Abstracts from the
53rd Annual Meeting of The Society of Rheology
Louisville, Kentucky
October 11–15, 1981

Plenary Lectures

P1. Kinetic Theories for Melt Rheology. R. Byron Bird, *Chemical Engineering Department & Rheology Research Center, University of Wisconsin, Madison, Wisconsin 53706.*

The network theories for polymer melts have their origins in the Green–Tobolsky publication of 1946. Later articles by Lodge (1956) and Yamamoto (1956–1958) developed the network theories more fully and applied them to nonlinear rheological properties.

The reptation theories are of more recent vintage, beginning with the Doi–Edwards papers of 1978–1979. The theory has been reformulated and further studied by Curtiss and Bird (1981).

The two classes of theories will be compared and contrasted, particularly as regards their usefulness in rheology and polymer fluid dynamics.

P2. Recent Studies of the Rheo-Optics of Polymers. Richard S. Stein, *Polymer Research Institute, University of Massachusetts, Amherst, Massachusetts 01003.*

The term "rheo-optics" was suggested over twenty years ago by Don LeGrand as pertaining to the application of optical techniques for the following rheological phenomena. Over the years we have used such methods involving birefringence, x-ray diffraction, infrared dichroism, and light scattering for the following of the deformation behavior of polymers. In recent years, methods have been extended to include small-angle x-ray scattering and neutron scattering. Experiments have been carried out during relaxation where samples have been held at constant length or during oscillatory experiments. The former have the advantage of being extendable to the high strain region, whereas the latter are susceptible to steady-state signal averaging over many cycles of vibration. Recent developments to be discussed in this paper include the use of computer techniques for signal averaging in dynamic experiments, the use of time-resolved FTIR techniques with dynamic infrared studies (in cooperation with S. L. Hsu), the use of one- and two-dimensional optical multichannel analyzers for rapid acquisition of light scattering data, the use of synchrotron sources for the rapid acquisition of x-ray diffraction data during relaxation, and the use of one- and two-dimensional position sensitive detectors for studies of time-dependent small-angle x-ray scattering. The utilization of small-angle neutron scattering in which a species is molecularly labeled with deuterium gives promise for studying single chain relaxation

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behavior within solids. In some cases, such as with dynamic light scattering from crystalline polymers, much experimental data have been gathered but these await theoretical advances for their interpretation. The present state of theory is discussed. The role of dynamic form birefringence and distortional birefringence is considered in the interpretation of experiments. Applications of the techniques are discussed for polyethylene, polystyrene, polyacrylonitrile copolymers, and polymer blend systems.

P3. Structure–Property Relations for Composite Materials–Some Critical Issues. J. L. Kardos, *Materials Research Laboratory and Department of Chemical Engineering, Washington University, St. Louis, Missouri 63130.*

The burgeoning technology of composite materials is now facing some crucial barriers toward rapid expansion into the structural materials area. Several of these issues will be identified for both short fiber and continuous fiber systems. The state of our current knowledge in these problem areas will be sketched and some possible new research directions will be explored.

Bingham Award Lecture

P4. Rheology and Structure Development in Polymer Processing. James L. White, *Polymer Engineering, University of Tennessee, Knoxville, Tennessee 37916.*

The application of rheological principles to the interpretation of melt flow behavior and structure development in polymer processing is described. Constitutive equations for homogeneous polymer melts and systems filled with high loadings of small particles are described. Comparisons are made to experimental data. The response of polymer melts in various processing operations such as extrusion and melt spinning are contrasted to theoretical predictions. Attention is also given to the specification and development of orientation and crystalline morphology in polymer melt processing. Orientation is related to the stress fields developed during flow. This is shown for melt spinning of fibers, tubular film extrusion, and molding operations. The characteristics of polymer liquid crystals are described.

Session A: Biorheology
Chairman: C. E. Miller

A1. Methodology for Forecasting Mechanical Failure of Prostheses; Sowing the Seeds For Future Research. W. H. Hoppmann, II,* Consultant, *U.S. AMSAA, Aberdeen, Proving Ground, Maryland 21005.*

A proposal for a methodology for forecasting mechanical failures of prostheses is presented. It grows out of past efforts to provide a similar methodology for U.S. Army

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material. With appropriate changes, the ideas, terminology, and rules of operation generated for one field can sometimes be shown to be quite natural for another. Such turns out to be the case for the present topics. The same model can be used for both.

A series of important items are considered to be necessary for the development of the methodology. These include (1) the relationship of the theory of probability and mathematical statistics to the design, production, and use of prostheses; (2) the introduction of an essential informational system; (3) the necessary use of applied science and deterministic methods; (4) the essential but limited testing and stochastic methods as aids to prediction; (5) the use of inspection data which arise in the process of production; (6) the use of inputs from quality assurance and quality control systems; (7) the meaning and use of forecasting in various contemporary activities; (8) the use of case histories and the influence of management on the production and use of prostheses; and (9) the impact of the concept of authority on the development, production, and use of prostheses.

It is considered that the following presentation will suggest various areas for research on the many problems associated with the process of forecasting failure of proposed or actual prosthetic devices. Contemporary studies indicate profound changes for the future use of prostheses and for the methods of predicting their failures.

A2. Continuous Axisymmetric Flow of Human Red Cell Membrane.* R. M. Hochmuth, E. A. Evans, H. C. Wiles, and J. T. McCown, *Department of Biomedical Engineering, Duke University, Durham, North Carolina 27706.*

Preswollen human red cells are sphered by aspirating a portion of the cell membrane into a small micropipet; and long, thin, membrane filaments or 'tethers" are steadily withdrawn from the cell at a point diametrically opposite to the point of aspiration. The aspirated portion of the membrane furnishes a "reservoir" of material which replaces the membrane as it flows as a liquid from the nearly spherical cell body to the cylindrical tether. The application of the principle of conservation of mass permits the tether radius R_t (ca. 200 Å or less) to be measured with the light microscope as the tether is formed and extended at a constant rate. The tether behaves as an elastic solid such that the tether radius decreases as the force or axial tension acting on the tether is increased. A dynamic analysis of the extensional flow process reveals that the tether radius must decrease as the velocity of the tether is increased and that the decrease depends on both the viscosity of the membrane (modeled as a Newtonian liquid) and the elasticity of the tether. The analysis also shows that these two factors (membrane viscosity and tether elasticity) are readily decomposed and determined separately when flow experiments are performed at different isotropic tensions.

For the range of values of R_t in these experiments ($100 < R_t < 200$ Å), the tether elasticity expressed as the slope of the tether-force, tether-radius line is -1.32 dyn/cm. The surface viscosity of the membrane as it flows from cell body to tether is 3×10^{-3} dyn s/cm. This viscosity is essentially constant for characteristic rates of deformation between 10 and 200 s^{-1}.

* This work was supported by NIH grant HL 23728.

A3. Stress Relaxation and Birefringence Studies of Fibrin Film. Fred J. Roska and John D. Ferry, *Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.*

Fibrin film, prepared by compaction of a clot of bovine fibrin, is a structure of coarse fibers lying primarily in the plane of the film and composed of parallel bundles of protofibrils formed by self-assembly of unit molecules 450 Å long. Anastomosis of the bundles forms a branched network. The film typically contains 13–22% fibrin; the remainder (plasticizer) may be an aqueous salt solution or glycerol. The units in the protofibrils are joined, and the protofibrils in the bundles adhere, by noncovalent forces (unligated) unless additional covalent bonds have been introduced by the enzyme fibrinoligase (ligated). The film can be stretched up to 100% in uniaxial extension and, if ligated, recovers with little or no permanent set. Extensive measurements have been made, on both ligated and unligated films, of stress relaxation and birefringence, at uniaxial stretch ratios λ from 1.2 to 1.5. In ligated films held at constant λ, stress decreases and birefringence increases up to 10^2 s, then both remain constant up to 10^4 s. In the constant (plateau) region, stress is proportional to $\ln \lambda$ and birefringence to $2\lambda^2/(\lambda^2 + 1) - 1$. At longer times, stress and birefringence decrease somewhat and small-angle x-ray scattering measurements show that the unit molecules increase in length. In unligated films, the relaxation of stress is more rapid throughout; at long times, the birefringence relaxes but less rapidly than the stress. Conclusions can be drawn concerning the mechanism of elastic energy storage (not rubberlike elasticity) and the mechanisms responsible for relaxation of stress and birefringence.

A4. The Dynamic Morphology of Blood Flow: Implications for Rheology. Edward H. Bloch, *Department of Anatomy, School of Medicine, Case Western Reserve University, Cleveland, Ohio 44106.*

The determination of the flow characteristics of blood requires precise information of the dynamic structure of its container—the vessels and the fluid—the blood—as they exist in the organism, on a temporal basis. Ideally, the rheology of blood should be determined in its normal environment, in health and disease. It is especially important to be aware of how blood is altered in disease as both its suspension stability and adherence of cells to the vessels can significantly alter the flow characteristics: some of these characteristics have not been sufficiently considered or measured by *ex vivo* methods.

The major characteristics of vessels and blood (Homo) are a cardiovascular system that consists of ca. 1.2×10^9 vessels, ca. 99% of which have a diameter from 500 to 5 μm, arterial and venous vessels that have a taper of ca. 1°–2°/branch, the former decreasing toward the capillaries and the latter increasing toward the heart. In the arterial system a pulsatile flow of 72/min av (Homo) which may be as high as 650/min in small animals. To reach the cylindrical capillaries blood must flow through terminal vessels whose bore measures but 1.5× (max) the diameter of the specie's red cell (8 μm, Homo). (Usually each red cell deforms before it enters a capillary.) In disease, cells aggregate. The aggregates consist of red cells, leucoytes, and/or platelets, are equal or varied in size, are only slightly larger than their normal size or several times larger. They may involve any fraction of the circulating cells from a few to 100%, vary in plasticity and rigidity, plug vessels temporarily or permanently, as well as sediment in them. These normal and pathological characteristics of the blood and vessels will be illustrated by motion picture films taken at framing rates of 12–3600 frames per second.

A5. Effect of Delta Gluconolactone on the Rheology of Cementitious Grouts Used in the Disposal of Intermediate-Level Liquid Radioactive Waste.* E. W. McDaniel, *Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.*

The Oak Ridge National Laboratory uses cementitious grouts to dispose of radioactive waste by the hydrofracture technique. In this process, the waste is mixed with cement and other additives to form a grout which is injected into a deep hydrologically fractured, horizontal shale bed. Delta gluconolactone, a sugar, is used as an agent to regulate the set time of the grout. Studies of the properties of the grout showed that the grout thickening time, flow behavior index, and phase separation increased, and the yield value decreased, as the quantity of sugar was increased. Specifically, 0.04 wt % sugar in the dry mix grout extended the thickening time by more than 8 h. Further, increasing the delta gluconolactone concentration from 0.01 to 0.08 wt % in grouts containing 720 g/L solids decreased the yield value from 30 to 2.5 dyn/cm^2 but increased the phase separation from 5 to 25 vol %.

