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Symposium PO Poster Session

Organizer: Lewis E. Wedgewood

Wednesday 5:30 Legislative

PO1

STICK-SLIP TRANSITION OF HDPE RESINS ON MOLECULARLY SMOOTH WALLS IN SLIT DIE FLOW

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44106-7202

We use a slit die (with the two inner walls made of silicon wafers) to provide for the first time a microscopically smooth surface and study the influence of surface condition on flow behavior of polymer melts. By comparing bare metallic walls with silicon walls, we show that the influence of metallic surface roughness on an extensively studied stick-slip transition phenomenon [1] is insignificant. A molecular weight dependence study of the transition characteristics allows us to propose a more detailed physical picture of the interfacial adsorption state at a PE/wall boundary: There is a saturated layer of chain adsorption containing many loops that entrap unbound chains before a disentanglement transition when the unbound chains undergo a coil-stretch transition. 1. S.Q. Wang and P.A. Drda, *Macromol. Chem. Phys.* 198, 673 (1997).

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PO2

MOLECULAR CHARACTERISTICS OF SHARKSKIN DYNAMICS IN CAPILLARY EXTRUSION OF METALLOCENE POLYETHYLENES [1]

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A series of metallocene polyethylenes is studied with a controlled pressure capillary rheometer. Because of their narrower molecular weight distributions, several distinctive features are observed in comparison to conventional LLDPE. The sharkskin distortion appears to be more sharply defined and the stick-slip transition is rather gradual instead of being abrupt with respect to the applied stress. More importantly the sharkskin dynamics are investigated as a function of molecular weight. We find that the sharkskin wavelength is essentially independent of the molecular weight in agreement with a simple theoretical description of the sharkskin dynamics. To lend a powerful and convincing support for the previously proposed molecular mechanism for sharkskin formation [2], we show that the sharkskin period not only changes with temperature as the inherent molecular chain relaxation time does but also scales with the molecular weight as the chain relaxation time does, which is independently measured from oscillatory shear in a planar Couette cell. 1. C. Depraserticul 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.

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PO3

THE ROLE OF CONDUCTION IN THE ELECTORRHEOLOGY OF BARIUM TITANATE SUSPENSIONS**P. J. Rankin and D. J. Klingenberg**

Department of Chemical Engineering and Rheology Research Center, University of Wisconsin, Madison, WI 53706

The electrorheology (ER) of barium titanate particles (BaTiO_3 , dielectric constant = 2000) in insulating oils was studied. Barium titanate suspensions perform poorly in D.C. fields despite the large particle dielectric constants. However, as predicted by Maxwell-Wagner theory, ER activity improves dramatically with increasing field frequency. A dynamic yield stress of over 500 Pa is obtained for 20 vol. % suspensions with electric field strengths of 2000 V/mm at 1 kHz. To probe the frequency dependence and the role of surface conduction, BaTiO_3 particles were modified by grafting various chemical species on their surfaces, thereby making the surfaces hydrophobic. These surface-treated particles exhibited no noticeable change in their ER activity. However, when surfactants are instead added, ER activity decreases. This suggests that untreated BaTiO_3 has at most a small surface conductivity, and that the Maxwell-Wagner dispersion is controlled by bulk conduction.

Evidence also suggests that nonlinear conduction occurs in the continuous phase. Maxwell-Wagner theory predicts that the dielectric dispersion should occur at frequencies much smaller than we observe. This suggests that the continuous phase conductivity is increased substantially by the electric field. Furthermore, this nonlinear conduction is frequency dependent. The dielectric dispersion shifts to larger frequencies with increasing field strength. We also find that the dynamic yield stress is proportional to E^m where m increases with frequency. These results indicate that the fluid conductivity, which depends on both field strength and frequency, plays an important role in the ER response of suspensions with large dielectric constant particles.

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PO4

POLYMER-MODIFIED RHEOLOGY OF PULP FIBER SUSPENSIONS**S. Zauscher and D. J. Klingenberg**

Department of Chemical Engineering and Rheology Research Center, University of Wisconsin, Madison, WI 53706

Above a critical concentration, cellulose fibers in suspension form three-dimensional networks (flocs). Strong flocculation at high fiber concentrations compromises sheet uniformity and thus papermaking in this regime is avoided.

