Mathematics University of Windsor, Windsor, Ontario, Canada N9B 3P4

The purpose of this presentation is to employ the two fluid mixture theory, (by considering polymeric solutions to be mixtures of two continua) to study the flow of a polymeric solution between two parallel plates and through a circular pipe. A comparison of the theoretical results with the corresponding experimental observations shows that not all the prevailing constitutive equations predict the observed behaviour.

Thursday 11:00 Senate MX7

RHEOLOGY OF IMMISCIBLE POLYETHYLENES

Ibnelwaleed A. Hussein and Michael C. Williams

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta

The miscibility of two types of polyethylenes was investigated by measuring the rheological properties of the melt in a Rheometrics Mechanical Spectrometer (RMS-800). Low-density polyethylene (LDPE, MI = 0.75) and linear low-density polyethylene (LLDPE, butene, MI = 1.0) were selected for study. Small strain (10%) dynamic oscillatory measurements were carried out in the range 0.01 to 100 rad/s at 190oC using a cone (0.1 rad; 25 mm dia.) and plate (C&P). Results were checked for reproducibility in the C&P as well as the parallel plates geometries. The measurements were in perfect agreement regardless of the geometry or the direction of the frequency sweep (ascending or descending). The 3as-received² samples were blended in a Haake Rheocord 90 Mixer equipped to measure melt temperature (Tmelt) and torque. A two-level four-variable factorial design approach was adopted to determine "optimum" blending conditions (speed of blades, temperature, time of operation). The "optimum" conditions were defined as avoiding chemical degradation (color appearance) and high viscous heating and achievement of steady-state torque (tss) in minimal time of shearing (minimizing shear degradation). The number of variables and their levels for the experimental design were chosen based on our previous experience, and their combinations were established using a standard fractional factorial design matrix. The optimum blending conditions (50 rpm, 190oC, 10 min.) were used for blending LDPE/LLDPE pair for miscibility study. Samples (25 mm dia., 2 mm thickness) were prepared in a Carver Press under fixed thermal and mechanical histories. The variation of the viscous component of the complex viscosity, h¢, with composition showed positive deviation (PD) from linear additivity in the composition range (10 to 90%w LLDPE) over the range 0.01 to 1 rad/s (0.4 to 20 kPa) with a sharp maximum at 70%w LLDPE. For the rest of the range linear additivity was obeyed . The same behavior was manifested in the storage modulus, G¢, in the range 0.01 to 10 rad/s (0.4 to 80 kPa) with linear variation with composition over the range 10 to 100 rad/s (80 to 100 kPa). A similar result was obtained with tss and DT (Tmelt - Tset) during the blending process, a totally different flow field. The existence of PD, accompanied by a sharp maximum, in Eta', G', tss and DT is taken as evidence of phase separation (immiscibility) between the blend components. The reasons for immiscibility are discussed in terms of classical thermodynamics and the possibility of ordered microstructures in the pure polyethylene melts.

Thursday 11:25 Senate MX8

THE RHEOLOGY OF VISBROKEN REACTOR PRODUCED IMPACT COPOLYMERS

Chun Lee, Ramesh Shroff, and Mani Shanker

Millennium Pertochemicals Inc., Allen Research Center, Cincinnati, Ohio 45249

A rheological characterization of visbroken (peroxide treated) reactor produced impact PP copolymer resins was carried out using dynamic and steady state viscosity and melt relaxation measurements. The variation of the rheological parameters with increased visbreaking can be explained by two simultaneous mechanisms: 1) chain scission of the PP chain and 2) grafting in E-P copolymer chain, producing a network type structure in the melt. With an increase in visbreaking, chain scission of the PP portion results in a decrease of viscosity and moduli at higher frequencies or shear rates. At the same time, grafting in the E-P copolymer portion leads to unusual up-turns in viscosity as well as in both storage and loss modulus. This observation results in slower stress relaxation at longer times. We also describe experiments designed to elucidate the nature of a network structure as exhibited in viscosity and moduli up-turns. Specifically, polymers are subjected to varying levels of low rate steady-state or high dynamic strain just prior to making low strain dynamic melt rheological measurements. A systematic and dramatic decrease in the extent of up-turn is observed. This so-called network destruction is reversible in that the material reverts back to its original, unmodified state - to a structure that existed prior to pelletization.

Thursday 11:50 Senate MX9

THE DYNAMICS OF MIXING AND MECHANO-CHEMISTRY IN AN ORGANO-CERAMIC COMPOSITE

J.A. Walberer and A.J. McHugh
Department of Chemical Engineering, University of Illinois, Urbana, Illinois, 61801

Torque rheometry in a Banbury mixing system has been used to monitor the evolution of paste formation and microstructure in an organo-ceramic composite material based on a calcium aluminate cement and a phenolic resin. Measurements of the mixing torque versus time reveal a mechano-chemical interaction between the organic and reactive ceramic phase characterized by an induction period of flat torque followed by a period of rapid paste stiffening. The behavior of the induction and stiffening periods as a function of mixing rate, temperature, and pH suggests that a specific sequence of chemical events is responsible for paste development. Dissolution of the cement during the induction period increases the pH of the paste causing the resin to ionically interact with the cement particles and rapidly increase the paste stiffness. The development of paste rheological properties with mixing was correlated with measurements using an equibiaxial extensiometer and a capillary rheometer.