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A6. Future Trends in Biorheology. Frederick R. Eirich, *Polytechnic Institute of New York, Department of Chemistry, Brooklyn, New York 11201.*

The statement "The future is what happens when one expected it otherwise" is as true for biorheology as for any other field. Even so, controversial as it must be, a chart of active, neglected, or as yet embryonic currents will be drawn.

From this, some topics of blood flow, mucoid streaming, motion in plants, membrane transport, cycloplasnic motion, and muscle contraction will be specially pointed out, and possible or desirable directions briefly discussed, with emphasis on the rheologists' preoccupation with correlations of macroscopic and microscopic observations with molecular processes.

Session B: Numerical Simulation of Material Processes
Chairman: B. Caswell

B1. Numerical Results for Plane Flows of BKZ Fluids Using Finite Elements. B. Bernstein and D. S. Melkus, *Department of Mathematics, Illinois Institute of Technology, Chicago, Illinois 60616.*

We have developed techniques to compute solutions to problems of steady flows of fluids with memory of the BKZ type. We employ the integral constitutive equation directly and make use of the "drift function" method of following particle histories. Recent investigations have shown that the Maxwell model in integral form provides a convenient test problem, but the solutions obtained do not differ dramatically from the Newtonian. This talk will discuss new results extending our techniques to constitutive equations which involve shear thinning as well as normal–stress effects. In particular, we will discuss results obtained using an equation of Wagner type with exponential damping and one of the Doi–Edwards/Currie type.

B2. Experimental and Theoretical Investigation of Polymer Flow in Converging Channel. A. I. Isayev, R. K. Upadhyay, and S. F. Shen, *Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, New York 14853.*

An experimental investigation of the isothermal flow of a viscoelastic fluid (polyisobutylene Vistanex LM-MH) converging with an angle of 29° from a large to small slit (width ratio 7.4) has been conducted using a rheo-optical method. The buildup and relaxation of birefringence along the center line, and distribution of birefringence at different cross sections, have been measured with the simultaneous recording of the flow rate and pressure. It is observed that the birefringence maximum along the center line occurs immediately before the entrance to the small slit, and full or incomplete relaxation, depending on the Weissenberg number, occurs before the exit.

A theoretical investigation has been made on the basis of the Leonov constitutive equation. Storage and loss moduli as a function of frequency in the linear region of oscillatory shear flow, and shear stress and first normal stress difference versus shear rate in steady-state flow have been measured. The dynamic data have been used to fit the model parameters while the steady-state data have served as a preliminary check on the predictive capability of the model. A special numerical scheme with streamwise integration of the constitutive equation and the finite element method has been used to compute the velocity and stress field in converging flow at high Weissenberg number. The stress–optical law has been applied to predict the observed birefringence during flow.

B3. Numerical Analysis of Glass and Polymer Fiber Spinning. R. I. Tanner and H. B. Phuoc, *Department of Mechanical Engineering, University of Sydney, Sydney, N.S.W. 2006 Australia.*

In many polymer processing applications the generation of heat by viscous losses in the flowing molten polymer is often significant. In the forming of glass fibers the variation of viscosity owing to temperature variations is also significant, and has the effect of coupling the momentum and energy equations. The temperature rise reduces the viscosity of the melt sharply, and the flow patterns are different from the isothermal case. In this paper a finite element scheme based on the Galerkin method is used to explore the effects of thermally induced property changes in fiber spinning.

After solving the isothermal spinning problem, the more realistic temperature-dependent problem was tackled. The boundary conditions on the free surface for nonisothermal spinning include convection and radiation losses; the latter are significant with glass fiber drawing. The results obtained for glass fiber spinning show the importance of having available accurate heat transfer information, especially for the radiative transfer.

B4. Die Entry Flow of a Maxwell Fluid. Bruce Caswell and Arie Cohen, *Division of Engineering, Brown University, Providence, Rhode Island 02912.*

The die entry flow of a Maxwell fluid has been computed by the finite element method using a memory integral formulation. In this work finite strain computations are carried out by following the motion of particles originally located at spatial integration points. Finite strains are computed by the composition of deformation gradients of the many small deformations computed along particle trajectories. Particular attention is given to the verification kinematical consistency.

B5. Numerical Simulation of the Curing Process for an Epoxy Resin.* C. E. Hickox, D. K. Gartling, J. W. Nunziato, and K. R. Hirschbuehler, *Sandia National Laboratories,*† *Albuquerque, New Mexico 87185.*

The transition of an epoxy resin from an initial liquid state to a relatively solid gel is, in general, a complex transient process that involves chemical reaction kinetics as well as heat and mass transfer. A finite element-based fluid mechanics code that utilizes the Boussinesq approximation has been modified and used for the numerical simulation of the gelation process associated with a particular epoxy resin. The modifications were concerned primarily with the implementation of the Arrhenius reaction kinetics which are assumed to describe the gelation process.

The specific gelation process chosen for simulation is one for which a limited amount of experimental data is available. An epoxy resin and a curing agent are combined, at constant temperature, in a small cubicle container (5 cm on a side) and placed in a constant temperature oven. As the curing process proceeds, heat is generated as a result of the exothermic nature of the reaction, convection cells are observed in the container, and a gelation process is subsequently initiated near the top of the container. Once initiated, a planer gel front propagates rather rapidly through the container (in approximately 5 min). The entire curing process requires approximately 75 min at an oven temperature of 344 K. The epoxy resin used in the experiments was DEGBA (diglycidylether of Bisthenol A), and the primary amine curing agent was TETA (triethylene tetramine).

Computed streamlines, isotherms, and contours depicting the extent of reaction and hence gelation were obtained and compared with experimental observations. Reasonably good qualitative agreement was obtained between experimental and numerical results. Specific difficulties encountered in the simulation process are enumerated.

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B6. On the Flow of a BKZ Fluid in an Orthogonal Rheometer. K. R. Rajagopal, *Department of Mechanical Engineering, The Catholic University of America, Washington, D.C. 20064,* and A. S. Wineman, *Department of Mechanical Engineering and Applied Mechanics, University of Michigan, Ann Arbor, Michigan 48109.*

The motion occurring in the orthogonal rheometer has been studied by several authors. Recently, it has been established by Rajagopal that the equations of motion of a general simple fluid give rise to a differential equation of the same order as the Navier–Stokes equation because of the assumed form of the velocity field. Here we study the problem due to the flow of a BKZ fluid and obtain a numerical solution for the velocity field.

B7. Analogy among Heat and Momentum Transfer For Non-Newtonian Fluids in Laminar Flow Through Pipes. Bahman Ghorashi and Bela Hirsch,* *Department of Chemical Engineering, Cleveland State University, Cleveland, Ohio 44115.*

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The heat transfer to a non-Newtonian fluid, flowing in a heated pipe in the range of $300 \leq G_z \leq 800$ was studied. A polyacrylic-water system which falls in the category of pseudoplastic fluids was used. Until recently, attempts to describe nonisothermal momentum and energy transfer to these fluids have been limited by certain assumptions or restrictions. The laminar flow equations have been solved with restrictive conditions for various non-Newtonian models, characterized by the empirically observed relationships between shear stress and velocity gradient.

In this work an attempt is made to obtain an analogy among heat and momentum transfer using the generalized power law function, valid for all time-independent non-Newtonian fluids. The difference between the Nusselt numbers found experimentally and those determined by the Metzner–Vaugh–Houghton relationship was considered to be due to the free convection, since effects of viscous dissipation of energy and heat generation owing to the internal sources were insignificant for the range of flow rates considered. The free convection, which determined approximately 17% of the total heat transfer, was accounted for by modified forms of Grashof and Prandtl numbers. A new term which includes the modified Grashof and Prandtl numbers is added to Metzner–Vaughn–Houghton relationship in order to include the effect of free convection. It is believed that the resulting equation would describe more adequately the heat transfer to this type of system.

Session C: Nontraditional Experimental Techniques for Determining Viscometric Functions
Chairman: J. J. Ulbrecht

C1. The Use of Nearly Viscometric Techniques to Measure The Normal Stress Function. R. I. Tanner, *University of Sydney, 2006 Sydney, Australia.*

The measurement of the viscometric functions at high shear rates presents several problems. The present paper discusses the measurement of N_1 by using a lubrication geometry. It is shown that the measurement of a single force, a single speed, and a single displacement is sufficient to deduce N_1 at a known shear rate provided the viscosity function is known. Preliminary results with a prototype apparatus show the feasibility of the technique. The use of a fan flow geometry for measuring N_2 at higher shear rates is also suggested, and progress is reported.

C2. The Measurement of Viscoelastic Functions Associated with Shearing at High Strain Rates. J. M. Dealy and S. S. Soong, *McGill University, Montreal, Canada.*

At present, the use of transient shear flows to characterize viscoelastic fluids is limited to rotational rheometers in which the strain rate is limited to low values by edge effects. This is a serious limitation, as many commercial processes involve shearing at large strain rates. Capillary rheometers can be operated at high shear rates, but can only measure viscosity. A new melt rheometer is described that can be used to carry out such tests as stress growth, stress relaxation, and large-amplitude oscillatory shear. The problems arising from rotational flows are avoided by using rectilinear flow, and edge effects are minimized by the use of a shear stress transducer of novel design to measure local wall shear stress.

C3. A New Automated Linear Rheometer. J. M. Starita, *Rheometrics, Inc., Union, New Jersey 07083,* and C. W. Macosko, *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455.*

Most rheological testing is done in torsion. It is often advantageous, however, to use a linear motion. A new rheometer incorporating a linear motor, position sensor, and microprocessor has been developed. The rheometer has a force level of 100 N, displacement of ±5 mm, and frequency range of 0.002–100 Hz. It can operate under displacement or stress control. Application of the rheometer to linear viscoelastic testing of solids in three-point bending, tension, and compression are discussed. Thermal expansion and creep during testing over extended temperature and time scales is accommodated by maintaining the static tension on the sample proportional to the modulus. Viscoelastic response of liquids can also be studied using a shear sandwich and with lubricated squeezing flow (equibiaxial extension).

C4. Differential Rheometry: A New Method for Detecting Changes in Material Functions. M. T. Shaw and W. F. Gebhardt, *University of Connecticut, Storrs, Connecticut 06268.*

Frequently the rheologist is interested not primarily in the absolute value of material functions but in the change of these functions with aging, manufacturing process, molecular weight, etc. By exploiting the simplicities of the squeezing flow geometry, an instrument has been devised that measures directly the differences in viscosity and dynamic mechanical properties of two samples. By careful design and operation of the differential rheometer, property differences in the 1% range can be detected easily, which compares very favorably with the typical 5–10% error associated with conventional instrumentation. A complete analysis of the dynamics of the instrument has been performed, pointing to design changes for increased sensitivity.

C5. A Simple Viscoelastic Tester. W. J. Fenrick, S. J. Armour, and G. A. Hill, *Defense Research Establishment, Suffield, Ralston, Alberta, Canada.*

A simple device for measuring the viscoelastic properties of liquids has been designed and developed. This device has the advantage of requiring only small sample volumes and is suited for use with toxic, corrosive, or pathologically active materials. The device monitors the variation in force applied to a thin metal rod as the test liquid moves relative to it. These force–time signatures are unique to each combination of viscosity and elasticity. A detailed mathematical analysis of the force–time signatures which permits the determination of the complex viscoelastic moduli and the relaxation modulus will be described. The data obtained from this device will be compared with that obtained from more complex rheological test equipment.