In this presentation, we describe how the rheology of highly concentrated fiber can be controlled by the addition of small amounts (1-3 wt%; wt/wt fiber) of high molecular weight water-soluble polymer. We studied the influence of polymer (sodium carboxymethyl cellulose) concentration on the rheology of a bleached softwood pulp using a controlled strain rheometer to make small amplitude oscillatory shear measurements and steady shear measurements at small strain rates. These measurements indicate that the presence of unadsorbed polymer in the suspension reduces the strength of fiber flocs. This is consistent with the hypothesis that water-soluble polymers alter the interactions at fiber contact points. We also show how atomic force microscopy can be used to measure fiber interaction forces, and present results showing how water-soluble polymers affect the dynamic interactions between model cellulosic surfaces and fibers.

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PO5

ON THE MODELLING OF A PIB/PB BOGER FLUID IN EXTENSIONAL FLOW**Richard Verhoef*, Ben van den Brule*, Martien Hulsen****

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We will report on elongational flow measurements of a PIB/PB Boger fluid in a filament stretching device. Attention will be paid to both inception of elongational flow and subsequent relaxation. The results will be compared against predictions from various differential constitutive equations, including Oldroyd-B, Giesekus,

FENE-P and the recent models put forward by Hinch and Rallison that include a viscous contribution to the stress. We will propose an improved model of the latter type which gives satisfactory predictions for both start-up and relaxation.

Wednesday 5:30 Legislative PO6

METHOD OF DISTURBANCES FOR VISCOELASTIC FLOWS IN LONG CHANNELS WITH COMPLEX CROSS-SECTIONS

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It is well-known that rectilinear flows in long channels with complex cross-sections do not generally exist. This is due to the occurrence of non-zero second normal stress difference. Nevertheless, all observations and recent numerical simulations indicate that the secondary flows are very weak and can be considered as small disturbances of a basic quasi-rectilinear flow (BRF). The BRF can then be found using a simple variational procedure, and the secondary flows, from a linear set of PDEs, with coefficients depending on the BRF. Simple and effective analytical-numerical procedures have been developed for solving respective boundary problems, when using a nonlinear multi-mode viscoelastic constitutive equation of differential type. The results of calculations are compared with experimental studies for two polyisobutylenes at high Deborah numbers.

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AN EXPERIMENTAL/THEORETICAL INVESTIGATION OF LINEAR AND WEAKLY NONLINEAR STABILITY OF MULTILAYER CHANNEL FLOWS

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The majority of prior studies on interfacial stability of multilayer flows have dealt with the linear stability of this class of flows. In order to gain an understanding of the mechanism(s) that give(s) rise to these instabilities as well as the influence of nonlinear effects, our present investigation has centered around the analysis and observation of these instabilities in model multilayer polymeric flow systems. Specifically, in this study we have examined the linear and weakly nonlinear stability of multilayer pressure driven flow of viscoelastic fluids both theoretically and experimentally. The theoretical portion of this work examines the linear and weakly nonlinear stability of these flows to 3-D disturbances by utilizing asymptotic techniques (i.e., regular perturbations, method of multiple scales), bifurcation analysis and spectrally based numerical methods. Based on these studies, the effect of various parameters such as viscosity and layer depth ratio as well as first and second normal stresses on the linear and weakly nonlinear stability of this class of flows has been identified. We have also investigated the mechanism(s) of interfacial instabilities by performing a rigorous energy analysis. In our experiments, both polymer melts and Boger fluids have been used to examine the stability of this class of flows. Upon comparison of theoretical and experimental results, it is shown that a constitutive model that can accurately predict the steady and dynamic rheological properties of the test fluids is capable of providing an accurate picture of the interfacial stability both in the linear and weakly nonlinear regime.

Wednesday 5:30 Legislative PO8

IMPACT OF PHYSICAL AGING ON CRAZE GROWTH UNDER STRESS RELAXATION CONDITIONS

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Crazing is a dilatational phenomenon in glassy polymers that can be the precursor to failure in long term performance conditions. Craze initiation and propagation are known to be related to the viscoelastic properties of the bulk material and are resultingly sensitive functions of such parameters as temperature that influence these properties. Therefore, one would also expect the physical aging process, in which viscoelastic properties are observed to change due to, e.g., densification of the polymer after a quench, to also impact the craze process. Here

we present the first examination of the effects of physical aging on the growth in length of crazes. Craze growth tests were performed on a styrene-acrylonitrile copolymer in stress relaxation conditions by bending a strip of material over a known elliptical geometry (Bergen Jig). In each experiment a range of strains from 0 to 0.016 was obtained. Samples were aged isothermally for times from a few to 1000 hours prior to applying the deformation. The temperatures examined varied from ambient to 330 K. A video system attached to a microscope was used to capture images that were analyzed to obtain craze growth data. The craze length was found to vary linearly in the logarithm of the loading time and the logarithmic rate of growth was found to depend on both aging time and temperature. The results will be discussed in the context of current viscoelastic models of crazing.