Symposium LC
Liquid Crystals: Structure and Rheology

Organizers: Davide A. Hill and Lynn Walker

Thursday 8:05 Executive LC9

EFFECT OF THE MOLECULAR WEIGHT ON THE RHEOLOGICAL BEHAVIOR OF THERMOTROPIC LIQUID CRYSTALLINE POLYMER

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While much is known about the rheology of lyotropic liquid crystalline polymers (LCPs) subjected to shear flow, the effect of molecular characteristics on the rheological behavior and microstructure of thermotropic LCPs are relatively less understood. To a large extent, this situation reflects the experimental difficulties associated with high nematic-isotropic transition temperature, thermal degradation, transesterification and recrystallization processes in the commercial thermotropic LCPs. An attractive model thermotropic LCP that has been established to avoid these problems is a main-chain nematic polyether with a methyl stilbene mesogen and flexible aliphatic spacers (DHMS-7,9; Tc=95 C, Tni=197 C). For this study we have synthesized DHMS-7,9 with molecular weights ranging from approximately 5K to 60K. The effect of the isotropic-nematic transition on the relaxation spectrum of unaligned samples is reported as a function of molecular weight. For comparison with previous studies on lyotropic LCPs, the behavior of the nematic phase is probed as a function of flow history. Relatively low molecular weight (9K) DHMS-7,9 shows a recovery in its storage and loss moduli that are reminiscent of those reported by Mewis and coworkers for lyotropic HPC solution. This behavior is more difficult to observe in high molecular weight (60K) DHMS-7,9 because the contribution of macromolecular distortion to the dynamic moduli is so large at the experimental accessible frequencies. This has the consequence that the relative contribution of the texture to G* (and its recovery after shear) becomes unobservably small. Rheological results for various molecular weight polymers will be compared with optical microscopy study of their texture under shear flow.

Thursday 8:30 Executive LC10

ORTHOGONAL SUPERPOSITION MEASUREMENTS OF LYOTROPIC LIQUID CRYSTAL POLYMER SOLUTIONS DURING AND AFTER SHEAR FLOW

Lynn M. Walker*, Jan Vermant, Jan Mewis** and Paula Moldenaers****
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Measurements of the evolution of the dynamic moduli of lyotropic liquid crystal polymer (LCP) solutions after cessation of shear flow have proven instrumental in understanding the influence of shear on the anisotropic texture of these materials. In this study, an RMS-800 has been adapted to apply a small amplitude oscillatory flow orthogonal to the shear-gradient plane and measure the resulting moduli. These orthogonal moduli probe a different plane of the shear field than is typically studied rheometrically, a factor important in studying anisotropic structures like those observed in LCPs. Orthogonal moduli measured *during* flow also retain physical meaning as they may be decoupled from the primary flow. The orthogonal moduli have been studied during and after cessation of shear flow for solutions of PBG in m-cresol and HPC in water. Results are compared to moduli measured parallel to the flow direction. At low concentrations, results agree qualitatively with the interpretation of structural evolution developed from previous mechanical and optical measurements. At higher concentrations, results are less clear but provide a new perspective of the complications induced by increasing the concentration of lyotropes.

Thursday 8:55 Executive LC11

STRUCTURE AND LINEAR VISCOELASTIC BEHAVIOUR OF THERMOTROPIC POLYMERS. INFLUENCE OF MOLECULAR WEIGHT

A. Romo-Uribe*, T. J. Lemmon and A. H. Windle
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We present our investigation on the influence of molecular weight on the ordering processes and linear viscoelastic properties of a series of thermotropic polymers. The polymers are aromatic copolyesters based on random units of 75 mol% 1,4-hydroxybenzoic acid (B) and 25 mol% 2,6- hydroxynaphthoic acid (N). Thermal characterisation results show that annealing below 290 C gives rise to a secondary endotherm. Hot-stage diffractometry enables us to identify this endotherm with a phase transformation from pseudohexagonal to orthorhombic structure. When annealing is carried out above 290 C only one endotherm is observed, showing that all transitions are completed by 310 C, the temperature for the rheological characterisation. Oscillatory measurements show that the B-N copolyesters exhibit a linear viscoelastic (LVE) regime similar to that observed in common flexible chain polymers. Interestingly, it is found that the linearity extends only up to strains of about 10%, independently of the molecular weight. Dynamic experiments within the LVE regime reveal a rubber-like region, suggesting that the B-N copolyesters behave like lightly crosslinked materials, adding thus support to the elastic network hypothesis.