C6. The Use of Controlled Jet Instability for Elongational Rheometry. P. Schümmer and K. H. Tebel, *Rheinisch-Westfallische Technische Hochschule Aachen, Institut für Verfahrenstechnik, 5100 Aachen, Federal Republic of Germany.*

A novel stretching technique realizing uniaxial elongational flow of dilute polymer solutions has been designed and developed. The elongational rheometer is based on the behavior of viscoelastic liquid jets emerging into air from a cylindrical nozzle under the influence of external vibrations. The frequency of the vibrating nozzle is an additional operating parameter which adjusts the purely elongational flow. Polymer solutions with shear viscosities lower than 100 mPa s can be elongated in the free jet elongational rheometer.

In general there is no unique deformation history but for suitable operating conditions a transient elongational flow with an approximately constant rate of strain sets in. In any case convenient comparative elongational parameters can be obtained. Furthermore, a new method occurs for measuring low relaxation times by describing the so far undesired effect of increasing filament stability as an elongational flow of an upper convected Jeffreys fluid.

C7. Ultrasonic Rheometry from Pulse-Echo Acoustic Velocity and Attenuation Data. C. K. Jennings and D. O. Harper, *University of Louisville, Louisville, Kentucky 40208.*

In hopes of determining viscoelastic properties of liquids equivalent to those exhibited at very high shear rates, experimental work has been initiated using acoustic wave transmission in the ultrasonic range (MHz). A Panametrics intervalometer permits the accurate measurement of acoustic velocity and attenuation with the pulse-echo overlap technique.

Using longitudinal wave transducers with nominal frequencies of 1.0, 5.0, and 10 MHz and three viscosity standards from Brookfield (49, 507, and 4800 mPa s) the acoustic velocities were found to be about 1000 m/s. These velocities are known to be temperature dependent; they are also slight functions of frequency, viscosity, and acoustic path length. The absorption (or attenuation) coefficients were found to vary inversely with path length and to be slightly dependent upon viscosity; they appear to be independent of frequency. Spurious effects were observed at very short path lengths, effects that increase with increasing frequency.

A similar study using shear wave transducers in the same range of frequency will be performed before the meeting dates.

A demonstration of the device can be arranged after the session.

C8. Novel Method for Dilute Polymer Solution Characterization Using Orifice Flow Techniques. M. Barigah and D. H. Fruman, *University of Paris, France;* and A. Quibrahim, *Ohio State University, Columbus, Ohio 43210.*

It is by now well substantiated that the anomalous effects displayed by dilute polymer solutions in extensional flows are a direct evidence of their viscoelastic properties. The excess energy dissipation versus strain rate behavior of these solutions, in extensional flows (sink flow and stagnation point flow), has been described in terms of three viscoelastic characteristic parameters: an anomalous stress magnitude, a relaxation time, and a power law index. In order to test the validity of such a description, a systematic research has been conducted using a 0.1-mm orifice rheometer for solutions of a large number of polymer compounds (PEO, PAM, HPAM, Guar Gum) and various concentrations and solvent salinity and pH.

To take into account the eventual contribution to the energy dissipation of the non-Newtonian viscosity of some of the solutions, tests were also performed with inelastic solutions of Carbopol.

The analysis of the results confirms and extends to very dilute solutions (2.5 ppm in the case of HPAM) the three parameters description and allows an interpretation in terms of polymer type and molecular weight and conformation. The orifice flow technique looks like a promising tool for the rheological characterization of dilute polymer solutions.

C9. Capillary Rheometry with Annular Dies. P. Kalivoda, *University of Stuttgart, Stuttgart, Federal Republic of Germany.*

Annular capillaries offer several advantages over the circular or the slit capillaries: (1) the rotational symmetry of the die favors precise manufacturing tolerances as well as exact measurement of the die geometry; (2) interchangeable cores (inner cylinder) allow variation of slit width and length; (3) because the shape of an annular die allows that pressure transducers be positioned along its periphery, a direct and very exact measurement of the axial pressure gradient in the die is possible. As well, when measuring the upstream pressure of the capillary, the entrance pressure loss can be directly monitored by transducer; and (4) in contrast to slit dies, no edge effects occur with annuli; stagnation zones at the entrance are avoided.

Limiting factors of annular capillaries include the pressure has to be measured through pressure holes, which are disadvantageous for some polymers; and the influence of curvature complicates the evaluation of the data. It might be ignored for $r_i/r_a = 0.9$.

The influence of the properties of the annular capillary will be estimated.

Session D: Solid-Phase Forming and Novel Processing Techniques
Chairman: M. R. Kamal
Co-Chairman: L. A. Utracki

D1. The Techniques of Ultradrawing. Roger S. Porter, *Polymer Science and Engineering Department, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003.*

The general properties of a novel process for producing high-modulus polyolefins are discussed. The technique is an extrusion drawing involving a crystal–crystal transformation which produces chain extension and efficient crystal orientation. The principal tests have been made on polyethylene, and the guidelines have been established for extending the technique to other polyolefins. The preparation and characterization of such materials is discussed extensively, particularly in light of the concept of continuous crystals.

D2. The Extrusion Drawing of Poly(ethylene Terephthalate). Jose R. C. Pereira and Roger S. Porter, *Polymer Science and Engineering Department, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003.*

Uniaxially oriented poly(ethylene terephthalate) (PET) films have been prepared by solid-state coextrusion surrounded by polyethylene in the temperature range 40–120°C, well below the PET melting temperature and in some cases well below its glass transition temperature. The effect of the initial morphology on the properties of the drawn PET has been investigated by coextruding PET with different initial crystallinities (33 and 50%) to extrusion draw ratios up to 4.8.

D3. Analysis of the Solid-Phase Forming of Semicrystalline Polymers. G. W. Halldin and Y. C. Lo, *Department of Mechanical Engineering, University of Wisconsin, Madison, Wisconsin 53706.*

To exploit fully the solid-phase forming processes, it is necesary to be able to generate a complete solution to the deformation problem. An integral part of each solution is the flow curve or relationship for the material, i.e., the true stress–true strain relationship. There has been a good deal of controversy over the form of this relationship with respect to whether a drop in the true stress occurs upon yielding. Experimentally determined room temperature flow curves will be presented for a wide range of semicrystalline polymers. No drop in the flow stress upon yielding was observed, i.e., the necking behavior of semicrystalline polymers is shown to be a case of geometrical strain softening. Mathematical models for this behavior will be reviewed.

D4. Flow-Induced Crystallization and Orientation. J. R. Collier,* B. Pandya, L. Ankrom,† and S. K. Upadhyayula,‡ *Chemical Engineering Department, Ohio University, Athens, Ohio 45701.*

Highly oriented fibers and ribbons of polyethylene and polypropylene were formed in a process using a single-screw plasticizing extruder as the melt source. These extrudates exhibited properties typical of highly oriented semicrystalline polymers resulting from solid-state and hydrostatic extrusion: transparency, fibrous morphology, elevated melting temperatures, and high initial and secant moduli and yield strength. This process has demonstrated the capability of imparting controlled levels of uniaxial and apparently biaxial orientation, which range up to exceptionally high values. A conditioned polymer melt is fed to specially designed and operated dies where it experiences elongational flow to impart orientation in the desired direction(s), and at least the outer sheath of the extrudate is crystallized in the fixed boundary land of the die prior to exiting.

Elongational flow occurs in the shaping section of the die. The effects of geometry of the shaping section on the extrudate properties and processing conditions were investigated, including the effect of diverging flow in the transverse direction simultaneously with converging flow in the machine direction. The flow behavior in one of the dies used in this process has been modeled illustrating the streamlines that exist.

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D5. Hydrostatic Extrusion of Glass-Reinforced and Unreinforced Celcon POM. J. Kastelic, P. Hope,* and I. Ward, *Celanese Research Co., Summit, New Jersey 07901.*

Several of the solid-state shaping methods developed for metals have been found applicable to polymers. When applied to plastics, such methods as rolling, drawing, and hydrostatic extrusion can impart substantial molecular orientation, consequently enhancing physical properties. Of these techniques, hydrostatic extrusion may have advantages in that glass-filled resins may be employed and more complex profiles may be produced, including hollow sections. Here, we investigate the processing speeds and physical properties attainable by hydrostatic extrusion of glass-reinforced and unreinforced Celcon polyoxymethylene. Large size scale and modest 2–10 area reductions are explored so that commercially feasible production rates can be approached. Both resins can be processed successfully by hydrostatic extrusion. Furthermore, at these modest reductions, significant gains in physical properties are achieved. The strongest beneficial effects are found in tensile and impact strengths. Surprisingly, the elongation of the glass-filled resin is also improved. Glass fiber breakage is not experienced, but a modest amount of debonding is suggested by an observed decrease in modulus at very low reduction ratios (<3). In both resins transverse properties are reduced unless biaxial dies are used. Pressures required for extrusion are found to vary linearly positive with increasing reduction ratio and linearly negative with increasing extrusion temperature.

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D6. Vented Compression Molding: A New Method for Molding Particulates. John McCree and Lewis Erwin, *Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.*

Application of the molding process is usually limited liquid phase processing, since large-scale flow is required to fill a cavity uniformly and reproducibly. Molding of particulates presents a challenging problem, since the large shear strengths and compressible nature of the material make large-scale flow of particulates difficult to achieve. The primary difficulties encountered in molding particulates are nonuniform material distribution in the mold, and nonuniform compaction.

A new process for molding of particulates, vented compression molding, has been developed. Vented compression molding is a modification of standard compression molding that uses a perforated surface as the molding surface. The mold cavity is filled with an excess of material, which is forced out through the openings in the surface of the mold, as the mold closes. The resulting frictional forces, which can be determined approximately by Mohr–Coulomb yield criterion, generate the pressure that compacts the material. Thus, the pressure in the mold is governed by the geometry of the openings and the mechanical properties of the particulate, and not the displacement of the ram. This uncoupling of the pressure–displacement relationship allows uniform material distribution and compaction without requiring large-scale flow of the particulates. An analysis of the mechanisms of vented compression molding is presented.

Although developed primarily for ablative materials used in the space shuttle program, the method is general, and can be applied to a wide variety of materials.

D7. Solid-State Rolling of Linear Polyolefins. D. M. Bigg, E. G. Smith, M. M. Epstein, and R. J. Fiorentino, *Battelle Columbus Laboratories, Columbus, Ohio 43201.*

Solid-state rolling of semicrystalline polymers is shown to be an effective method of producing high-strength, high-modulus tape at acceptable production rates. High-density polyethylene tape was produced having a tensile strength exceeding 300 MPa and a tensile modulus of 8.7 GPa at production rates exceeding 8 m/min. A significant factor in producing high-oriented tape by the rolling process is roll temperature. Increasing the roll temperature from 25 to 125°C not only increases the maximum extent of orientation achievable, but also increases the mechanical properties at a given degree of thickness reduction. Internal frictional heat development limited the maximum thickness reduction ratio of polypropylene to 6.6:1. This reduction was reached by rolling at 150°C. The resultant tape had a tensile modulus of 5.1 GPa and a tensile strength of 300 MPa.

