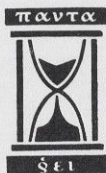


# RHEOLOGY BULLETIN

Publication of the Society of Rheology

Volume 35 No. 1



January, 1966

## ANNUAL WINTER MEETING OF THE SOCIETY OF RHEOLOGY

U.S. NAVAL POST GRADUATE SCHOOL  
MONTEREY, CALIFORNIA

JANUARY 31 THROUGH FEBRUARY 2, 1966

### Accommodations

Pre-registration is encouraged. Reservations may be obtained at the nearby Mark Thomas Inn through the local arrangements chairman (below). The Inn is booked to capacity for the night of February 2. If this creates a problem for you, two other motels in the nearby area are—Western Motel, 2041 Fremont, Monterey and Lazy Lake Lodge, 55 Camino Arguajito, Monterey. Reservations may be obtained individually.

### PROGRAM COMMITTEE

Local Arrangements: RODNEY BEYER, United Technology Corporation  
P.O. Box 358, Sunnyvale, California

General Chairman: DALE J. MEIER, Shell Development Company  
1400 53rd Street, Emeryville, California

THOR L. SMITH, Stanford Research Institute  
Menlo Park, California

ROGER S. PORTER, Chevron Research Corporation  
576 Standard Avenue, Richmond, California

### EXECUTIVE COMMITTEE MEETING

OCTOBER 24, 1965

WADE PARK MANOR

1. The meeting was called to order at 2:30 P.M. Executive committee present were J. T. Bergen, R. S. Marvin, J. C. Miller, T. L. Smith, R. R. Myers. Others present included I. Krieger, S. Prager, J. Brodnyan, D. Meier, V. William, Director of AIP.
2. Minutes of the previous meeting were accepted as mailed to the Executive Committee.
3. The Secretary-Treasurer made a financial report. It was pointed out that although publishing of 900 pages

for 1965 in the Transactions was excessive, this does not create an immediate crisis because of the balance, sixteen sustaining members and fact that the bill for Transactions 9, part 2, will not be paid until 1966. Action must be taken within the next year if the Society continues to expand its publishing activities. A motion was made, seconded and passed to limit the number of pages in the Transactions to 800 pages.

4. A number of proposals to increase the amount of money available for publishing were presented. These included
  - a. Raise dues
  - b. Increase meeting charges
  - c. Change publishers (to AIP)
  - d. Introduce a page charge
  - e. Limit number of pages
  - f. Negotiate a new charge from Wiley & Sons.

The following courses of action were agreed upon for immediate action. AIP would send estimates of costs to Myers, and Marvin and Miller would talk with Wiley about renegotiating the agreement.

5. The possibility of having quarterly issues of the Transactions was considered. The decision was reached to continue with the semi-annual publication to coincide with the meetings.
6. The American Institute of Physics requested action on four items in accordance with the Constitution of AIP. The Society of Rheology must approve or disapprove before action is final.
  - a. Application by the American Crystallographic Association for admission to AIP as a Full Member. Moved, seconded and passed unanimously.
  - b. Application by the American Astronomical Society for admission to AIP as a Full Member. Moved, seconded and passed unanimously.
  - c. A change in the AIP Constitution to make individual members of Member or Associate Member Societies, individual members of AIP. Moved, seconded and passed unanimously.
  - d. A change in AIP Constitution which will change the formula for determining the Governing Board representation. Moved, seconded and passed unanimously.

Of particular interest to the Society is the fact that the new formula will give the Society of Rheology only one member on the Governing Board which is more in line with the number of members.

(Continued on Page 10)

RHEOLOGY BULLETIN  
 Raymond R. Myers, Editor  
 Chairman, Department of Chemistry  
 Kent State University  
 Kent, Ohio, 44240

PROGRAM OF 1966  
 WINTER MEETING OF  
 THE SOCIETY OF RHEOLOGY

REGISTRATION:

6:00-9:00 p.m., January 30 Mark Thomas Inn  
 8:00-8:45 a.m., January 31 U. S. Naval Postgraduate  
 School

8:30-9:00 a.m. February 1 U. S. Naval Postgraduate  
 School

OPENING REMARKS: 8:50 a.m., Monday, January 31

MONDAY, JANUARY 31, 1966

GENERAL SESSION A

9:00-12:15. M. C. WILLIAMS, Chairman, University of California, Berkeley, California.