Thursday 9:20 Executive LC12

FRANK-ELASTICITY-INDUCED INTERPARTICLE FORCES IN LIQUID CRYSTALS: SQUEEZING FLOW AND "NEMATIC LEVITATION".

Ana Schwendt* and Davide A. Hill
Department of Chemical Engineering, University of Notre Dame du Lac, Notre Dame, IN 46556.

Incommensurate anchoring boundary conditions on neighboring surfaces confining a liquid crystalline medium result in permanent distortion of the interstitial director profile. Forces are thus generated between such surfaces driven by the change in Frank's distortional free energy with separation. We experimentally study this problem by monitoring the gravity-driven approach of a thin, circular glass plate towards a bottom plate of larger dimensions in nematic MBBA. The anchoring boundary conditions on both surfaces are tangential, with a 90 degrees twist. For this configuration, theory predicts final settling of the top particle at a finite, non-zero equilibrium separation ("nematic levitation"). The separation between the two plates is experimentally monitored (in an indirect fashion) by measuring the dielectric permittivity from a capacitive sensor photolithographically patterned at the bottom surface. This dielectric technique is sensitive to separations of the order of micrometers (though, as we shall discuss, this

method poses non-trivial challenges when applied to liquid crystals). The experimental results seemingly confirm the attainment of a non-zero equilibrium separation between the plates of the same order as that predicted by theory. A mathematical model, based on Stefan's equation for squeezing flow with an additional term describing Frank repulsive interactions is employed to decipher the experimental transients.

Thursday 10:10 Executive LC13

RHEO-OPTICAL RESPONSE OF BIPHASIC SOLUTIONS OF PHIC

Sanaul K. Siddiquee and Jan W. van Egmond
Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003

The rheo-optical response of highly concentrated solutions of poly(n-hexyl) isocyanate (PHIC) of molecular weight 60,000 in TCE was investigated. The techniques used were dichroism, small angle light scattering and shear microscopy. As the concentration is increased from the concentrated isotropic regime, the solution passes into a biphasic nematic in isotropic region and then into a biphasic isotropic in nematic regime. Further increasing the concentration results in the attainment of a single phase nematic solution. This study was primarily interested in the rheological response of the biphasic regions. The biphasic isotropic in nematic solution showed an unusual relaxation corresponding to a transitionary structure orienting perpendicular to flow with a long time structure oriented in the flow direction. The strength and duration of the transitionary structure was shear dependent. The magnitude of the dichroism during relaxation increases with shear rate and the time at which this maxima occurs decreases with shear rate.

Thursday 10:35 Executive LC14

SUPPRESSION OF THE RAYLEIGH CAPILLARY INSTABILITY BY RIGID-ROD MICROSTRUCTURE

Gregory M. Forest* and Qi Wang**
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**Department of Mathematical Sciences, I.U.P.U.I, Indianapolis, IN 46202

We study the effect of microstructure on the capillary instability of cylindrical jets. We duplicate Rayleigh's classical linearized stability analysis but applied to Doi-type kinetic equations for flows of liquid crystalline polymers (LCPs). We focus on the highly aligned "prolate" equilibrium phase of rodlike molecules, which exists at sufficiently high LCP density; this phase is stable to possible uniaxial and biaxial orientation-dominated instabilities, so is the primary candidate for stabilizing cylindrical jet flows. We show that orientational coupling reduces all growth rates while increasing the dominant wavelength of instability. Two critical scaling parameters are identified: an LCP capillary number which measures the ratio of LCP free surface energy to interfacial surface tension; and an anisotropic drag or friction parameter. For large capillary number (with a precise condition given) the linearized growth rates are reduced considerably; by additionally making the drag more anisotropic, the growth rates can be uniformly reduced arbitrarily close to zero. For capillary numbers below a critical value, the growth rates are reduced, but less than above; there again is further reduction due to anisotropic friction. However, there is a finite, positive growth rate curve that gives a sharp lower bound so the instability is trapped between the Rayleigh rate and this lower bound. The upshot of these calculations is the prediction that an oriented versus isotropic fluid jet which undergoes capillary breakup will yield bigger drops that form on longer time scales.

Thursday 11:00 Executive LC15

INVESTIGATION OF NEAR-WALL STRUCTURE EVOLUTION IN TUMBLING 8CB BY MICRODIELECTROMETRY.

Davide A. Hill and Vinaya Sequeira
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We have probed near wall dielectric anisotropy during flow in 8CB, a low molecular weight liquid crystal of the tumbling type. The experimental apparatus consists of a microdielectrometry sensor flush mounted to the bottom plate of a parallel disks, torsional flow device [J.S. Fodor and D.A. Hill, J. Rheol., 38(4), 1071 (1994)]. The sensor enables measurement of dielectric anisotropy of the liquid in the immediate vicinity (15 micrometers) of the solid surface. Dielectric-thermal analysis under steady shear, inception of flow and flow reversal experiments are

indicative of transient tumbling and the development of out of plane orientation. The experimental results are in good qualitative agreement with simulations by Han and Rey [J. Rheol., 38(5), 1317 (1994); 39(2), 301, (1995)] of the 3-D Leslie-Ericksen problem.