D8. Sequential Forming of Thermoplastic Parts. Richard Kafue Okine and Nam P. Suh, *Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.*

A sequential forming process (SFP) for high-speed production of three-dimensional thermoplastic parts was investigated theoretically and experimentally. In this process, an extruded plastic sheet or profile, at an initially high temperature, is passed through and progressively formed in a series of dies as it cools to room temperature. The development of this method provides an attractive alternative to the injection-molding process in that it has no limitations owing to part thickness and potentially offers low equipment cost and process cycle times. Inadequate knowledge and control of the time–temperature-dependent behavior and large elastic springback of polymers, however, have made similar processes very difficult to implement in the past.

Both the theoretical and experimental aspects of this investigation have involved modeling of plastic viscoelastic behavior to enable the successful prediction of nonisothermal strain recovery. A fundamental understanding of this recovery behavior is essential to the SFP. A two-stage sequential-forming system was designed, constructed, and used to demonstrate the feasibility of the sequential-forming concept to produce fairly complicated polycarbonate and polypropylene parts.

D9. Rheology of Flat Film Coextrusion. C. D. Han, Y. J. Kim, and H. B. Chin, *Department of Chemical Engineering, Polytechnic Institute of New York, Brooklyn, New York 11201.*

An experimental study was carried out to investigate the coextrudability of a number of thermoplastic resins, including low-density polyethylene, high-density polyethylene, nylon 6, ethylene vinyl acetate (EVA), poly(ethylene terephthalate) (PET), polycarbonate, poly(vinylidene fluoride), and poly(methyl methacrylate). For the study, the rheological properties of the individual resins were determined at high shear rates (or high shear stresses) that are of practical interest in coextrusion operations. Measurements of wall normal stresses along the flow direction of the flat-film die permitted us to determine the shear stress at the interface between the layers inside the die. Experimental correlations were obtained to explain the onset of an unstable interface in terms of the rheological properties of the individual components being coextruded, and of the processing variables. It was found that interfacial instability occurs when the viscosity ratio (and elasticity ratio) of the components at the interface exceeds certain critical values.

D10. Direct Extrusion of Polymer Latex Emulsions. R. J. Nichols and R. K. Senn, *Welding Engineers, Inc., King of Prussia, Pennsylvania 19406.*

The preparation of many polymers, such as the terpolymer, acrylonitrile–butadiene–styrene, can be accomplished by dispersing the monomer(s) to be polymerized in water (usually with the aid of a surfactant). The monomer(s) is (are) then polymerized by the introduction of a free radical catalyst, to produce a latex of the polymer. This paper describes a process in which a twin-screw extruder is used to coagulate such polymer latex emulsions. The present commercial practice for the coagulation of a polymer latex to form a dry product typically involves many steps. Several of these steps require substantial transfer of heat into or out of the product. This cyclic heat history is generally detrimental to finished product quality.

The process described combines all of these separate steps into one continuous process, in which the total heat requirement is greatly reduced because the dewatering, drying, and melt extrusion steps are combined. Further, the total quantity of coagulant required is reduced, since the coagulation is much more rapid and complete because of the high shear mixing of the screws. This in turn leads to reducing washing requirements, since washing is used primarily to remove impurities introduced by the coagulant. Additional energy efficiency is maintained by separating the water from the polymer mechanically, in liquid form, rather than vaporizing it. This is accomplished by employing twin-screw mechanical filters in combination with variable back-pressure valves.

Several critical process parameters are identified and discussed in this paper. These include the pressure profile through the coagulation zone, the relationship of coagulation zone pressure with upstream melt seal pressure, and the relationship of the polymer seal dimension to the proportion of water removed. The interaction with the final devolatilization zone and the melt pumping zone are also described. Examples of pilot plant scale experimental data for ABS and acrylic polymers are discussed.

D11. Melt Flow of PET/Nylon 6,6. L. A. Utracki and G. L. Bata, *NRCC-IMRI, Montreal, Quebec, Canada*, and V. Tan and M. R. Kamal, *Department of Chemical Engineering, McGill University, Montreal, Quebec, Canada.*

Capillary, rotational, and dynamic measurements of poly(ethylene terephthalate)–polyamide–6,6 blends were carried out in the range of 240–300°C. The steady-state shear and dynamic viscosities for shear rates between 10^{-2} and 10^{5} s^{-1} and the shear moduli in a range of frequency from 10^{-1} to 10^{2} rad/s were determined. The kinetics of thermal degradation at 260–300°C was also studied.

Of a 47×10^{9}-kg total production of plastics in 1975, $\frac{3}{4}$ were thermoplastics, of these 86% were made up of PE, PVC, PS, and PP. Polymer blends constituted 2%. The projected production of thermoplastics in 1990 is 140×10^{9} kg with an increasing share of the four polymers. This, along with the general decrease of introduction of new polymers on the market, will force the producers to rely more heavily on polymer blends and composites. Indeed the projected production of blends for 1983 is 13% of the total volume of thermoplastics. Alloying provides better flexibility and economics. Unfortunately, so far progress has been made primarily by trial and error. Systematic studies of blends are needed to allow generalization of the phenomena. In this paper we want to report on the progress of work on the flow properties of poly(ethylene terephthalate)-polyamide-6,6 blends. The work constitutes a part of a thorough investigation of the system, which will include study of thermodynamics, rheology, processability, and properties of the finished products.

D12. Endochronic Theory of Plastic Fluids. K. C. Vallanis, *College of Engineering, University of Cincinnati, Cincinnati, Ohio 45221.*

The purpose of the present paper is the application of the endochronic theory to the response of metals undergoing flow, resulting in large deformation. We use the term "large" very advisedly and in a very special context. We imply in fact that the material in question has undergone flow to such a degree that its original atomic structure has been seriously disarranged. In this sense, it is reasonable to argue that the metal in such a highly deformed state has no memory of its reference configuration. It falls therefore within the class of fluids.

We wish, however, to retain the property of plasticity in the context of strain rate independence of the stress response, but history dependence of the current state of stress on the previous history of the deformation.

For the sake of brevity and for the purpose of discussion we call a metal with the above properties a plastic fluid. The derivation of constitutive equations appropriate to plastic fluids is pursued in the setting of irreversible thermodynamics and the endochronic theory of constitutive response. We limit the analysis to isothermal conditions.

Some properties of the plastic fluids are illustrated by application to a simple shearing flow under conditions of large deformation.

Session E: Rheology of Suspensions of Two-Phase Flows
Chairman: J. D. Goddard
Co-Chairman: C. D. Han

E1. New Approach to Predict Concentration Distribution in Fine Particle Slurry Flows. II. M. C. Roco, *Department of Mechanical Engineering, University of Kentucky, Lexington, Kentucky 40506,* and C. A. Shook, *Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0W0.*

The distribution of solid particles in the cross section of slurry pipelines and channels determines both the hydraulic parameters and secondary effects such as wall abrasion. The known diffusion or gravitational models gave satisfactory prediction of the phenomena only at relatively low concentration of the mixture.

The paper suggests a new differential equation governing the mechanism of turbulent suspension, derived from the dynamic equilibrium of the two phases in an elemental volume. The gradient of concentration results from the influence of gravitational force, hindered turbulent motion of carrier liquid, mixing effects owing to solid particle interaction and dispersive forces in the flowing suspensions. Neglecting the last two terms the equation takes a form equivalent with the Schmidt–Rouse diffusion model.

The computational algorithm was tested with experimental data in pipes of various sizes (51.5, 263, and 495 mm) containing flowing fine sand (0.165 mm)–water mixtures. Experiments performed with another sort of uniform sand (d = 0.43 mm) in the 51.5-mm pipeline show the influence of particle diameter. The proposed approach improves the prediction of concentration distribution, especially at high concentrations, and reveals some specific elements of the two-phase structure.

E2. Flow of a Suspension in a Vertical Circular Tube.* S. L. Passman, J. W. Nunziato, and P. B. Bailey, *Sandia National Laboratories,*† *Albuquerque, New Mexico 87185.*

We present a theory for a mixture of a granular material with a fluid, based on classical continuum theory of mixtures and the theory of flowing granular materials of Goodman and Cowin [*J. Fluid Mech.*, **45**, 321 (1971)]. It is assumed that the mixture is saturated, that each component is incompressible, and that the grains are essentially spherical.

We examine some of the implications of the theory by considering the boundary value problem of flow in a tube of circular cross section. For simplicity, the flow is driven by a body force parallel to the axis of the tube. The problem is governed by a system of nonlinear differential equations sufficiently complex so that closed-form solutions are not obvious. We use a modified shooting method to solve them numerically. We consider a range of parameters sufficiently wide to represent both flow through a deformable porous medium and flow of concentrated and dilute solutions. Generally, the solid particles tend to concentrate toward the center of the tube. The fluid exhibits a high velocity gradient toward the walls, where a no-slip boundary condition is satisfied, and a much smaller gradient over the remainder of the cross section, exhibiting a balance between its tendency to assume a parabolic velocity profile in the absence of solid particles, and the resistance to flow in the region of relatively high particle concentration. The solid particles, on the other hand, are dragged along in the region of higher fluid velocity.

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† U.S. Department of Energy facility.

E3. Characteristic Compositions in the Melt Rheology of Binary Mixtures of Polymers. Andrew P. Plochocki, *Polymer Engineering, University of Tennessee, Knoxville, Tennessee 379162.*

Certain characteristic compositions, defined in terms of extrema in plots of melt viscosity versus composition, were first observed in the mid-1960s for mixtures of isolatic polypropylene and linear polyethylene. Since that time the present author has found similar characteristic compositions in other rheological properties, notably normal stresses, relaxation times, and relaxation spectra, for a comprehensive set of polyolefin mixtures. In the present paper the sensitivity of various measures of melt elasticity, including the rate dependence of such measures, is discussed for several types of polymer mixtures and for commercial blends of polyolefins. Specifically, the measurements have to do with the stress–temperature–composition dependence of extrudate (die) swell, the recoverable strain–shear stress–composition relationship, and the specific volume–composition behavior as related to the structure of mixtures. Finally the implications of the characteristic compositions in selecting components, blending ratios, and manufacturing process parameters for an industrial blend of polymers are discussed.

Polymer Blends, D. R. Paul and S. Newman, Eds., Academic, New York, 1948.

E4. Rheological Properties of Dispersions of Fumed Silica in Polydimethylsiloxane. R. S. Ziegelbaur and J. M. Caruthers, *School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907.*

The steady-state viscosity and primary normal stress difference were measured for dispersions of fumed silica in polydimethylsiloxane. The shear viscosity of the unfilled polydimethylsiloxane fluid was essentially independent of the shear rate; however, the filled fluid was shear thinning even when the volume fraction of the filler was exceedingly small. Both the shear viscosity and the primary normal stress difference of these filled materials exhibited thixotropic material behavior. After each experiment the dispersion was allowed to recover in the undeformed state. The viscometric properties increased as the time allowed for recovery was increased. The rate of recovery was retarded, when the dispersion was sheared during the recovery period. The magnitude of the viscometric properties, the degree of shear thinning, and the rate of recovery increased as the volume fraction of filler was increased. Transient rheological properties of these filled fluids were also studied. For a constant recovery time, the stress growth function exhibited a maximum that increased with decreasing shear rate. The strain associated with the maximum in the stress growth function was shifted to lower values of strain as the shear rate was increased.