A-1

9:00-10:00. INVITED LECTURE: "A Molecular Approach to Non-linear Rubberlike Viscoelasticity," J. C. HALPIN, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

A-2

10:00-10:30. "Statistical Mechanics and Elastic Behavior of an Entangled Chain," STEPHEN PRAGER, University of Minnesota, Minnesota 55455, and H. L. FRISCH, Bell Telephone Laboratories, Murray Hill, New Jersey 07971.

Consider a polymer chain of length  $l$  with one end held at a distance  $r$  from an infinitely long straight bar. If the other end is now joined to the first, what is the probability  $P_e$  that the loop so formed will be entangled with the bar? This question can be answered exactly if one disregards the possibility of knots in the chain. The result is in the form of a complicated triple integral, which may, however, be bounded from above and from below:

$$(1-4/\pi^2) \operatorname{erfc}(2r/\sigma^{1/2} l^{1/2}) < P_e(r, l) < \operatorname{erfc}(2r/\sigma^{1/2} l^{1/2}),$$

where  $\sigma$  is an effective segment length.

If a force directed radially away from the bar is exerted on a segment of a loop entangled with the bar, the response is that of a non-linear spring. As the applied force increases, the effective spring constant first decreases, then increases again, asymptotically approaching two thirds of its initial value. This non-linearity is an intrinsic property of the entanglement, and not merely the result of the polymer chain approaching a fully extended configuration.

A-3

10:45-11:15. "A Crystalline Loss Mechanism in Semi-crystalline Poly(ethylene Terephthalate), by RICHARD M. IKEDA, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

The mechanical behavior of partially crystalline poly(ethylene terephthalate) was studied with a torsion pendulum. The mechanical loss maximum in the 100°C. region was found to vary as much as 38°C. depending upon the crystallinity level and orientation. This is similar to the results found by other investigators who have attributed the loss peak to the glass transition. Differential thermal analysis data for our samples indicate that the Tg's do not vary by more than 5° to 10°C. This same conclusion was also obtained from tensile modulus (1% stress) versus temperature plots. The initial fall-off of the moduli with temperature occurs in the same temperature range (80° to 90°C.) for two samples with loss maxima at 98° and 118°C. This information has led us to believe that the glass transition cannot account for the entire loss maximum in question.

The tensile modulus versus temperature curves show a second fall-off in moduli occurring at somewhat higher temperatures thus indicating a second loss mechanism. The data indicate that this second mechanism occurs at different temperatures for the two samples and the relative temperatures are similar to that found with the mechanical loss peaks. We speculate that this second loss mechanism is responsible for the large shifting of the mechanical loss peaks and is associated with the crystalline portions of the polymer. This assignment is compatible with the observed increase in peak areas with crystallinity and might also explain the large increase in peak areas brought about by biaxial orientation. Although these observations and our results with a one-way stretched sample suggest a crystalline slip type of mechanism, a delineation of the exact loss process cannot be made with the information at hand.

A-4

11:15-11:45. "Photographic Light Scattering from Ringed Spherulites Subjected to a Constant Rate of Strain," by R. S. MOORE and C. GIENIEWSKI, Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey.

In previous photographic light scattering studies, two types of experiments were carried out on films of polyethylene containing well-defined ringed spherulites. In the first type the sample was subjected to successive fixed increments of strain and light scattering patterns and photomicrographs were obtained as a function of time. In the second type a sample was subjected to uniaxial stress and the scattering patterns were obtained while sample elongation was continuously recorded by means of a transducer. Results of the first type of experiment indicate that accompanying spherulite deformation the ring spacing increases in the direction of tensile stress and decreases at right angles to the stress direction. Results of the second type of experiment indicate that although the spherulites deform, the changes in ring spacing as determined by light scattering are less at the same strain than in the first type of experiment.

To assess the effect of the type of deformation experiment on the mode of spherulite deformation, an apparatus

was constructed by means of which a sample could be subjected to a constant rate of strain while scattering patterns were taken. The results at different rates of strain are presented as well as data pertaining to samples with poorly ordered spherulites. An analysis in terms of suggested mechanisms of spherulite deformation is given.