Thursday 11:25 Executive LC16

MECHANICAL RHEOMETRY STUDY OF A POLYMER LIQUID CRYSTAL MONOLAYER

Carlton F. Brooks, Joe S. Hur, Gerald G. Fuller, Curtis W. Frank, and Channing R. Robertson
Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025

We've constructed a constant surface stress rheometer to apply an oscillatory stress on a Langmuir monolayer. A magnetized rod resides at the air-water surface and its motion is induced with a magnetic field gradient. With this device the rheology of a "hairy rod" polymer, phthalocyaninatopolysiloxane (PcPS), dissolved in arachidyl alcohol was investigated when subjected to an oscillatory surface stress. The alcohol solvent by itself exhibited Newtonian-like properties over the range of frequencies probed (0.1 to 10 rad/s). The presence of the polymer at 7 mol% increased the rigidity of the film by an order of magnitude. At a surface pressure of 20 mN/m the surface storage modulus, G_s', and loss modulus, G_s'', are comparable in the low frequency regime, but at high frequencies the film is more elastic than viscous. At 30 mN/m, G_s' dominates over the entire frequency range. Applying the Cox-Merz relation to our dynamic data, the addition of polymer produces shear thinning behavior. Previous work with this polymer system indicated that at rest, the film exhibited nematic liquid crystalline behavior [1]. When subjected to flow the direction of orientation could be controlled and the orientational order increased. These results and the transient behavior were successfully modeled by Maffetone *et al.* [2], using a two-dimensional analog of the rigid rod model. Our rheometer measurements agree with this model that predicts the resistance to flow should decrease as the rod molecules align in the flow direction.

1.) M.C. Friedenberg, G.G. Fuller, C.W. Frank, and C.R. Robertson, *Macromolecules*, v 29 (1996) p 705.

2.) P.L. Maffetone, M. Grosso, M.C. Friedenberg, and G.G. Fuller, *Macromolecules*, v 29

Thursday 11:50 Executive LC17

OPTICAL RHEOLOGY AND A FLOW-INDUCED NEMATIC STRING PHASE IN WORMLIKE MICELLE SOLUTIONS

Ignatius A. Kadoma, Socratis G. Kalogrianitis and Jan W. van Egmond
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Recently, the possible formation of multi-connected networks due to transient cross-links between entangled micelles with sufficient counter-ion concentration has attracted much interest. In these networks, the connection points are transient and free to slide along the micelle backbone much like a one dimensional gas. In this paper, we present a combination of flow-induced phenomena in a semi-dilute solution of connected wormlike micelles. These phenomena include a local isotropic-to-nematic transition and a flow-induced string phase. The experimental techniques include small angle light scattering and three-dimensional flow birefringence and enable a differentiation between contributions of convection, stress and diffusion to the structural evolution and relaxation. We are also reporting an increasing ratio of the normal stresses (-N2/N1) as a function of shear rate.

Symposium FM
Non-Newtonian Fluid Mechanics

Organizers: Gary L. Leal and Frank Baaijens

Thursday 8:05 Judicial FM22

VISCOELASTIC INSTABILITIES OF RECIRCULATION FLOWS NEAR SOLID SURFACES AND INTERFACES

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Recirculation flows near solid surfaces and interfaces are extremely important in industrial processes from injection molding and polymer processing to coating flows. Our investigations of the stability of coating flows with an eccentric cylinder geometry for both a viscous Newtonian fluid and an ideal elastic Boger fluid will be discussed in terms of three classes of phenomena. First, we have discovered several new transitions in traditional fingering instabilities, including a novel saw-toothed cusped pattern. Secondly, we have found that purely elastic bulk flow instabilities in the neighborhood of air-fluid interfaces can cause surface deformations if the secondary flow is of sufficient strength. Finally, these interfacial flows are found to display a new class of purely elastic instabilities which appear to be independent of traditional viscous fingering instabilities and elastic bulk flow instabilities. We found that indeed elasticity has a dramatic effect on the stability of interfaces, not only changing the manifestation of traditional fingering instabilities, but causing new purely elastic interfacial instabilities. We shall discuss these phenomena in turn along with possible mechanisms for their occurrence.

Thursday 8:30 Judicial FM23

PURELY ELASTIC INSTABILITY OF PIPE FLOWS

H.J.Wilson and J.M.Rallison
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Extrusion flows are commonly used in industrial processing of polymeric fluids. The co-extrusion of two elastic fluids has been shown in some configurations to be unstable to long wave perturbations (Hinch, Harris & Rallison, JNNFM 43 (1992) 311-324) and for the specific case of the Oldroyd-B model, for most parameter values, unstable to short waves in the absence of surface tension (Wilson & Rallison, in press, JNNFM (1997)). These inertialess instabilities are driven by a jump in the first normal stress difference at the interface.