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PO9

INVESTIGATION OF FLOW-INDUCED MORPHOLOGY OF IMMISCIBLE POLYMER BLENDS

H. Yang, P. Van Puyvelde, P. Moldenaers and J. Mewis

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Linear conservative dichroism and small-angle light scattering (SALS) have been used to probe the flow-induced morphology of dilute immiscible polymer blends (PDMS/PIB). In a sufficiently strong shear flow, i.e. capillary number larger than twice the critical one, the dichroism evolves in a complex manner, displaying both a maximum and a minimum. This evolution is attributed to elongation, break-up and coalescence of droplets. The initial fast increase of the dichroism depends only on strain and has been modeled. When the flow is suddenly interrupted at this stage, the dichroism decreases with time in a specific way. The corresponding SALS pattern shows multiple streaks due to the Rayleigh disturbance on the surface of the elongated droplets. Using a suitable scattering model, the position and the intensity of the streaks can be used to deduce the wavelength of the disturbance and the size of the droplets.

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PO10

TWO FLUID MODEL OF THE APPARENT SLIP IN POISEUILLE FLOW

Lourdes de Vargas*, Arturo F. Méndez-Sánchez* and José M Tejero**

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A two fluid model was developed to simulate the apparent slip phenomenon in Poiseuille flow. The fluids were considered inelastic and the fluid near to the wall obeyed a power law behavior. The equations of motion were solved by assuming no-slip at the wall. Also, that the velocity field is continuous through the whole die section. The obtained slip velocity expression predicts a non-linear dependence on the reciprocal of the die gap size. The shear rate function of the core-fluid free from the apparent slip, and the fluid parameters for the fluid in contact with the wall can be evaluated by non-linear fitting.

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PO11

FORCED REPTATION RHEOLOGY MODEL

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A rheology model has been developed which brings together Graessleys concept of treating entanglements as couples, the framework of molecular network theory developed by Lodge, and the concept of reptational pathways first introduced by de Gennes. The model predicts a zero shear viscosity - molecular weight scaling of 3.5; far closer in agreement with experiment (3.4) than the classic reptation model (3.0). A description of this new model will be presented along with linear and non-linear viscoelastic predictions for various polymer systems.

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PO12

THE WORK OF ADHESION OF POLYMER/WALL INTERFACES AND ITS ASSOCIATION WITH THE ONSET OF WALL SLIP

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The interfacial characteristics of a variety of polymer/wall interfaces were measured by using the sessile drop method in order to calculate the work of adhesion. Polymers included linear low-density as well high-density polyethylenes, while wall substrates included clean stainless steel and modified stainless steel by applying two different fluoropolymers in order to alter its surface energy. It was found that the work of adhesion of the various interfaces scales linearly with the critical shear stress for the onset of slip of the corresponding polymers under shear in agreement with theoretical predictions by Hill et al. (1991) and Hatzikiriakos et al., (1993). In the present work, the experimental results are interpreted in terms of parameters defined by these two theories. It is suggested that small deviations from the no-slip boundary condition in the case of polymer melt flow are due to a stress-induced chain detachment/desorption of polymer chains from the wall.

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PO13

HOW BUBBLY MIXTURES FOAM AND FOAM CONTROL USING A FLUIDIZED BED

***Jose Guitian, *Daniel Joseph, and **Clara Mata**

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In hydrocracking and other foaming reactors, the foam rises to the top because it has a higher gas fraction than the bubbly mixture from which it comes. The high gas hold-up in foams is undesirable in chemical reactors because it strongly decreases the liquid residence time and in hydrocracking reactors also promotes the formation of coke. To study foams we built a cold slit bubble reactor which when used with aqueous anionic surfactants gives rise to foam. This reactor reproduces the foaming processes which are characteristic of the commercial system CANMET from PetroCanada. We discovered a critical condition for foaming; when the gas velocity exceeds a critical value which depends on the liquid velocity, a foam interface appears at the top of the reactor, with foam above and bubbly mixture below. The interface is very sharp and it moves down the reactor as the gas velocity is increased at a constant liquid velocity. This is the way reactors foam, with the bubbly mixture being consumed by foam.