A-5

11:45-12:15. "Dynamical Aspects of Viscoelasticity," by JULIAN J. DAVIS, Polymer Research Branch, Plastics and Packaging Laboratory, Picatinny Arsenal, Dover, New Jersey.

There is a compelling need to develop a mathematical theory of dynamic loading of plastic materials sufficiently generalized to handle a wide variety of boundary conditions ranging from impulsive loading to periodically applied loads over long time periods. Thus far no such satisfactory theory has been developed, in large part due to the varied nature of the boundary conditions. However, a host of mathematical problems has arisen, in various stages of solution, in an attempt to solve specific problems.

In this paper we describe some of these problems in an attempt to show how some powerful methods in boundary value problems in partial differential equations can aid us in a search for such a generalized theory. In particular we describe a three dimensional linearized dynamical viscoelastic theory for a certain class of constitutive equations and apply this to the viscoelastic vibrations of spheres and cylinders under certain boundary conditions. Certain eigenvalue problems thereby arise whose solutions yield viscoelastic vibrations described by the dependence of phase velocity on frequency. Another class of problems discussed concerns the application of asymptotic expansion methods in partial differential equations to stress wave propagation in viscoelastic media.

## MONDAY AFTERNOON

### SESSION B

#### NON-NEWTONIAN FLOW AND NORMAL STRESSES.

Chairman: J. F. Johnson

Chevron Research Company, Richmond, California.

#### B-1

2:00-2:30. "Non-Newtonian Tangential Flow in Cylindrical Annuli", Z. TADMOR, Engineering Research Center, Western Electric Company, Inc., Princeton, New Jersey.

The shear stress profile, velocity profile, and flow rate were derived for tangential pressure flow with constant angular pressure gradient and for a power law model fluid. The solutions for the angular or tangential velocity and for the flow rate were obtained in terms of infinite series. The radius at which the shear stress assumes a value of zero is numerically calculated for different ratios of the outer and inner radii and for different exponent values in the constitutive equation. Velocity and shear stress profiles for dilatant, Newtonian, and pseudoplastic fluids are compared.

This type of flow is of interest in screw extruders. The conventional screw extrusion theory is based on Newtonian flow between infinite parallel plates. In this theory a

forward drag flow is linearly added to a backward pressure flow. These two terms then are independently corrected for wall effects, curvature, and helix angle. Although this procedure is strictly valid only for Newtonian fluids,<sup>1</sup> the influence of curvature on a pure drag flow and pure pressure flow for a non-Newtonian fluid may still be very helpful in analysing screw extruders.<sup>2</sup>

By comparing the pressure flow rates between parallel plates and concentric cylinders, it was found that if the pressure gradients are equaled at the arithmetic mean radius, the flow rates will not differ appreciably except for very pseudoplastic fluids and very high ratios of outer to inner cylinder radii.

The error in linear addition of tangential pressure and drag flows of a non-Newtonian fluid is also examined.

<sup>1</sup>Kroesser, F. W. and Middleman, S., *Polymer Eng. & Sci.*, **5**, 231 (1965).

<sup>2</sup>Jacobi, H. R., "Screw Extrusion of Plastics," Iliffe Books, Ltd., London, 1960.

#### B-2

2:30-3:00. "Correlation of the Weissenberg Rheogoniometer With Other Methods," by W. PHILIPPOFF, ESSO Res. & Engr. Co., Linden, N. J., and R. A. STRATTON, Mobil Chemical Co., Metuchen, N. J.