Using a generalized Oldroyd-B model, the jump in normal stress may be "blurred" into a continuous profile. For steep profiles the instability is still observed.

We investigate the stability of pipe flow for a White-Metzner constitutive model with power-law viscosity.

Thursday 8:55 Judicial FM24

DYNAMICS AND STABILITY OF VISCOELASTIC FLOWS: A TIME-DEPENDENT SIMULATIONS APPROACH

R. Sureshkumar, Mark D. Smith, Robert A. Brown and Robert C. Armstrong
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In this work, we explore the suitability of direct time-dependent simulations to study the dynamics and stability of viscoelastic flows. The numerical algorithm uses finite element techniques for spatial discretization and the semi-implicit theta method for integration in time. Two flow geometries are considered: the plane Couette flow where the non-normal linear dynamics can be well-characterized through linear stability analysis results and the pressure-driven flow past a linear array of cylinders in a plane channel, where the complex geometry and multiple inhomogeneous flow directions present a formidable computational challenge. We first show that the critical eigenfunctions of the plane Couette flow of an Upper Convected Maxwell (UCM) fluid are non-orthogonal to each another in the sense of the conventional inner product. Subsequently, it is shown that the non-normality of the linear viscoelastic operator could result in transient growth of initial perturbations even in the absence of non-linear effects. Similar conclusions can be drawn for the Oldroyd-B fluid as well using the (numerical) linear stability analysis results and direct time-dependent simulations. Moreover, direct time-dependent simulations show that non-linear effects can further amplify the transient energy growth. For the cylinder in a channel geometry, we conduct two types of studies. In the first part, we explore the suitability of the time-dependent simulations to evaluate steady state solutions at relatively large Weissenberg numbers. We also perform calculations to investigate the linear stability of the flow against symmetric/non-symmetric two-dimensional perturbations. The computational results are used to decipher the mathematical behavior of the critical eigenvalue as a function of the Weissenberg number.

Thursday 9:20 Judicial FM25

ROLE OF FLUID ELASTICITY AND DYNAMIC MODULATION ON STABILITY OF MULTILAYER VISCOELASTIC FLOWS

C. T. Huang and B. Khomami

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In this study we have theoretically investigated the effect of fluid elasticity and dynamic modulation on the stability of multilayer pressure driven channel flows as well as multilayer flows down an inclined plane by utilizing asymptotic analysis and spectral based numerical techniques. In absence of dynamic modulation, our results indicate that for slow multilayer flows down an inclined plane (i.e., stable free surface) a stable flow to longwave disturbances can only be obtained when the elasticity gradient is in opposite direction of the gravitational field (purley elastic) and viscosity gradient is in the direction of the gravitational field (purley viscous) provided the most viscous fluid is adjacent to the wall and the most elastic fluid is in the top layer. This is in contrast to multilayer channel flows where the depth ratio plays a significant role in determining the stability of the interface. However, in both class of flows the interactions between the viscous and elastic forces determine the stability of the interface at intermediate-and- shortwaves. Hence, the stability of multilayer channel and inclined plane flows of viscoelastic liquids to disturbances with moderate to high wavenumbers can not be determined by simply examining the purely viscous and elastic stability of the system. Utilizing Flouqet theory, we have also shown that dynamic modulation can significantly affect the stability of multilayer channel and inclined plane flows. Specifically, in presence of dynamic modulation flows that are otherwise unstable for extensive range of viscosity and elasticity ratios, can be stabilized or visa-versa. In particular, in a certain parameter range resonance between a free surface and an interface or between various interfaces gives rise to an extremely rich dynamics and early transition to chaos.

Symposium SL
Rheology of Solids

Organizers: Gregory B. McKenna, Robert Shay and Omar A. Hasan

Thursday 10:10 Judicial SL15

USING THE SPIN TENSOR IN CONSTITUTIVE EQUATIONS FOR POLYMERIC LIQUIDS

William E. VanArsdale

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Constitutive equations are investigated which involve an objective part of the spin tensor. Constraints on the inclusion of such variables are reviewed in the context of these models. One approach generates an objective skew rate that is bounded by the symmetric part of the spatial velocity gradient. An isotropic function of these rates completely characterizes the response of any "simple" fluid in motions with constant stretch history. The dissipation inequality requires a positive viscosity but does not fix the sign of terms in this function associated with the primary normal stress coefficient. A similar result is obtained for a modified upper convected Maxwell model. This three-parameter constitutive equation is similar to the differential form of the Johnson-Segalman model. Predictions are

similar in shearing flows, except the proposed model gives more realistic results in step shear and large amplitude oscillatory shear. Generalizations of the integral form will be discussed in the context of shearing flows.