The foam may be destroyed by increasing the liquid velocity backing up against the foaming threshold. The reactor partitions into two phase, two phase flow with bubbly mixture below and foam above. The bubbly mixture is dispersed gas in water plus surfactant; the phase above is a foam through which large gas bubbles rise. Constant state theories for the bubbly mixture, the foam and the position of the foam interface are derived and semiempirical correlations are presented.

Foaming may be strongly suppressed by fluidizing hydrophilic particles in the bubbly mixture below the foam. The suppression is achieved by increasing the liquid hold-up by bed expansion; by increasing the wetted area of solid surface (walls and particles) and by decreasing the gas hold-up by increasing the effective density of the liquid-solid mixture. Even greater suppression of foaming can be achieved by fluidizing hydrophobic particles.

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PO14

PARTICLE TRACKING VELOCIMETRY STUDIES OF BUBBLE PENETRATION THROUGH VISCOELASTIC FLUIDS IN CAPILLARY TUBES

Vishal Gauri and Kurt W. Koelling

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The penetration of a long inviscid bubble through ideal elastic fluids in a capillary tube geometry is studied using Particle Tracking Velocimetry (PTV). Experiments are performed to characterize the fluid kinematics around the bubble tip. Streamlines and contour plots of constant shear rates and extension rates are presented for both the Newtonian and Boger fluids in the recirculation and complete bypass flow regimes.

The residual coating thickness for Newtonian fluids is a function only of the Capillary number ($Ca=U_b\eta/\sigma$). The ideal elastic Boger fluids exhibit a substantially higher fractional coverage at large Ca . This can be attributed to the elastic and extensionally thickening nature of the fluids. At a Deborah number of $De = \lambda \cdot d\gamma/dt \approx 1$, the coating thickness deviates from Newtonian behavior. A region of extensional flow is observed close to the interface. Local extension rate in this region is approximately half the magnitude of the local shear rate. Since the fluid extensionally thickens at $\lambda d\epsilon/dt \approx 1$, this suggests that the extensionally thickening response of the Boger fluids has a significant effect on the fractional coverage.

Flow field simulations for the Newtonian fluids are conducted using POLYFLOW. A comparison of the results from experiments and simulations is presented in order to validate experimental techniques.

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PO15

X-RAY SCATTERING STUDY OF MOLECULAR ORIENTATION IN A MODEL THERMOTROPIC LIQUID CRYSTALLINE POLYMER DURING STEADY AND TRANSIENT SHEARING FLOWS

Victor M. Ugaz and Wesley R. Burghardt

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We use *in-situ* x-ray scattering techniques to directly measure the effect of flow on molecular orientation in a model thermotropic LCP. This model material, synthesized by Chang and Han [*Macromol.* 29 (1996): 2383-2391], consists of rigid mesogens randomly copolymerized with flexible spacer chains of two different lengths. This architecture effectively suppresses melt recrystallization while giving the LCP an accessible isotropic transition temperature, thereby allowing a well-defined thermal history to be established prior to application of shear flow. We present measurements of molecular orientation in steady shear flow, during relaxation upon cessation of shear flow, and in the transient period during shear flow inception. In the transient experiments, x-ray scattering patterns were collected using a high-speed electronic position sensitive detector which provided exceptional time resolution. The evolution of molecular orientation observed during shear flow inception appears to be consistent with flow aligning behavior. This conclusion is supported by calculations using the Ericksen transversely isotropic fluid model.

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PO16

MICROMECHANICS OF CELLULAR STRUCTURES USING SYNCHROTRON TOMOGRAPHY

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The mechanical properties of cellular structures have been calculated by large-scale finite-element simulations, using up to 17 million elements. Accurate representations of the microstructure were obtained by synchrotron tomography; samples studied include human trabecular bone and aluminum foams. The calculated elastic constants of these samples were found to agree with experimental measurements.

The tomographic images show that the architecture of trabecular bone is quite different from that of surface-minimized structures such as aluminum foam. In particular the mean coordination number in trabecular bone is 3 whereas in aluminium foam, and other surface-minimizing structures, it is 4.

The variation in elastic stiffness with density has been studied for several samples, by uniformly removing or adding material to the surfaces. We find significant deviations from classical scaling laws, which are based on the mechanics of beam bending. Trabecular bone reorganizes its structure by biological remodeling, in order to reduce stress; a consequence of this remodeling is an increase in direct compressional resistance in the primary load direction. In the other orthogonal directions, the scaling is consistent with bending of trabecular elements.