E5. Electrostatic and Hydrodynamic Interactions between Rigid Rods. W. B. Russel and D. L. Berry, *Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544.*

Suspensions of charged rigid rods provide a reasonable model for a variety of intrinsically stiff or highly charged water-soluble polymers, such as CMC, Xanthan gum, or DNA. Here we extend earlier descriptions of the rheology at infinite dilution [e.g., L. G. Leal and E. J. Hinch, *J. Fluid Mech.*, **55,** 745 (1972)] to include pair interactions. The hydrodynamic interactions are weak but long range, while the electrostatic interactions are strong but only at short range, effectively decoupling the two.

The results indicated that hydrodynamic interactions accentuate the non-Newtonian behavior predicted at infinite dilution. At high rates of strain the effects disappear in simple shear but increase rapidly in uniform extension. The predictions agree quantitatively with recently published data for Xanthan gum [G. Chauveteau, *J. Rheol.* (1981)].

Electrostatic interactions have been analyzed only in the low shear limit. Significant increases in the effective viscosity are predicted but comparison with data remains qualitative.

E6. The Influence of Water-Soluble Thickeners on Colloidal Stability and Flow Properties of Latex Paints. G. R. Zeichner and D. F. Massouda, *Hercules Inc., Wilmington, Delaware 19899.*

Hydroxyethylcellulose is commonly used as a thickener in latex paints. In the high shear regime, the polymer-thickened aqueous phase properties control brush drag and spatter characteristics. In the low shear regime, the unadsorbed polymer contributes to colloidal instability which leads to an aggregated dispersed phase and advantageous thixotropic flow behavior. The characteristics of polymer-induced aggregation were investigated using only a model system of latex and thickener. We find in small-amplitude oscillatory flow a plateau in the storage modulus G'. The plateau occurs over a frequency range characteristic of the shear rates for sag and leveling. The effects of polymer molecular weight and concentration on paint properties are accounted for by the magnitude of the plateau modulus and the relaxation time of the aggregated network.

E7. Foam Flow. Robert K. Prud'homme, *Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544.*

Gas–liquid foams are being used as fracturing fluids in oil well drilling because, being compressible, they can store energy. They are being tested as vehicles for paper coating chemicals because, since foams are mostly air, much less energy is used in drying the coatings than in drying conventional aqueous coatings. And they are being considered for the pipeline transport of pulverized coal because foams, having a yield stress, suspend solids easily and the pipeline transport of foams containing coal would require less water than aqueous slurry transport.

The mechanism of foam flow involves bubbles moving past each other in a series of jumps from one equilibrium position, through an unstable state, to a new equilibrium position. The energy barrier between the stable and unstable states results in the observed yield stress in foams. The value of this yield stress can be evaluated from this geometry of the cellular structure.

Experiments have been conducted on the flow of foams through tubes. From data taken with different-sized tubes and through an analysis similar to that of Rabinowitz, the magnitude of the apparent wall slip can be determined as well as the viscosity of the foam at the shear rate that occurs at the wall.

E8. Stability of Double Emulsion Droplets in Shear Flow. Pieter Stroeve, Padma Prabodh, and Jarda Ulbrecht, *State University of New York at Buffalo, Amherst, New York 14260.*

Double emulsions are of considerable interest because of their use as separation media or as shear-sensitive fluids. Double emulsions, also known as liquid membrane dispersions, have been tested extensively for wastewater treatment, toxin removal, and valuable mineral recovery. The selectivity and capacity of the double emulsion droplets can be augmented by addition of reversible carriers and sink species which combine preferentially with a compound of interest. The stability of the double emulsion droplets in shear flow is of importance not only in separation processes, but also in the utilization of these emulsions as shear-sensitive fluids. As an example for the latter case, reactants can be released from the droplets if a desired shear intensity level is reached, i.e., when the droplets break up. The released material could then polymerize with another compound already present in the continuous phase.

In this work, the breakup of double emulsion droplets has been studied in a counterrotating plate-cone viscometer mounted on an inverted microscope. Image analysis of the double emulsion droplets was performed with a Quantimet System 23. Droplet breakup was studied as a function of dispersed phase and continuous phase viscosity, interfacial surface tension, and the shear rate. The critical Weber number can be correlated with the ratio of the apparent viscosity to the continuous phase viscosity. The results in this type of plot can be used to predict emulsion stability against droplet breakup.

E9. Rheology of Unstable Liquid–Liquid Dispersions. Steven A. Zoeller and Dean O. Harper, *Department of Chemical and Environmental Engineering, University of Louisville, Louisville, Kentucky 40292.*

This study was conducted in order to evaluate various models for predicting the viscosity of two-phase liquid–liquid systems. Such information was needed for related work on the performance of a new emulsification device. Unstable xylene-in-water dispersions were formed in this device at xylene (dispersed phase) volume fraction levels of 11, 20, and 30%.

The viscosity of these unstabilized dispersions was determined by capillary rheometry. The data were compared with the predictions of 11 viscosity models for two-phase systems. All of these equations include the dispersed-phase volume fraction and the viscosity of the continuous phase. Five of them also incorporate the viscosity of the dispersed phase.

Over the range of shear rates investigated, 500–2400 s^{-1}, the dispersions showed Bingham-plastic behavior with initial yield stresses of 0.5–0.75 Pa. The Bingham viscosities were volume fraction dependent and were 1.86, 2.49, and 2.97 mPa s for the levels studied—11, 20, and 30%, respectively. The Hatscheck equation, $\eta_e = \eta_1/(1 - \alpha^{1/3})$, provided the best fit for the current data; however, it underpredicted literature data for this system at higher levels of dispersed phase fraction. It appears that modifications of this model, similar to that made by Sibree, multiplying the α term by a constant other than unity, may yield even better predictions for such systems. None of the models which incorporated the dispersed phase viscosity came close to the data.

E10. Boiling of Suspensions of Solid Particles in Water. Yu Min Yang and Jer Ru Maa, *Chemical Engineering Department, Cheng Kung University, Tainan, Taiwan, Republic of China.*

Saturated pool boiling of suspensions of Al_2O_3 particles of 0.05–1 μm in water is studied by heating the slurries with a stainless steel tubular electric heater of 3.2 mm o.d. Hysteresis of boiling curves, which does not appear in the case of pure water, is found in the boiling of slurries of all concentrations. Experimental results also show that the heat transfer rates of the suspensions are significantly higher than those of pure water. This enhancement of boiling heat transfer happens only in the region of nucleate boiling. It is more pronounced when the concentration of the solid particles is higher and when the particle size is smaller. The fluctuation of surface temperature of the heating element is also stabilized by the addition of the suspended solid particles.

Mechanisms for this behavior are proposed, based on the rheological properties of the suspensions.

E11. Rheology of Concentrated Suspensions of Particulates in Unsaturated Polyester Resins. C. D. Han and K. W. Lem, *Department of Chemical Engineering, Polytechnic Institute of New York, Brooklyn, New York 11201.*

Measurements were taken of the bulk rheological properties of concentrated suspensions of particulates in unsaturated polyester resins, using a Weissenberg rheogoniometer. The particulates were clay, calcium carbonate, and milled glass fiber. Shear thinning was observed at low shear rates, as the concentration of particulates was increased. However, when the particulates were treated with a coupling agent, the shear thinning tended to disappear. This implies that the shear thinning observed with untreated particulates resulted from "crowding." Support was provided by photomicrographs showing the state of dispersion in a steady shearing flow obtained by using a transparent cone and plate on the rheogoniometer. Observations could be made at or near the apex of the cone and also at other points across its radius.

Suspensions of high-density polyethylene (HDPE) powder in unsaturated polyester resin were found to give positive values of normal stress at low concentrations, but negative values of normal stress above a certain critical concentration. We are of the opinion that the negative normal stress observed with the concentrated suspensions of HDPE powder in unsaturated polyester resins are beyond doubt an artifact, and we hope that continuing investigations will unravel their physical origin.

E12. Melt Rheology of Glass Fiber-Reinforced Polypropylene. D. Tyagi, *Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061,* and A. Mishra, *School of Material Sciences and Technology, Indian Institute of Technology, New Delhi, India 110017.*

Rheological behavior of glass fiber-reinforced polypropylene was investigated. Though end correction increased with glass fiber content, it showed a nonuniform dependence on shear rate. The corrected viscosity data was used to formulate an equation with empirically determined constants. The equation can be used to describe the flow behavior in the non-Newtonian region for the glass fiber-reinforced polypropylene melts as a function of temperature, shear rate, and glass fiber content. The calculated values from the equation were in good agreement with the experimental values. From the melt fracture and the die swell behavior, existence of a critical glass composition was noted. Beyond this critical concentration, the die swell decreases with shear rate and the force required tends to level off.

E13. Use of the Lodge Model with a Strain-Dependent Memory Function to Describe the Shear Flow Behavior of Reinforced Nylon Melts. R. Pisipati and D. G. Baird, *Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061.*

A study of the steady shear, dynamic oscillatory shear, and transient stress growth rheological properties of particulate and fiber reinforced nylon 6,6 has been conducted. A Lodge rubberlike liquid model with a strain-dependent memory function is used to describe the nonlinear shear behavior of these systems. The time-dependent part is determined from dynamic moduli data obtained in the linear viscoelastic region. The strain-dependent term is obtained from the relaxation modulus that is calculated from stress relaxation following a sudden shearing displacement, and also from the stress growth experiments. This memory function is used in the Lodge model to predict steady shear viscosity and normal forces and the transient shear stress buildup and relaxation. It is found that the strain dependence differs for the fiber and particulate reinforced polymer.

E14. Dynamic Viscosity of Non-Newtonian Suspensions. P. Masi, L. Nicodemo, L. Nicolais, and G. Taglialatela, *Instituto Di Principi, Di Ingegneria Chimica, Facolta Di Ingegneria, Piazzale Tecchio, 80125 Napoli, Italy.*

The rheological behavior of glass bead suspensions PIB/decahydranaphthalene solutions, at different polymer concentration, and filler content, has been investigated.

The effect of the oscillatory flow on the viscosity of such systems has been studied over a wide range of frequency and amplitude.

The non-Newtonian dependency of the steady shear viscosity of the suspension seems to be dependent on the superimposed oscillatory flow. The experimental results are reported and discussed.

Session F: Rheo-Optics
Chairman: D. G. LeGrand

F1. Application of Infrared Dichroism to Molecular Orientation Measurements of Polymer Moldings. J. E. Huber and R. J. Samuels, *School of Chemical Engineering, Fracture and Fatigue Research Laboratory, Georgia Institute of Technology, Atlanta, Georgia 30332.*

The ability to characterize the microstructure of a semicrystalline polymer undergoing mechanical processing is prerequisite to theoretical understanding of the deformation mechanism controlling the process. Structure–process studies of thick injection-molded materials are severely constrained for lack of analytical techniques to measure molecular orientation. Current methods typically develop a qualitative description of molecular structure and orientation from analysis of thin films sliced from a molded specimen. With the exception of x-ray diffraction, the quantitative techniques developed for films and fibers have physical limitations which have prohibited their use in thick moldings.