The concept of "recoverable shear" has been used to correlate widely different experimental methods to measure the viscoelastic properties of polymer solutions. The Weissenberg Rheogoniometer (WRG) determines  $s = P_{11} - P_{22} / P_{12}$  from the measured stresses; in flow-birefringence, by  $s$  is given by measuring the extinction angle:  $s = 2 \cot 2\chi$  and the "recoil" in, say, a rotational viscometer gives  $s$  directly. Previous tests, together with some other methods, have shown the coincidence of the results obtained with these three methods. Recently a series of theories (termed constitutive equations) have cast doubt on the equality of  $s$  measured by these methods, specifically stating that the "recoil" values should be one-half of those calculated from the other methods. This discrepancy can be tested experimentally; further since the time these previous measurements were made, the WRG has been considerably improved. It seemed therefore of value to re-examine the situation. A number of viscoelastic liquids ranging from polydimethylsiloxane to polyisobutylene in white oil were used in a recent model of the WRG (RAS) and in the flow-birefringence instrument (FBR) (WP) together with flow curves and recoil measurements in a concentric cylinder viscometer. (WP). The results were (1) the WRG and FBR give identical values of  $s$ , providing an optically "matching solvent" is used. (2) In all cases,  $s$  measured in recoil is equal to the one calculated from either WRG or FBR. The maximum values of  $s$  were about 20 shear units, much in excess of anything measured in the field. Recoil measurements, apparently due to inertia effects, are only valid at low rates of shear,  $\dot{\gamma}$ , (below 1 sec<sup>-1</sup>) and at  $s < 1$ , higher values being systematically too low, the more so with increasing  $\dot{\gamma}$ ; all possible errors tend to decrease  $s$ . The equality of  $s$  measured with the three methods is independent of the relation between  $s$  and, say the shear stress or  $\dot{\gamma}$ , if it is linear or non-linear, whereas the men-

tioned theories have been developed for the linear case only (validity of linear viscoelasticity). This confirms and extends the previous findings, giving emphasis to the approach used before.

B-3

3:00-3:30. "Effect of Degradation by Pumping on Normal Stresses in Polyisobutylene Solutions," by G. K. PATTERSON, H. C. HERSHEY, C. D. GREEN and J. L. ZAKIN, The University of Missouri at Rolla, Rolla, Missouri.

Normal stress measurements were made on freshly prepared and previously pumped dilute solutions of high molecular weight polyisobutylene. Measurements were made with a jet thrust apparatus in which the thrust tube was mounted on the frame of an analytical balance. Thrusts as small as 0.1 gram could be measured with a repeatability of  $\pm 0.01$  grams.

The effect of degradation by pumping was to reduce ( $P_{11}$ - $P_{12}$ ) values by about one third. Drag reduction in turbulent flow in a one-inch tube was also decreased.

Normal stress measurements were also made on a medium molecular weight polyisobutylene. Even though these measurements were for a better solvent and a higher concentration than for the high molecular weight polymer, the normal stress differences were significantly lower indicating a strong molecular weight effect.

B-4

3:45-4:15. "Similarity Solutions for Non-Newtonian Fluids," by S. LEE and W. F. AMES, Department of Mechanical Engineering, University of Delaware, Newark, Delaware.

The boundary layer equations for non-Newtonian fluids are investigated. Similarity variables and equations for various flows are obtained by using transformation group methods. Similarity solutions are possible for power-law fluids in the following systems: (1) Momentum transfer in general Falkner Skan flows and Goldstein Flows; (2) Momentum and energy transport in (a) forced convection about a right angle wedge, (b) natural convection with constant heat flux at the boundary surface, (c) general Falkner Skan flows with non-constant heat conductivity and a restricted boundary temperature distribution; (3) Momentum and heat transfer of Eyring viscous flows about a right angle wedge.

The numerical calculations for a similarity solution of forced convection of power-law fluids past a right angle wedge are carried out. From these calculations the drag is obtained and an approximate expression is obtained for the local Nusselt number.

B-5

4:15-4:45. "Shear Stresses in Concentrated Polymer Solutions," by MICHAEL C. WILLIAMS, Department of Chemical Engineering, University of California, Berkeley, California.

A method is suggested for calculating the shear-dependency of stresses in flowing polymeric liquids. The expression for the stress tensor,  $\pi$ , presented recently by Fixman,

is used as a framework. It is shown to reduce to the appropriate form for very dilute solutions, but is evaluated in this work for the case of rather concentrated solutions. Thus emphasis is placed on the importance of intermolecular forces, derived from a smoothed interaction potential of mean force. This approach is expected to be valid up to concentrations at which extensive physical entanglements occur (polymer volume fraction exceeding about 0.1). One consequence seems to be a prediction that  $\pi$  is proportional to the square of polymer concentration, a result in agreement with experiment. The effect of shear rate ( $\dot{\gamma}$ ) is introduced through the shape of the segment distribution  $\nu(\mathbf{R})$ , and through a perturbation of the pair correlation function  $g(\mathbf{r})$  with Kirkwood's friction factor  $\xi$ .