Thursday 10:35 Judicial SL16

A SECOND PLATEAU IN DYNAMIC MODULI AT LOW FREQUENCY REGION FOR POLYMERS CONTAINING MULTIPLE BRANCHED MOLECULES

N. Nakajima and J.P. Varkey
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It is well known that for entangled polymers, between the terminal and the glass transition region there is a single plateau, which is called rubbery region. This observation is for linear or slightly branched and moderate-to-high molecular weight polymers. Our investigation has been motivated by the observation that the storage modulus G'(w) and loss modulus G"(w) curves of polymers containing significant amount of gels are concave upward in the low frequency region. On the other hand, for polymers that are "gel free," these curves in the low frequency (flow) region point downward with increasing slope. The significance of the G'(w) and G"(w) curves having concave upward shape in the low frequency region suggest the possibility of having a second plateau between the terminal and the rubbery region for these polymers. This work examines dilute and semi-dilute solutions of three different polymers, varying in gel content from, "gel free" to 70%. The concentration range was 3-20% and the temperature of measurement was 30 C. With dilution from 20 to 5% , in the case of polymers containing significant amount of gels, a second plateau was observed whereas no such plateau was observed for "gel free" polymer.

Thursday 11:00 Judicial SL17

SUB-TG RESPONSE OF POLYCARBONATE: DEVIATIONS OF THE EQUILIBRIUM RESPONSE FROM WLF EXPECTATIONS.

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While it is reasonably well known that the WLF expression is not truly valid as a description of the viscoelastic shift factors or viscosities below about Tg+10 K, the actual temperature dependence in the equilibrium glass below the nominal Tg has been very little studied. Here we review some prior results on an epoxy glass and present new results on a polycarbonate glass in which the sample is aged into equilibrium at temperatures as far as 15 degrees below Tg and the stress relaxation or creep responses are superimposed using time-aging time and time-temperature superposition principles. The results suggest that the equilibrium response of the polymers below the nominal Tg shifts in a fashion closer to Arrhenius than to WLF. This apparent transition will also be discussed in the context of a new model for the temperature dependence of viscosity based on the configurational entropy model of Gibbs and DiMarzio and that differs significantly from the Adam-Gibbs formulation.

Thursday 11:25 Judicial SL18

ELECTROSTATIC FORCES IN VISCOELASTIC SOLIDS

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Electrostatic forces in linear elastic solids depend on at least three dielectric parameters: the dielectric constant, and two derivates of the permittivity tensor with respect to deformation, a_1 and a_2. Features that determine the dielectric constant are well known, and values are tabulated for many materials. The other two properties, a_1 and a_2, had not been measured for many systems, and their dependence on chemical composition is not well understood. All three dielectric parameters influence the magnitude of electrostatic stresses, and our experimental and theoretical results show that a_1 and a_2 typically provide the largest contribution to electrostatic forces in solids.

In this presentation, we discuss electrostatic forces in viscoelastic solids. In these materials, the same dielectric parameters essentially describe the time-dependent electrostatic stresses. Since values of the parameters a_1 and a_2 are not known for many materials, we will discuss an experimental technique to measure these parameters and report experimental data for several kinds of polymers. The ability to control forces exerted by the electric field requires determining the relationships between material chemistry and the dielectric parameters. We present a microscopic model that relates the dielectric tensor to the microstructure of isotropic amorphous or crystalline materials. This microscopic theory agrees with experimental results for several kinds of viscoelastic polymers.

Thursday 11:50 Judicial SL19

PARTICLE-TRACKING MICRORHEOLOGY OF ACTIN GELS

Andre F. Palmer*, Thomas G. Mason*, and Scot. C. Kuo, and Denis Wirtz***
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Department of Biomedical Engineering, Johns Hopkins University, Baltimore, MD.

Actin is a 43 Kda globular protein which is present in all eukaryotic cells. This protein polymerizes at physiological concentrations of salt, into long semiflexible filaments in solution. These filaments have a very large aspect ratio, which allows them to form a gel. This gel forms the core of the subcellular cytoskeleton which provides rigidity to the cell. The viscoelastic properties of these gels are typically probed using mechanical rheometry by imposing a strain and probing the stress induced in the actin network. However, even strains as small as 5% can bundle, orient and even rupture actin networks. Using a novel high-resolution particle-tracking method, we avoid these limitations. Here, the local actin network dynamics is probed by measuring the mean-square displacements of a single particle imbedded in the network (particle-tracking microrheology). The quiescent rheological properties are probed in the frequency range of 1e-2 rad/s to 1e5 rad/s, much wider than that of conventional rheometers. Moreover, our single-particle-tracking technique only requires microliters of sample, which opens the way for the measurement of mechanical properties of the cytoskeleton of a living cell or of gels made of proteins that are either expensive or difficult to purify. Our experiments show that the motion of actin filaments making up the network is sub-diffusive on short-time scales. Moreover, the motion of the optical probe is shown to reach two separate plateaus corresponding to both the bending modes of the actin filaments and the long time scale motion of the diffusing actin filaments. We measure the plateau moduli as a function of actin concentration and compare these results with those obtained using mechanical rheometry measurements.