The purpose of the present talk is to show that infrared dichroism is a very practical, nondestructive technique for measuring molecular orientation in thick molded polymers, provided the infrared absorption phases and transition moment angles of the discrete absorption bands are known. Techniques will be shown, using isotactic polypropylene films and tensile bars as examples, for extending the applicability of infrared dichroism from films to specimens as thick as tensile bars. A structure–process study of the deformation of tensile bars at elevated temperatures will be used to demonstrate the utility of infrared dichroism as an analytical technique for thick moldings.

F2. The Rheo-Optics of Polymer Melts and Solutions, Possibilities, and Limitations. W. Philippoff,* *N.J.I.T. Newark, New Jersey.*

The theoretical and experimental foundations in the rheo-optics of viscoelastic liquids, such as polymer melts and solutions in flow, are critically reviewed. To expand the experimental results beyond obtaining (complicated) photographs to a quantitative analysis of the stress field in flow, a series of limitations have to be considered. These are mainly rheological, not optical. The foundation is the validity of the stress–optical law. But it is limited to flexible or nonpolar polymers. The two-dimensional flow field is a necessary requirement. The limitation to non-Newtonian liquids questions the suitability of such materials as aqueous suspensions of Milling Yellow or Bentonite. Established stationary flow is often difficult to achieve. Adiabatic heating in flow can invalidate the interpretation of results on viscous (10^4–10^6 poise) materials at reasonable flow rates. The application to theoretically untreated flow-field (such as cross-shaped ones) may lead to premature conclusions. These difficulties should be balanced against the unique possibility of obtaining with a relatively simple arrangement a complete two-dimensional stress field without interference by probes, giving the actual, not precalculated, one. For more dilute or less viscous solutions, the measurement of the normal stress difference N_1 is an asset, which can be expanded to low-stress regions, not measurable otherwise. The previously nearly exclusively investigated low-concentration range yields the stress–optical coefficient C, which presents some difficulties to a more elaborate analysis.

* Retired.

F3. On the Constitutive Relations for Birefringence in Viscoelastic Fluids. B. D. Coleman, *Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213,* and L. J. Zapas, *National Bureau of Standards, Washington, D.C. 20234.*

The general theory of optical behavior of viscoelastic dielectric fluids in nonsteady shear will be outlined with the emphasis laid on results that are independent of "the stress–optical law." It will be shown how birefringence measurements can be used to verify optical analogs of various relations that have been proposed for components of the stress tensor. Among the topics to be discussed are (1) Weissenberg's conjecture about the second normal stress difference, (2) Coleman and Markovitz's relations between the shear stress and the first normal stress difference, and (3) the range of validity in shear of the constitutive relation proposed by Bernstein, Zapas, and Kearsley.

F4. Streaming Birefringence in Converging Flow of a Viscoelastic Polymer Solution. Gregory D. Eisenbrand and J. D. Goddard, *University of Southern California, Department of Chemical Engineering, Los Angeles, California 90007.*

By means of laser optics we have measured flow birefringence and tracer-particle trajectories in a concentrated Separan AP-30 polyacrylamide solution just upstream of a small orifice.

For different orifice diameters and flow rates, we obtain a good correlation between birefringence and superficial extension rate, based on the orifice diameter and superficial velocity. For superficial extension rates between 10 and 80 s^{-1}, there is an evident nonlinear relation between these quantities.

Based on an analysis of tracer-particle streakline photographs, we conclude that the true extension rates are much smaller than the superficial ones. Also, we observe what appears to be flow instabilities, like those in the previous experiments of Cable and Boger (1978).

F5. Application of Flow Birefringence to Measurement of the Hole Pressure. D. Pike and D. G. Baird, *Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061.*

A study has been undertaken using flow birefringence to determine quantitatively various factors that affect the magnitude of the hole pressure for polymer melts and to assess quantitatively the assumptions in the Higashitani and Pritchard theory. In the first phase of this work, which is reported here, our interest is primarily in assessing the effect of asymmetry of the stress field on the theoretical predictions of Higashitani and Pritchard for flow over a slot. From measurements of the principal stress differences and principal stress directions for a polystyrene melt, the theory of Higashitani and Pritchard was evaluated directly. Values were also compared with the numerical solutions obtained by Crochet and Townsen. Our initial results indicate that the asymmetry has no significant effect over a large range of shear rates. Two methods for reducing the effect of asymmetry were also evaluated.

Session G: General

Chairman: K. F. Wissbrun
Co-Chairmen: H. H. Winter
M. G. Hansen
W. R. Schowalter

G1. Studies in Non-isothermal Rheology: Behavior Near the Glass Transition Temperature. C. J. Wust, Jr., P. Potnis, B. D. Snow, and D. C. Bogue, *Department of Chemical, Metallurgical and Polymer Engineering, University of Tennessee, Knoxville, Tennessee 37916.*

In prior work we measured stress response in an amorphous polymer (polystyrene) while simultaneously pulling the material and cooling it; in related work we determined the effect of cooling rate on the glass transition temperature T_g. In the present work we continue these kinds of studies with emphasis on frozen-in (nonequilibrium) volume effects and orientation effects, including especially the aging of these properties at temperatures near and well below T_g.

G2. Shear Rheological Behavior of Branched BPA–Polycarbonate. R. H. Colby and M. G. Hansen, *General Electric Company, Corporate Research & Development Center, Schenectady, New York 12301.*

A series of ten samples of branched BPA–polycarbonate synthesized with different amounts of chain stopper and trifunctional branching agent have been characterized in terms of molecular weight, dynamic melt rheology, and steady shear melt viscosity. Weight-average molecular weight has been determined with low-angle laser light scattering coupled to a GPC. Dynamic storage and loss moduli have been measured in the cone and plate geometry between 200 and 300°C, and master curves generated.

From this information, relaxation spectra and complex viscosity functions have been calculated. Steady shear viscosity has been measured using a slit rheometer between 250 and 300°C for five of the samples.

Comparison of these data have shown that zero shear rate viscosity can be expressed as a function of weight-average molecular weight over the range of samples studied. This functionality is extended to take into account the hydrodynamic size of the molecules ($g\overline{M}_w$). Flow activation energies have been found to be independent of molecular weight. The viscosity functions determined from dynamic measurements and steady shear measurements are compared using the Cox–Merz empiricism.

G3. Processability and End-Use Properties versus Nonlinear Viscoelasticity of Film-Grade Low-Density Polyethrene. Hui Chang, *Xerox Corporation, Webster, New York 14580.*

Improvement of LDPE film-grade resins by postreactor polymer processing showed the differences in the nonlinear viscoelastic properties of the film-grade LDPE. This postreactor polymer process was to pass a molten LDPE from a reactor through a long (l/d = 40) single-screw homogenizing extruder at a high screw speed and low melt temperature.

The blown-film processability and optical properties of two LDPE samples–one at low pressure separator (sample E) and the other after passing through a homogenizing extruder (sample S)—are different. Sample S can be processed at higher speed and drawn to a thinner film without breaking, and has better optical properties. These two samples are very similar in most molecular characterizations: intrinsic viscosity, GPC, and in viscous flow behavior of the melts, shear viscosity. They are, however, very different in melt index, die swell, elastic effects in extrusion flow, normal stress differences in cone-and-plate rheometer. Those differences were reversible after the sample S had been heated above the melting point of LDPE (230°C) for a period of time.

G4. The Influence of Molecular Weight Distribution on Melt Rheology of Polypropylene. G. R. Zeichner and P. D. Patel, *Hercules Incorporated, Wilmington, Delaware 19899.*

The influence of molecular weight and distribution on the rheological behavior of polypropylene was examined with 40 samples which ranged in $\overline{M}_w$ from 100,000 to 4,000,000 and $\overline{M}_w/\overline{M}_n$ from 2 to 9. Two parameters, determined from dynamic shear master curves, are shown to correlate viscosity, normal force, extrudate swell, and processing characteristics. A method of relating these parameters directly to $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ is presented. The partition model of Bersted has been applied to polypropylene to predict rheological parameters from molecular weight distribution curves.

G5. A New Method of Representing the Memory Functionals of Nonlinear Viscoelastic Materials. Part I. Theory. B. D. Coleman, *Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213,* and L. J. Zapas, *National Bureau of Standards, Washington, D.C. 20234.*

A new type of expansion will be proposed for nonlinear functionals possessing the smoothness assumptions appropriate for the response of viscoelastic materials with gradually fading memory. The first term in the expansion is in general nonlinear and has the form of the single integral functional in the relation proposed by Bernstein, Kearsley, and Zapas; the higher-order terms are iterated integrals of nonlinar functions. The relation of the expansion to others presented in the literature will be explained, and theorems will be given that suggest that the stress in a nonlinear viscoelastic material, far from its "rest history," may be given to a good approximation by just the first two terms in the expansion.

It will be shown how the expansion may be applied to characterize the stress in motions of extension and general shearing motions. It also will be shown that, in principle, each successive term in the expansion can be determined by an elementary set of experiments.

G6. A New Method of Representing the Memory Functionals of Nonlinear Viscoelastic Materials. Part II. Experiments. L. J. Zapas and G. B. McKenna, *National Bureau of Standards, Washington, D.C. 20234;* and B. D. Coleman, *Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.*

The theory presented in part I was developed to explain the differences between experimental results and the currently existing theories for the nonlinear behavior of viscoelastic materials. In this work we present experimental results for a selected epoxy resin. The torsional responses of cylindrical bars were measured for various multistep stress relaxation histories. From these data we obtained the memory functionals necessary for the calculation of the response in other torsional histories. Constant rate of strain (loading followed by unloading) experiments were obtained and compared with calculated values. Some data will also be shown for PMMA cylinders and PIB solutions which show the usefulness of this new theory.

G7. A Constitutive Theory for Fluids Based on Microstructural Slippage. D. M. Binding, *Universidad Nacional Autónoma de México, Facultad de Ingeniería, División de Estudios de Posgrado y Division de Ingeniería Mecánica y Eléctrica, Mexico.*

In recent years there has been a growing interest in constitutive relations which incorporate the ideas of "microstructural slip" or which utilize strain measures different from the usual Cauchy and Finger strain tensors. This paper considers a continuum constitutive theory based on such an "effective" strain measure.

It is assumed that the state of stress may be expressed as a function of an "effective" deformation which is determined in terms of the imposed macroscopic motion and a microstructural slip motion. A special case is analyzed for several simple flow situations, including simple shear, small-amplitude oscillatory shear, extensional flows, and stress relaxation. In this special case it is assumed that the slip velocity gradient is linear in both the effective deformation and the imposed rate of strain. It is also assumed that the fluid is instantaneously a hyperelastic material with respect to the effective deformation. The corresponding elastic strain energy function is taken to be a linear function of the involved invariants.