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PO17

EVOLUTION OF COMPOSITIONALLY-INDUCED CHANGES IN THE MORPHOLOGICAL AND RHEOLOGICAL PROPERTIES OF TRIBLOCK COPOLYMER BLENDS

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Depending upon composition, triblock copolymers may exhibit a range of morphologies (cylindrical, lamellar, etc.) and chain conformations (looped versus bridged mid-blocks). Moreover, for a given lamellar triblock copolymer, it is also possible to alter the morphology and chain conformation through the addition of miscible homopolymer or diblock copolymer. In this study, the evolution of the physical characteristics of poly(styrene-*b*-isoprene-*b*-styrene) (SIS) triblock copolymer are examined for its blends with homopolyisoprene (hI) and poly(styrene-*b*-isoprene) diblock copolymer (SI). Blend composition, hI molecular weight, and I-block molecular weight of the SI diblock have been systematically varied. Rheological measurements are used to infer possible scenarios of compositionally-induced changes in chain conformation. Identification of blend morphology is accomplished through transmission electron microscopy and small angle x-ray scattering.

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PO18

EFFECT OF JUNCTION FUNCTIONALITY ON THE RHEOLOGY OF ASSOCIATIVE TRIBLOCKS IN MICROEMULSION SOLUTIONS

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Our goal is to gain a better understanding of the physics of associative systems, to determine which parameters best tune the rheology of solutions for specific applications. The system is a water-in-oil microemulsion, with sodium 2-diethyl hexyl sulfosuccinate (AOT) as the surfactant and decane as the oil. The addition of associative triblock polymers with short hydrophilic endgroups of polyethylene oxide and longer midblocks of polyisoprene forms a transient network. Since the polymers are insoluble in decane, the composition determines the junction functionality, unlike micellar solutions, in which thermodynamics controls. At lower junction functionalities we approach the limit of a classical reversible network, and oscillatory experiments show Maxwellian behavior with a single relaxation time. For higher numbers of polymers per droplet, we approach the limit of micellar solutions of associative polymers, with the droplets covered with a layer of polymer chains in a looped configuration. The rheological behavior in this case is much more complex. The high frequency modulus increases monotonically and roughly quadratically with junction functionality, as compared with the $3/2$ power dependence predicted by Semenov and co-workers. Both dynamic and steady shear experiments show evidence of two relaxation mechanisms, with the longer relaxation time due to dissociation of the endblocks which form bridges between the droplets. The faster relaxation appears to be caused by "hopping" or deformation of the droplets and the polymer chains looping between the droplets. We are planning experiments to isolate the two different mechanisms, including rheological studies of diblocks and systems with differing association strengths.

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PO19

NONLINEAR VISCOELASTICITY OF ABS POLYMER MELTS

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Experimental transient viscosity data for start-up of steady shear and uniaxial extension for commercial grade ABS polymer melt are presented. These data as well as stress relaxation data after both deformations were used to fit three nonlinear viscoelastic constitutive models based on linear viscoelastic spectrum of the melt obtained from oscillatory shear measurements. Phan-Thien and Tanner model resulted in the best overall fit, although it predicted nonphysical oscillations of steady shear viscosity at high strain rates. Qualitative differences between the first normal stress difference model predictions and experimental data for stress relaxation after uniaxial extension are discussed.

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PO20

SMECTIC RHEOLOGY**R. W. Connelly***, **R. H. Colby****, **C. K. Ober*****, **J. R. Gillmor***, **T. Duong***, **G. Galli******
and M. Laus*****

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We have studied the oscillatory shear response of three thermotropic smectic-A liquid crystalline materials with no external aligning field (other than the necessary presence of rheometer plates). Two are polymers (one main-chain and one side-chain) and the other is a small molecule smectic. All three exhibit the classical linear response to oscillatory shear characteristic of a viscoelastic solid at sufficiently small strain amplitudes and frequencies. However, for strain amplitudes exceeding a small critical value, these materials exhibit a strongly nonlinear response to strain, which is characterized in detail. While the low-strain moduli and the critical strain of the three smectics are considerably different, the nonlinear response has some universal character which is presumably related to the low energy for the formation of defects in smectic liquid crystals.