Symposium NP
Novel Polymer Systems

Organizers: Michael Mackay and Anthony J. McHugh

Thursday 8:05 Legislative NP5

DYNAMICS OF MULTIARM STAR POLYMER SOLUTIONS

D. Vlassopoulos*, G. Petekidis*, G. Fytas*, J. Roovers, and A. N. Semenov*****
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Star shaped macromolecules consisting of f linear homopolymers covalently joined to a common center represent model spherical polymer brushes with soft colloidal character. The resulting inhomogeneous monomer density distribution can lead to liquid-like ordering at the overlapping concentration. We study the dynamics of such solutions of polybutadiene stars with f=64 or 128 using photon correlation spectroscopy and rheology. We identify 3 mechanisms for the relaxation of concentration and composition fluctuations, namely cooperative diffusion, structural relaxation and self-diffusion. The former is typical in polymers, whereas the latter two are characteristics of colloidal particles. The self- diffusion behavior is consistent with the solution viscosity. The ordering persists at all high concentrations, even in the melt state. These materials exhibit a behavior intermediate between polymers and colloids.

Thursday 8:30 Legislative NP6

RHEOLOGY OF HYBRID STYRYL-POLYHEDRAL OLIGOMERIC SILSEQUIOXANE POLYMERS

A. Romo-Uribe, P. T. Mather, T. Haddad* and J. Lichtenhan**

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We present the rheological characterization of linear thermoplastic non-polar hybrid inorganic-organic polymers. These materials are synthesized through copolymerization of an oligomeric inorganic macromer with 4-methyl styrene. The inorganic portion of the material is a well-defined polyhedral oligosilsesquioxane (POSS),R7 (Si8O12) (CH2CH2C6H4CH=CH2), where R=c-C6H11 or c-C5H9. A series of 4-methyl styrene copolymers with 4, 8 and 16 mol % POSS macromer incorporation were investigated. Results show that the thermal properties of the polymers are modified as the percent of POSS incorporation increases. On the other hand, dynamic rheological measurements evidence a modification of the rheological properties with increase of POSS incorporation. These results suggest that interchain interactions between the massive inorganic groups are responsible for the modification of the polymer chains motion, a mechanism similar to the "sticky" reptation model described by Leibler et al. [Macromolecules (1991) 24, 4701].

Thursday 8:55 Legislative NP7

POLYMERIZED GELS TEMPLATED USING SURFACTANT CUBIC PHASES

Eric Paul*, Anahi Sommer-Grosse*, Jessica Hittle*, Robert K. Prud'homme* , Dvora Perahia, and Gregory G. Warr*****

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Gel structures have been synthesized based upon templating the polymerization of a water soluble monomers with surfactant cubic phases. Surfactant cubic phases are viscous isotropic oil/water/surfactant phases with bicontinuous oil and water networks. Polymerization of either the oil or the aqueous phase produces nanoporous hydrogels. These materials offer the potential of controlled release of larger molecules than can be released from conventional hydrogels. Since the pore sizes are tunable and it offers a vehicle for encapsulating enzymes or potentially whole cells. Also, the biocontinuous oil-water structure has the potential to function as very high interfacial area supports for phase transfer catalytic reactions. Gels templated on cationic and non-ionic surfactants have been obtained. The control of morphology during polymerization requires the control of the rate of polymerization and crosslinking to prevent the polymer from entropically destabilizing the cubic structure. The rheology of the cubic phase is crucial for the success of the process.

Symposium GN
General Session

Organizer: Robert L. Powell

Thursday 10:10 Legislative GN3

FLOW PROPERTIES OF "HAIRY-ROD" MONOLAYERS FORMED BY CELLULOSE DERIVATIVES WITH AND WITHOUT ATTACHED CHROMOPHORES

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A study of hairy-rod monolayers formed by several cellulose derivatives is presented. The rheological experiments are conducted within a Langmuir trough so that the surface pressure of the spread monolayers can be controlled.

Both Brewster angle microscopy (BAM) and dichroism measurements are used to investigate the orientational dynamics of the surface films when subjected to extensional flow generated by a four-roll mill. Some cellulose molecules have attached chromophores and are dichroic when oriented. This optical property is used to measure the orientation of the side chains and the rigid backbone. Orientation phenomena under flow are also visualized by BAM. Furthermore, this technique can be used to probe samples that do not contain attached chromophores and are therefore not dicroic. These uniform fluid monolayer show a strong alignment in the flow field indicated by drastic changes in reflectivity, especially in the regime of high shear rates. This indicates a flow-induced orientation in the direction of the polarization of the light. This orientation depends on both surface pressure and temperature. In addition, BAM was used to document the phase behavior of all samples.