A specific non-Newtonian viscosity model is derived from very simple choices of  $\nu(\mathbf{R})$  and  $g(\mathbf{r})$ . It contains only two parameters, a low-shear viscosity limit  $\eta_0 = \eta_0(n^2, \xi/kT)$  and a time-constant  $\lambda$ . Both parameters are regarded as empirical, although in principle they might be evaluated theoretically. The predicted viscosity, a complicated function of incomplete elliptic integrals, is displayed graphically as  $\eta/\eta_0$  versus  $\lambda\dot{\gamma}$ . Its limiting behavior is:  $\eta/\eta_0 \doteq 1 - \frac{9}{14}(\lambda\dot{\gamma})^2$  at low  $\lambda$ , and  $\eta/\eta_0 \doteq 5/(3\lambda\dot{\gamma})$  at high  $\dot{\gamma}$ . The latter is not entirely realistic, but apparently is a consequence of (a) certain linear approximations, (b) use of only one time constant, and (c) total neglect of intramolecular forces.

B-6

4:45-5:15. "Pitot Tube Measurements in Turbulent Viscoelastic Flow," by G. ASTARITA\* and L. NICODEMO, Istituto di Chimica Industriale, University of Naples, Italy.

The interpretation of Pitot tube readings in a viscoelastic turbulent stream is discussed. Apart from the possibility that the probe may alter the local structure of flow, it is shown that the actual local impact pressure is made up by the usual kinetic contribution, plus two contributions arising from time-average deviatoric normal stresses. These may be important when the liquid is viscoelastic, and they result in apparent velocities lower than true velocities. Experimental data relative to dilute aqueous solutions of a polymer show that the integrated apparent flowrates are indeed consistently lower than true flowrates. Several customary ways of plotting velocity distributions are discussed, and anomalous results to be expected are explained. A Momentum average correction factor to be used in overall mechanical energy balances is obtained from Pitot traverses, which is of direct physical relevance.

The theoretical analysis given includes the laminar flow case, and the case of turbulent flow of purely viscous non-Newtonian liquids. The second normal stress difference contribution is shown to be non-negligible even for liquids which approach the Weissenberg stress pattern in viscometric flow.

\*Present address: Chemical Engineering Department, University of Delaware, Newark, Delaware.

TUESDAY MORNING

FEBRUARY 1, 1966

SESSION C—GENERAL SESSION

B. Wright, Chairman

Shell Chemical Company, Ltd., Manchester, England.

C-1

9:00-10:00. INVITED LECTURE: "Time and Gradient Dependence of Viscosity of Dilute Polymer Solutions in Viscous Solvents," A. PETERLIN, Research Triangle Institute, Camille Dreyfus Laboratory, Durham, North Carolina.

C-2

10:00-10:30. "Time, Temperature and Molecular Weight Effects in the Environmental Stress Cracking of 0.95 Density Polyethylene," by GLENN E. FULMER, W. R. Grace and Co., Clarksville, Maryland.

Reduced variables of time, temperature and molecular weight are used to describe the stress relaxation failure of 0.95 density polyethylene in a stress cracking agent, Igepal. This method was previously shown to work for 0.96 density linear polyethylene. The 0.95 density polyethylene has an apparent activation energy for stress cracking of 38 Kcal. This is appreciably higher than the 22 Kcal found for 0.96 density linear polyethylene. A much higher dependence on molecular weight was also found. The 0.95 density polyethylene has a lifetime that is proportional to  $Mw^{5-8}$  while the 0.96 density polyethylene has a lifetime proportional to  $Mw^{3-4}$ . Some preliminary data is also shown which indicates a difference in the sensitivity to strain for the two materials. This can lead to appreciably longer lifetimes for the 0.95 density polyethylene at low strains.

C-3

10:45-11:15. "Pressure Dependence of Molecular Motion in Some Elastomers," by J. E. ANDERSON<sup>1</sup> and W. P. SLICHTER, Bell Telephone Laboratories, Murray Hill, New Jersey.