The present theory differs in many respects from previous ones advocating the use of the concept of microstructural slip. For instance, incompressibility is imposed on the slip motion as well as on the imposed macroscopic motion. Also, the slip velocity gradient is not restricted to a function of the rate of stretching tensor. The most notable difference, however, is that the present theory requires the calculation of the effective deformation.

The Newtonian fluid is seen to be a naturally limiting case of the theory.

G8. Nonlinear Rheological Properties of Entangled Polymeric Fluids—Extension of a Kinetic Network Model to Binary Blends of Monodisperse Components. Tony Y. Liu, David S. Soong, and Michael C. Williams, *Department of Chemical Engineering, University of California, Berkeley, California 94720.*

A molecular network theory incorporating the concept of entanglement disruption and regeneration was developed previously to describe not only steady-state but also transient rheological properties of monodisperse polymer melts and concentrated solutions. The viscoelastic responses of these systems are dominated by a rapid segmental motion at short times and a more sluggish, structure-dependent network relaxation process at long times.

In a binary blend of monodisperse fractions, the entangled network is composed of chains of two different lengths. The chain dynamics, and thus the characteristic response time, of each component in such a system is influenced by the presence of the coexistent component. This interaction is accommodated by a simple mixing assumption, which leads to accurate predictions of composition-dependent linear viscoelastic properties, such as zero shear viscosity. In addition, the model gives excellent description of the shear-rate-dependent viscosity curves of binary blends of various compositions and concentrations. Time-dependent viscoelastic properties, such as stress growth and relaxation functions, have also been simulated. Comparison of these results with experimental data will be discussed. The successful extension of this kinetic network theory to binary blends provides the critical step to predict ultimately the nonlinear rheological properties of polydisperse polymers from knowledge of their molecular weight distribution, as the proposed mixing rule can be easily generalized to account for multiple interactions among the constituent chains.

G9. The Significance of Temperature Changes in Rheological Deformation. Harry H. Hull, *Pittsburgh, Pennsylvania 15243.*

There is a close thermodynamic relationship among the compression of a gas, the stretching of rubber, and the deformation of a viscoelastic fluid. When these processes are adiabatic and followed by a relaxation without external work, the temperature changes that accompany these processes provide a means for expressing them in terms of thermodynamics. The heat generated in such deformations can be partitioned into reversible and irreversible. The reversible heat can again be partitioned into that generated by the internal work and that generated by a portion of the external work.

A thermodynamic model for a viscoelastic body is one dashpot and two springs in parallel. The work done by or against one spring represents the work done by or against the intermolecular forces (the internal work). The work done by or against the other spring represents the work done by or against the kinetic motion of the molecules. The two springs normally oppose each other.

G10. Failure of Viscoelastic Fluids During Shearing Flows. Hon Chung Lau and W. R. Schowalter, *Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544.*

As part of a continuing study of the mechanism by which shearing induces cohesive and/or adhesive failure of viscoelastic fluids, a systematic study of the nature of failure over a range of temperatures was conducted. Tests were performed with polyethylene melts, polybutadiene resins, and aqueous solutions of poly(vinyl alcohol) and sodium borate using cone-and-plate and parallel-plate viscometers.

In most cases the first manifestation of failure was cohesive, i.e., failure was initiated within the material rather than at the fluid/wall interface. At the onset of failure the continuum was broken down and the flow became nonlaminar. Failure began at the periphery of the apparatus and was often accompanied by healing. As the shear rate was increased, stick–slip behavior of the polymer at the plate or cone boundary was often observed. The effect of test geometry, wall roughness, molecular weight and temperature on the onset of failure was investigated.

A theory based on the network concept is proposed to explain the observed phenomenon. Failure is modeled as catastrophic breakage of a large number of network junctions. Essential to the model is the kinetics of junction formation and breakage, which is assumed to be an activated rate process.

Correlation between the proposed theory with experimental data as well as the relationship between failure in shear and the dynamic properties of the test materials will be discussed.

G11. Transient Shear Flow Behavior of Polymeric Fluids According to the Leonov Model. R. K. Upadhyay, A. I. Isayev, and S. F. Shen, *Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, New York 14853.*

The viscoelastic behavior of polymeric systems based on the Leonov model has been examined for (1) the stress growth and relaxation, (2) the stress relaxation after step–shear strain, and (3) the elastic recovery in shear flow. Using an effective least-squares procedure, a large number of modes have been conveniently incorporated through the determination of the model parameters from conventional rheological data obtained in steady-state (shear viscosity and first normal stress difference as a function of shear rate) or oscillatory (storage and loss moduli as a function of frequency in the linear region) flow. Six different materials, including polymer melts and polymer solutions, have been used with a different number of relaxation modes (maximum six modes). Results indicate that the stress relaxation experimentation is most sensitive to the accuracy of the model parameters. With sufficient number of modes, the predictions are in very good agreement with corresponding experiments in literature, including the recent data for cases (1) and (2) obtained by optical methods. The present theory also confirms the Lodge–Meissner relation $(\tau_{11} - \tau_{22})/\tau_{12} = \gamma_0$ in a step–shear experiment. In general, the present model leads to results that for these test cases are comparable to those from Wagner's theory, the latter having been most successful to date in describing the above-mentioned experiments. It is noted, further, that the Leonov model is considerably less difficult to apply, thus offering the possibility of analyzing flow problems of practical interest.

G12. Primary Normal Stress Difference–Shear Power Law Expression for Viscoelastic Fluids. L. Choplin, *Department of Chemical Engineering, Laval University, Quebec, Canada G1K 7P4,* and P. G. Carreau, *Department of Chemical Engineering, École Polytechnique, Montréal, Canada.*

The first normal stress difference (N_1) is well represented by a power law model with respect to shear stress (τ_{12}). This model has been tested with over 30 different fluids, and it has been shown to fit the data very well in all cases practically over the entire range of shear rate covered by a Weissenberg rheogoniometer. This model presents among others, the advantage of clarifying and emphasizing the doubts shed by various authors on the validity of the method of Abdel-Khalik et al. [*Polym. Eng. Sci.*, **14,** 859 (1974)].

Moreover, this $N_1 - \tau_{12}$ representation shows only a weak dependence on the polymer concentration and approximately no dependence on the solvent used. Strangely enough, for a variety of polymer solutions, a surprising behavior was observed in the sense that for a constant shear stress, the first normal stress difference is inversely proportional to the polymer concentration. This behavior was observed for concentrated solutions as well as for relatively dilute solutions, and is predicted by the finite extensible nonlinear elastic (FENE) model of Bird–Dotson–Johnson (the calculations were made with some available experimental data for dilute solutions). The implications and consequences of such a model and behavior are discussed.

G13. Linear and Nonlinear Viscoelastic Characterization with a Rheometrics System Four. A. C. Papanastasiou, C. W. Macosko, and L. E. Scriven, *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455.*

Several integral constitutive models propose that the memory function may be separable into a time-dependent, linear viscoelastic function and a strain-dependent, nonlinear viscoelastic part. We have developed a strategy for testing this hypothesis and determining these functions on polymer melts using a Rheometrics System Four rheometer. The linear viscoelastic function, $G(t)$, is determined first by stress relaxation. The instrument digitally records log $G(t)$ vs. log t data, suitable for fitting with various constitutive expressions. The short-time part of the function is supplemented with high-frequency sinusoidal data. Accuracy in the longtime part is improved by using creep. Stress relaxation after large step strain in shear is used to determine nonlinear viscoelastic dependence. Performance of the complete model is tested against steady shear stress and normal force data and extensional measurements.

G14. Large Elastic Deformations of Inflated Membranes with and without Contact. G. Canova, J.-M. Charrier, C. Kim, S. Shrivastava, and R. Wu, *Department of Chemical Engineering, McGill University, Montreal, Quebec, Canada H3A 2A7.*

Theoretical studies of the large elastic deformations of inflated plane, tubular, and spherical membranes have been conducted where in the course of the inflation the membranes come in contact with flat or cone-shaped rigid boundaries. Two different interface situations are considered: where no friction exists at the interface and where no slip occurs. In order to generate simple sets of dimensionless results potentially useful for the engineering design of thermoforming processes, incompressible elastic solids featuring only one elastic constant are considered. For cases where the geometry of axisymmetrically deformed membranes is not simple, different approaches are discussed and compared: mathematical approximation of the meridian shape, combined analytical and numerical approaches, finite elements approach.

G15. Dynamic Viscoelastic Properties of Crosslinked Styrene *N*-Butyl Methacrylate Melts. S. K. Ahuja and R. Nelson, *Xerox Corporation, Webster, New York 14580.*

Random copolymers of styrene/*n*-butyl methacrylate were crosslinked using different monomer ratios and levels of crosslinking agent, divinyl benzene. Dynamic shear moduli, elastic and viscous moduli, viscosities, and compliances were determined from measurement of forces in eccentric rotating disks (ERD) device of a Rheometrics mechanical spectrometer.

With increasing levels of crosslinking agent in the copolymer, distinction between terminal and plateau regions of elastic modulus reduces to the point of being nonexistent in the highly gelled polymer. Dynamic viscosity of the copolymer at lower levels of crosslinking agent shows both a Newtonian region and a non-Newtonian power law region. At the highest level of crosslinking agent in the polymer, two power law regions are discernible in the viscosity versus frequency curve. The relaxation modulus obtained by Schwarzl–Staverman numerical approximation shows an increasing breadth in the spectrum as the concentration of divinyl benzene in the polymer is increased.

Equilibrium compliances (J_e^0) obtained from elastic and viscous moduli at lower frequencies are about a decade higher in magnitude for the crosslinked polymer than the linear polymer. The Newtonian viscosity of the crosslinked polymer is lower than that of the linear polymer at the same molecular weight. The plateau modulus G_N is about the same for linear and crosslinked copolymers. This work on copolymers is consistent with earlier works on crosslinked and star-shaped polystyrene reported in the literature.

G16. Effects of the Glassy Phase Morphology on the Mechanical Properties of SBS Block Copolymers. John K. Bard and Chan I. Chung, *Rensselaer Polytechnic Institute, Troy, New York 12181.*

Triblock copolymers of styrene–butadiene–styrene (SBS) exhibit a microphase separation which gives them a two-phase structure consisting of a glassy polystyrene phase and a rubbery polybutadiene phase. The mechanical properties of a particular SBS sample depend on its morphology. This morphology can be changed by casting from solvents selective for one or the other of the blocks. In the present study, sheets of a SBS sample with about 25 wt % styrene (Kraton 1101) were cast from four different solvents. Transmission electron microscopy was used to evaluate the resulting morphologies, especially noting differences in size, shape, and degree of continuity of the glassy phase. Stress relaxation and tensile tests were carried out to determine the differences in mechanical properties. Large differences in morphology and mechanical behavior were observed. Samples cast from a polybutadiene-selective solvent had isolated polystyrene domains and exhibited the lowest modulus, hysteresis, and amount of relaxation. Less selective or nonselective solvents produced morphologies with more continuity in the glassy phase. A solvent selective for polystyrene produced a glassy phase with a high degree of continuity. With increasing continuity of the glassy phase, the modulus, hysteresis, and amount of relaxation increased. Deformation or disruption of the glassy phase during deformation seems to become more important with increasing glassy phase continuity, and this fact must be considered in any attempt to model the mechanical behavior of phase-separated block copolymers such as these.