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PO21

FROM SOLVENT TO SOLID - THE RHEOLOGICAL CHARACTERISATION OF POLYSTYRENE**U. T. Reinhardt**

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The applications of polymers cover an extremely wide range of concentrations. For drag reduction polymer solutions with concentrations of only a very few ppm are needed, while plastic materials for everyday use ideally consist of the pure material itself. Due to this wide range of applications a matching range of concentration is necessary for the full characterisation. In spite of the wide range of viscosity (0,6 mPa·s to 3,6 MPa·s), materials and testing methods (step strain, multiwave, intrinsic viscosity) a single instrument, i.e. the PHYSICA UDS 200, was sufficient to perform the measurements.

In order to examine the transitions between different states of solution polymer standards and rheo-optical techniques were employed. By calculating the theoretical orientation and comparing it to the observed one, information about molecular interactions were obtained.

To observe the practical influence commercial samples were tested at concentrations between 0 and 50 %. It was possible to distinguish dilute semi-dilute and concentrated solution and to calculate the critical concentration and the intrinsic viscosity.

The very same sample was used to demonstrate the transitions which take place during changes in temperature. Step strain and oscillation tests made it possible to observe the temperature dependent changes in the interactions between the molecules.

Furthermore a close look was taken at the kinetic of the polymerisation. Three decades of frequencies were used in a multiwave frequency time experiment to investigate changes during the reaction. Self accelerating effects in the course of the radical polymerisation were observed and explained.

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PO22

TUBE MODEL: EFFECT OF DEFORMATION ON TUBE CROSS SECTION**G. Ianniruberto and G. Marrucci**

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While the tube model of Doi and Edwards certainly captures many aspects of the rheological response of entangled polymers, it also predicts a major instability in steady shear (close to the onset of nonlinear behavior) which is in fact not observed. Rather, the well known Cox-Merz rule applies. We here investigate on the effect that different assumptions on tube deformation may have on shear and normal stresses in steady flow. Indeed, one of the questionable assumption of the classical theory is that the tube keeps its cross section unaltered in spite of deformation. Also, the mean effect of the convection of the surrounding chains is not accounted for in the basic theory. It is here shown that a judicious choice of how to account for the missing effects can perhaps explain the available evidence. One important ingredient seems to be the non-circularity of the tube cross section.

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PO23

ELECTRORHEOLOGICAL BEHAVIOR OF DIVERSE PARTICLE SUSPENSIONS**S. W. Henley and F. E. Filisko**

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ER active suspensions have previously contained one type of particle. However there has been speculation, based in one instance on Sillars work, that particles of non-spherical shapes may enhance ER behavior. His work shows that elliptical particles produce dielectric dispersions of greater intensity which have been related to ER activity. In this study we are investigating suspensions of particles of various shapes and mechanical properties as well as standard ER suspensions containing small amounts of these particles. Significant improvements in ER activity were observed with some of these particles. Small amounts of "soft" particles as well as particles which were chemically modified to be ER active showed dramatic improvements. We relate this behavior to selective segregation of the minor particles toward slip planes due presumably to hydrodynamic and/or electrical forces.

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PO24

MELT RHEOLOGY OF POLY(LACTIDE)**Jinlin Wang*, Robert Kean*, Jed Randall*, and David Giles****

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The rheological behavior of a biodegradable polymer, poly(lactide), was characterized using a stress controlled rheometer. The steady state viscosity, dynamic shear modulus, and dynamic viscosity were measured at different temperatures and shear rates. The Cox-Merz rule was used to relate the dynamic viscosity to the steady state viscosity. An empirical equation was developed to correlate the zero shear rate viscosity with molecular weight and tacticity of poly(lactide). Using the time-temperature superposition principle, a master curve for the linear poly(lactide) was constructed. The results from rheological measurements showed that the chain branching and molecular weight distribution have a significant effect on the shear thinning viscosity of poly(lactide). The flow properties and activation energy calculated from rheological data were compared with commodity thermoplastics. The effect of thermal degradation on the viscosity of poly(lactide) melts was also studied.

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PO25

COMPUTER SIMULATION OF THE YIELD STRESS OF STRONGLY AGGREGATING DISPERSIONS**Robert A. Lionberger**

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The yield stress is an important property in the processing of many different suspensions and as it is easily measured it is often used as a simple characterization. However the relation between the yield stress, interparticle forces and suspension microstructure are as yet unclear. Even the observed inverse square dependence of yield stress on

particle size is not well explained. We are measuring the yield stress via computer simulations which allows a complete characterization of the suspension microstructure for a given interparticle force law.