Thursday 10:35 Legislative GN4

THE INVALIDITY OF STRAIN-TIME SEPARABILITY AT SHORT TIME SCALES

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Strain-time separability, i.e., the factorability of material response to step strains into time and strain dependent parts, has been widely used as a convenient basis for the specification of viscoelastic constitutive equations. Experimental data for well characterized polymer melts such as LDPE Melt I appear to validate such separability upon cursory examination and have even served as the basis for the proposal of several popular integral constitutive equations. A closer examination of the data indicates that projection of the measured step strain response to very short time scales will result in what is perhaps the simplest manifestation of Hadamard instability. The invalidity of strain-time separability at short time-scales was noted at the outset in step-strain experiments on polymer solutions. This was also recognized by Doi and Edwards in their reptation model based constitutive equation. For polymer melts however, the extension of strain time-separability to short time scales has been often been made without any experimental or physical justification. It will be shown that any strain-time separable constitutive equation that is purported to properly describe step strain data for several popular polymer melts will ironically be Hadamard unstable in its instantaneous response. Interesting examples of the step response of polymer solutions will be provided to illustrate that deviations from strain-time separability at short time scales are consistent with the requirement of Hadamard stability. Experimental damping functions for polymer melts will also be discussed to demonstrate the complications arising from extrapolating experimental trends to short time-scales.

Thursday 11:00 Legislative GN5

A THIN-FILAMENT MELT SPINNING MODEL WITH RADIAL RESOLUTION OF TEMPERATURE AND STRESS

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Existing one-dimensional (1-D) non-isothermal thin-filament melt spinning models treat temperature as a cross-sectionally averaged quantity, varying only with axial distance. Such models accurately simulate processes in which the melt has high thermal conductivity relative to the surface heat loss, or in which the ambient air temperature equals the melt temperature. These characteristics are not true of industrial melt spinning processes. Here we extend existing 1-D melt spinning models to include radial as well as axial resolution of temperature by positing an evolving radial temperature profile which can accommodate realistic temperature variations within the fiber and between the fiber and ambient air. This 2-D resolution of temperature yields a corresponding 2-D resolution of stress in the fiber, while retaining the advantages of 1-D computation. We also improve modeling of viscosity and specific heat by allowing pointwise dependence of these quantities on the radially varying temperature. We conclude that models which neglect the leading-order radial variation in temperature generate 1-D velocity, temperature, and stress profiles that are in error, and that the model developed in this article generates predictions that depend on polymer thermal conductivity, a parameter that is missing from conventional models.

Thursday 11:25 Legislative GN6

A STANDARD REFERENCE NONLINEAR FLUID STANDARD: A PROGRESS REPORT

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NIST is in the process of developing a new Standard Reference material that replaces and goes beyond the certification of the old SRM 1490 Nonlinear Fluid Standard. The purpose of the material and its development is two-fold: first, to help equipment manufacturers and researchers in different laboratories to better understand the inherent lab-to-lab variability in their measurements and consequently help reduce these; and second, to provide a standard fluid that is useful to researchers and analytical laboratories alike as a research material and as a secondary standard because it is homogeneous and has well known material properties. We plan to decide what the material property ranges of interest are through consultation with the Rheology Community, a process that is already underway and has led to a preliminary selection of polyisobutylene in oligomeric isobutylene. NIST will perform preliminary measurements on this material and will then conduct round robin testing that will help to determine if the chosen material properties are acceptable to those participating in the round robin and to bring a consensus as to the lab-to-lab variability in the measurements. Based on these results, a large batch of a fluid will be made and certified for the shear rate dependence of viscosity and first normal stress difference over a temperature range of approximately 50 K. The linear viscoelastic responses will also be certified along with the temperature dependence of the shift factors and the zero shear viscosity. Here we will present progress in the material development up to the date of the meeting.

Thursday 11:50 Legislative GN7

DETERMINATION OF THE MOLECULAR WEIGHT DISTRIBUTION WITH INCOMPLETE LINEAR VISCOELASTIC RHEOLOGICAL DATA

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In order to rigorously apply the double reptation or weight average mixing rule to determine the molecular weight distribution of systems of linear flexible polymers, the dynamic moduli must be measured from the fully terminal region through the entire plateau region. The dynamic range required for a MWD that spans ~2 decades in M will span ~7 decades in the time/frequency domain. As a practical matter, such a large dynamic range is frequency inaccessible. We describe methods for extending the effective dynamic range of conventional rheometers by exploiting the different intrinsic sensitivities of stress controlled and strain controlled rheometers. When only partial dynamic moduli data are available, which is typically the case with commercial polymers, conventional numerical schemes for inverting the mixing rules **cannot** be used. This work describes numerical methods for extracting MWD information from partial dynamic moduli data. Specifically, we illustrate methods of introducing additional a priori information about the system such that an inversion of the mixing rule can be realized. We demonstrate that reliable molecular weight distributions can be determined when one has some a priori knowledge about the shape of the MWD, as is typically the case for commercial polymers produced from specific catalyst systems.

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