G17. Effect of Extending Oil on Viscoelastic Behavior of Elastomers.

N. Nakajima and E. R. Harrell, *B.F. Goodrich Chemical Group, Technical Center, Avon Lake, Ohio 44012.*

In spite of the fact that extending oils have been used very widely for many years, no fundamental work has been done to elucidate how they affect the viscoelastic behavior of elastomers. We have performed viscoelastic measurements of the oil–polymer system over the range of polymer concentration from 2.5 to 100% and temperature range from 30 to 150°C. Polymers were ethylene–propylene copolymer rubbers, which had been chosen to represent very different chain structures. Sample A has a relatively narrow distribution of molecular weight (MWD) and the least branching, whereas sample B has a broad MWD with some long branching. The temperature–superposition principle was determined to be applicable for these data, allowing the construction of master curves of elastic and loss moduli over eight decades of frequency. The data encompass the rubbery plateau and flow regions. We have discovered that the concentration–superposition applies to only a limited range of data, when the polymer contains long branching. Nevertheless, the two superposition principles provide a basic framework for describing the material behavior, especially when the significance is attached to the manner of deviation from the concentration–superposition. The observed viscoelastic behavior was interpreted in terms of processability as well as the polymer structure.

G18. Viscoelastic Behavior of a Multicomponent System.

S. K. Ahuja, *Xerox Corporation, Webster, New York 14580.*

Polyamide, poly(ether maleic anhydride), and carbon black were mixed in an extruder with different ratios of the two polymers. Banbury/roll mill, extrusion, and spray-drying conditions were used for blending equal concentration of polyamide and poly(ether maleic anhydride).

As the concentration of polyamide in the blend is increased, both elastic and viscous moduli go through a minimum. Downstream feeding of the polyamide in the extruder results in higher viscosity than when polyamide is fed upstream. The freely mixed extruded blend, spray-dried blend, and the material blended with Banbury/roll mill show distinctly lower viscosities than the blends formed from the Banbury-blended copolymer ether and carbon black with downstream feeding of polyamide in the extruder. These results are compared with mechanical and thermal behavior in solid state. The behavior of this system is analogous to the phenomenon of low critical solution temperature.

G19. Determination of Molecular Weight of Nylon 6,10 from Viscosity Measurements and Computations. Raja H. Abu-Samn and Mosbaḥ S. Zwuita, *Chemical Engineering Department, Riyadh University, Riyadh, Saudi Arabia.*

The polyamide nylon 6,10 is prepared in the laboratory by an interfacial polymerization reaction between sebacoyl chloride (SC) dissolved in carbon tetrachloride and a hexamethylene diamine (HMD)–sodium hydroxide solution. The polymeric film formed at the interface of the two solutions is continuously wound up by a mechanical windup device.

Different molar ratios of HMD:SC were applied (1:1, 1.5:1, 2; 1, 3:1, 1:1.5, 1:2, and 1:3) to produce polymers of different molecular weights. The relative viscosity of different concentrations of synthesized nylon 6,10 were experimentally determined by a calibrated glass capillary viscometer for each of the above molar ratios.

The specific (intrinsic) viscosity is computed and plotted against concentration. By extrapolating the limiting viscosity number is computed.

The molecular weight of each concentration for each molar ratio is calculated by means of the Mark–Houwink–Sakuracla equation: $[\eta] = KM^{a}$, where $[\eta]$ is the limiting viscosity number, M is the molecular weight of polymer, and K and a are constants.

All the molecular weight values obtained, except one, are in good agreement with literature.

It is concluded that the degree of polymerization of nylon 6,10 is increased by increasing the ratio of SC and decreased by increasing the ratio of HMD.

G20. Residual Stresses and Birefringence in Injection Molding. J. Greener and G. H. Pearson, *Eastman Kodak Company, Rochester, New York 14650.*

A simple mathematical model for predicting residual stresses in injection molding has been constructed. The use of a nonlinear viscoelastic constitutive equation allows the model to yield better quantitative results than previously obtained. The model fails to predict the existence of birefringence along the centerline of the part which is thought to be due to nonuniform cooling (i.e., thermal stress).

G21. The Determination of "Die Swell" of Polymers without End Effects. D. J. Plazek and R. Kannabiran, *Department of Metallurgical and Materials Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.*

Polymer melts and their concentrated solutions exhibit an increase in cross-sectional area after they are extruded from a tube or through a die. An attempt has been made to determine if entrance or exit effects play a significant role in the determination of this so-called "die swell." The effect of the entrance is avoided by filling a tube with polymer from a reservoir at a temperature well above its glass temperature, for example, polystyrene at 190°C. Thereafter, the driving pressure is removed and the polymer is allowed to relax. Previously made creep recovery measurements determine how long a relaxation time is necessary. The pressure is reapplied at a lower temperature, about 40°C above T_g, where the rate of deformation is low. After only a fraction of the original material residing in the tube is extruded, the temperature of the well-stirred oil bath in which the tube is immersed is lowered through the polymer's T_g. The applied pressure is maintained constant during the cooling so that the state of stress of a given polymer volume elements stays constant. The glassy rod is removed from the tube and sectioned. Thus, the degree of molecular orientation in the polymer is not affected by the removal. The sections are annealed 60°C above T_g while being supported in a nonsolvent liquid with a similar density. The ratio of the diameters before and after annealing are compared with the results obtained from conventional "die swell" measurements made with an extrusion viscometer.

G22. Influence of Porous Media in the Entry of a Capillary on Capillary Flow. D. S. Done and D. G. Baird, *Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*, and A. E. Everage, *Monsanto Textiles Co., Pensacola, Florida 32575.*

Porous media placed within small distances (e.g., 0.25–0.075 in.) of a capillary entrance are observed to have an interesting effect on the flow of polystyrene through a capillary. In particular, the pressure drop across the capillary is reduced by a factor of at least 3 as compared to that across the capillary with no porous media in the entry region. The onset of melt fracture is delayed so that flow rates three times greater than ordinary can be obtained. Some effect on die swell is also observed. Two mechanisms have been proposed to account for this phenomena. One involves the temporary breakup of entanglements in the porous media. The other is associated with the modification of the entry flow pattern.

G23. Variation of the End Correction Factor with Flow-Induced Crystallization in Various Rubbers. F. Aramburo and L. F. Ramos-De Valle, *Centro de Investigación en Química Aplicada Aldama 351 Ote., Saltillo, Coah., México.*

Capillary rheometry was used to analyze the variations in end correction as a function of shear rate and temperature, in five different rubbers: natural guayule and hevea rubbers (GR and HR), synthetic polyisoprenes SN-600 (high cis) and IR-309 (low cis), and SBR-1503.

For GR, HR, and SN-600 end corrections increase as the temperature is lowered. This trend reaches a maximum from where the effect is reversed, i.e., end correction decreases. This effect is detected at temperatures and shear rates near the occurrence of flow-induced crystallization. This phenomenon was not observed in IR-309 and SBR-1503 at the temperatures used in this experiment (40–140°C) and crystallization of these two rubbers was not observed. Hence, the variations in end correction for GR, HR, and SN-600 has been attributed to the occurrence of incipient flow-induced crystallization.

G24. Solvent Effects on the Rheology of Aqueous Polyacrylamide Solutions. Y. I. Cho, J. P. Hartnett, and Y. S. Park, *Energy Resources Center, University of Illinois at Chicago Circle, Chicago, Illinois 60680.*

The influence of solvent chemistry on steady shear viscosity and first normal stress difference for aqueous polyacrylamide solutions (Separan AP-273) was investigated in the Weissenberg rheogoniometer and capillary tube viscometer.

The zero shear rate viscosity of the 1000-wppm Separan solution with distilled water was greater than that of tap water by a factor of 25. However, when the shear rate was increased, the viscosity of the distilled water solution approached that of the tap water solution. The addition of 100-wppm NaOH to the tap water resulted in a 100% increase of the viscosity in the low shear rate range. In contrast, the addition of 4% NaCl to the tap water reduced the viscosity of the Separan solution over the entire range of shear rate by a factor of 4–25 depending on the shear rate. The first normal stress difference measurements of the 1000-wppm Separan distilled water solution was greater than that of the tap water solution by a factor of 2. The addition of 4% NaCl to the tap water resulted in a considerable decrease in the first normal stress difference, reflecting a substantial decrease in the elasticity.

The effect on viscosity by the addition of NaOH, NH_4OH, or H_3PO_4 to the tap water also was investigated and the results are presented on viscosity versus pH curves at fixed shear rates. These curves indicate that for base additives there is an optimum pH number (approximately 10.5) which maximizes the viscosity of the Separan solution. For acid additives, an increasing concentration of acid was always accompanied by a decrease of viscosity.

G25. Rheology and Ignition Properties of Jet Fuels with Antimisting Additives.

K. K. Chao, C. A. Child, M. C. Williams, and E. A. Grens, *Chemical Engineering Department, University of California, Berkeley, California 94720.*

Suppression of fuel mists created in aircraft crash landings is vital to preventing fires in these circumstances. This can be accomplished by the addition to the fuel of small amounts of polymers with very high molecular weight, known as antimisting (AM) agents. We report here an experimental study of the mist- and ignition-suppression phenomenon. Among the factors investigated were the molecular features of the AM agents, their influence on a spectrum of dilute solution rheological properties, the correlation of this rheology with AM activity, and the ultimate connection between mist modification and ignition prevention.

Among the most useful results we have obtained, is a simple rheological test for prediction of the misting and ignition properties for any fuel–polymer solution; no knowledge of polymer molecular properties is required. High- speed photos of sprays created by wind shear of a fuel stream in a special chamber will be displayed and used to demonstrate effects of the polymer nature and concentration. In the best case, 10 ppm of a high-molecular-weight polyisobutylene achieves significant suppression of the (spark) ignition of Jet A fuel, and 100 ppm achieves vastly reduced fuel flammability. This suggests that the currently favored technology of using 4000 ppm of a different additive could be improved, with reduced costs.

G26. Rheological Equations of State of Progressively Shear Thickening Solutions.

S. T. J. Peng and R. F. Landel, *California Institute of Technology, Pasadena, California 91103.*

FM-9 (the commercial name of an ICI product) in organic solvent exhibits a strong time-dependent thickening behavior. The time needed to induce the thickening strongly depends on the shear rate and the concentration. In this paper we derive the rheological equations of state to describe this very unusual behavior in the framework of Rivlin–Ericksen formulation with considerations that the equations depend on the progressive buildup of structure in the solution as the shearing continues.

G27. Ultrasonically Induced Agglomeration of Gas Bubbles. Robert K. Prud'homme, *Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540.*

Two gas bubbles pulsating under the influence of an ultrasonic field experience an attractive force independent of the rheology of the surrounding fluid, causing them to move toward each other and collide. Movies of bubble agglomeration induced by ultrasonic fields will be shown, and comments will be made on the applicability of ultrasonic fields to the devolatilization of polymeric solutions.