There are large amount of measurements of the yield stress for systems with well characterized interparticle forces for which existing empirical models of the yield stress (Kapur, Scales, Boger, and Healy AICHe J. (43) 1171 (1997)) describe the volume fraction dependence. However, the connection of the physical parameters of the models with reality is tenuous. From the simulation, structure parameters such as the coordination number, distribution of interparticle separations, fractal dimension, and the number of stress bearing interparticle contacts can be measured directly and connected to the yield stress. The magnitudes of the yield stresses extracted from the simulation are in accord with the measured values. The microstructure of these strongly aggregating suspensions is characterized by dense regions and voids, with the length scale for the inhomogeneities decreasing at higher volume fractions.

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PO26

STUDY OF MONODISPERSE POLYMER DEGRADATION IN A FAST TRANSIENT EXTENSIONAL FLOW

John D. Clay and Kurt W. Koelling

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The mechanochemical degradation of monodisperse polystyrene solutions is studied. High molecular weight polystyrene ($M_w = 1.1 \times 10^6$, $M_w/M_n = 1.06$) is dissolved in 1-methyl-naphthalene or polystyrene oligomer (Boger fluid). The solutions are passed across an axisymmetric sharp contraction using an opposed pistons device. The flow field is inhomogeneous, with pure extensional flow at the centerline. The sharp contraction geometry results in an impulse jump in the extension rate. The magnitude of the extension rate is varied by adjusting the piston speed and contraction ratio. Degradation is measured by analyzing the molecular weight distributions using gel permeation chromatography. Comparisons are made about the effect of different concentration regimes and different solvent viscosities on flow-induced chain scission.

The experimental work is combined with simulations of the flow field. The type of flow has a profound effect on stress transfer in macromolecular solutions. Extensional flows are much more effective in deforming the microstructure compared to shear flows. In this study, the flow character in a sharp contraction flow is calculated and mapped onto the flow field. The flow field character is represented with a scalar parameter proposed by Astarita. This scalar differentiates between different deformation mechanisms. The flow classification parameter will be used as a measure of the effectiveness of important flow variables leading to molecular degradation.

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PO27

EXTENSIONAL AND SHEAR RHEOLOGY OF DILUTE, BIMODAL POLYMER SOLUTIONS

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Rheological behavior of polymer solutions is highly dependent upon molecular weight distribution. The purpose of this study is to determine the effect of varying individual polymer concentrations in bimodal solutions of monodisperse polymers on transient extensional and shear properties. A filament stretching rheometer is used to measure extensional properties of dilute, bimodal polymer solutions in uniaxial extensional flow. The properties of interest are the transient extensional viscosity, transient Trouton ratio, and Hencky strain. The polymer solutions consist of combinations of 1.24×10^6 g/mol M_w ($M_w/M_n = 1.06$) and 8.99×10^6 g/mol M_w polystyrene ($M_w/M_n = 1.23$) in Hercules A-5 oligomeric polystyrene 430 g/mol M_w . Total polymer concentrations are fixed at 0.2 wt%. Solutions are measured at extension rates ranging from 0.65 to 2.5 sec^{-1} . Ratios of both monodisperse polymers are varied in each solution (polymer weight fractions of 1/0, 0.90/0.10, 0.77/0.23, 0.64/0.36, 0.52/0.48, 0.39/0.61, 0.26/0.74, 0.13/0.87, 0/1 for 1.24×10^6 M_w and 8.99×10^6 M_w polystyrene respectively). Rheometrics RMS-800 and RFS-II rheometers are used to measure shear viscosity temperature and shear rate dependence, first normal stress coefficient, and dynamic loss and storage modulus. Transient extensional results are then compared with transient shear results.

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PO28

COMPARATIVE STUDY OF FILM CASTING OF BLENDED AND CO-EXTRUDED POLYETHYLENE FILMS**Baigui Bian and Albert Co**

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The combination of two or more polymers by blending or coextruding provides desirable film properties that are difficult to achieve with pure materials. Several investigators have studied the difference in the mechanical properties of blended and coextruded films. However, the difference in their processing behavior is rarely considered. This study investigates the difference in the film casting of blended and coextruded films. The single layer films are made from blends of a LLDPE and a LDPE. The three-layer (A/B/A) coextruded films are made from the same resins with the same mass ratios as those in the blended films. The effect of mass ratios on molten film tensions and velocity profiles in both single layer blended films and three-layer coextruded films are examined. The differences in the processing behavior of blended films and coextruded films are observed.

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PO29

MORPHOLOGY AND PROPERTIES OF MODEL PRESSURE SENSITIVE ADHESIVES**D. W. Giles, R.-M. Ho and C.W. Macosko**

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The morphology and rheology of a model pressure sensitive adhesive (PSA) blend system was studied with transmission electron microscopy (TEM) and dynamic mechanical analysis (DMA). The studies provide a basis for understanding structure/property relationships, and illustrate useful methods for improved PSA formulation. The model PSA blend system we used was a Kraton SIS triblock copolymer with midblock and endblock associating resins. The use of midblock associating resins as tackifiers to reduce the rubbery modulus to the level low enough for effective PSA performance is well known; we also illustrate the use of endblock associating resins as stiffeners to raise the glass transition of the styrenic endblock, with the goal of increasing the temperature range and holding power of the PSA. The morphology and rheology provide clear indications of the miscibility or immiscibility of the two resin types in the block copolymer microstructure. They confirm whether candidate resins are midblock or endblock associating (or both). TEM directly shows the effect oligomer resins have on the morphology (the microstructure and/or macrophase separation). DMA is a sensitive indicator of the effect on the glass transition (as well as the modulus, and the order-disorder transition) so is a key tool in formulating for increased temperature range. General methods for studying the complex mixing phenomena in mixtures of oligomers in block copolymers are shown.

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PO30

EFFECTS OF POLYMER-SURFACTANT INTERACTIONS ON ATOMIZATION AND ELONGATIONAL VISCOSITY OF "SOLUBLE OIL" MACHINING FLUIDS**S. M. Yurgelevic, J. M. Smolinski, E. Gulari, and C. W. Manke**

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The control of machining fluid mist produced by liquid breakup during high-speed machining operations is an issue of increasing concern in metalworking industries. Small mist particles (< 5 microns diameter) are easily entrained in the surrounding air, leading to worker exposure to machining fluid mist via inhalation. Small concentrations of dissolved high molecular weight polymers can act to reduce the misting of machining fluids by modifying their rheology. In straight oil machining fluids, the antimisting effectiveness of the polymeric additive has been correlated directly with the elongational viscosity contributed by the polymer. The behavior of "soluble oil" machining fluids (which are oil-in-water emulsions stabilized by petroleum sulfonate surfactants) containing antimisting polymers is more complex because the fluid contains a dispersed phase, and because chemical associations may develop between the polymer and the surfactants present in the fluid. Here we examine the influence of polymer-surfactant interactions on the atomization characteristics and elongational viscosity of polyethylene oxide (PEO)-treated model

"soluble oil" systems in which paraffinic oil is emulsified with a range of surfactants including petroleum sulfonates and Triton co-surfactants. The atomization experiments are conducted with a coaxial airblast atomizing nozzle, and droplet size distributions in the sprays are evaluated by an optical particle sizer. The elongational viscosity of the PEO-treated emulsions is measured by a Rheometrics RFX extensional rheometer. Both the atomization experiments and the elongational viscosity measurements reveal strong interactions between PEO and petroleum sulfonate surfactants.

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PO31

MOLECULAR STRUCTURE AND CREEP RECOVERY BEHAVIOR OF POLYETHYLENE MELTS

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Elastic properties of melts of a long-chain branched low density polyethylene (LDPE) with a broad molecular mass distribution and a short-chain branched linear low-density polyethylene (LLDPE) with a more narrow molecular mass distribution were investigated by creep recovery measurements in shear. The results obtained by means of a magnetic bearing torsional creep apparatus in the linear-viscoelastic region, showed that the steady state recoverable compliance of the LLDPE is greater by a factor of two than that of the LDPE. In the short-time region up to 1000 seconds, however, the time-dependent recoverable compliance of the LDPE is higher than that of the LLDPE. The retardation times for the LLDPE are considerably longer than for the LDPE. For the LDPE the temperature dependence of the entanglement transition is consistent with that of the terminal zone of the creep compliance. The activation energy of 58 kJ/mole lies in the typical range for long-chain branched polyethylenes. In the case of the LLDPE the creep compliances can be shifted to give a mastercurve with an activation energy of 34 kJ/mole, whereas the recoverable compliances do not follow the time-temperature superposition principle. The molecular characterization using TREF showed that the LLDPE has a bimodal branching structure. In addition to a short-chain branched component, a low percentage of a linear constituent with high molecular mass was found. It is postulated that this linear component forms a dispersed phase in the matrix of the short-chain branched constituent. The resulting interfacial tension could be the reason for the long retardation times, the high steady state recoverable compliance and the fact that the time-temperature superposition principle is not fulfilled in the case of the LLDPE investigated.