Nuclear magnetic resonance (NMR) spectroscopy has shown itself to be useful for studying relaxation processes of polymers in certain high-frequency portions of the relaxation spectrum, but with the notable exception of Nolle's study of polyisobutylene,<sup>2</sup> these measurements have been carried out at atmospheric pressure. Nevertheless, such studies offer promise of useful information on thermodynamic properties and mechanism of relaxation.

We have investigated molecular motion in natural rubber, polyisobutylene, poly-cis-butadiene, and an ethylene-propylene copolymer, using pulse methods of NMR, over a pressure range of 1-680 atm and at temperatures from -100° to +135°C. In all these elastomers, except polybutadiene, the motion of substituent groups dominates the NMR relaxation at low temperatures. In these studies, however, emphasis was given to the temperature intervals in which the relaxation depends on motion of the main chains. Viewing these motions as thermally activated processes, we have determined enthalpies and volumes of activation, and have compared the pressure dependence of

NMR relaxation in these elastomers with information from the literature on viscoelasticity. Increasing pressure shifts the NMR dispersion to higher temperatures. The shifts are represented quite well by expressing the effects of temperature and pressure with reduced variables. The results support the assignment, from viscoelastic measurements,<sup>3</sup> of a portion of the compressibility coefficient to changes in local structures and decrease of free volume.

<sup>1</sup>Present address: Scientific Laboratory, Ford Motor Co., Dearborn, Michigan.

<sup>2</sup>A. W. Nolle and J. J. Billings, J. Chem. Phys. 30, 84 (1959).

<sup>3</sup>J. E. McKinney, H. V. Bolecher, and R. S. Marvin, Trans. Soc. Rheology 4, 347 (1960).

C-4

11:15-11:45. "Linear Free Energy Effects in the Poly(vinyl Chloride)-ester System From Creep Compliance, Melt and Solution Viscosity Techniques, E. M. SMOLEY and R. J. HAMMOND, Armstrong Cork Company, Lancaster, Pennsylvania.

Current literature indicates that considerable effort is being made to relate the rheological behavior of various materials to molecular mechanisms of flow. Implicit in the viscoelastic spectra of various substances is the molecular configuration and motion that gives shape to the stress relaxation or creep compliance curves. In dilute solutions or concentrated melts at higher temperatures flow curves give indications of molecular arrangements present causing deviation from some previously defined rheological standard. Research on high polymers has generally taken the course of investigations into pure one component or two component solvent-polymer systems. Experimental evidence obtained can thus be used for purely phenomenological, molecular or general processing application depending on the objectives of the program. In research on poly(vinyl chloride) melts, complications arise due to the presence of necessary impurities (thermal stabilizers and secondary plasticizers). While it is possible to describe the flow properties of these melts and solutions by suitable empirical equations, it is difficult to predict beyond any gross qualitative aspect what general chemical or physical property will result from small changes in the basic formulation. It is, therefore, quite impossible to explore the rheological behavior of poly(vinyl chloride) without understanding and evaluating the magnitude of effect of these added substances. Our primary considerations here are directed at understanding the nature of the interaction of ester-type plasticizers with poly(vinyl chloride) through tensile creep compliance, dilute solution and melt viscosity characteristics. The method employed represents a departure from conventional thought in that the rheological behavior has been successfully correlated to both Hammett and Taft substituent constants as implied in Eyring's concept of absolute reaction rates. While changes in interaction free energies and enthalpies evolve simply and naturally from this technique, the significant conclusion obtained from these data is that the generally accepted "hydrogen-bonding" interaction hypothesis of poly(vinyl chloride) with esters is clearly absent.

11:45-12:15. "Thermistor Analog Study of Dynamic Shear in Model Viscoelastic Materials," G. E. MUELLER, Department of Electrical Engineering, University of Delaware, Newark, Delaware, and I. J. GRUNTFEST, Re-Entry Systems Department, General Electric Company, P. O. Box 8555, Philadelphia, Pennsylvania, 19101.

This report is one of a series describing exploratory studies of the mechanical behavior of materials which have temperature dependent properties. Electric analog computer methods are used to simulate the dynamic shear of a Maxwell model viscoelastic slab. As in earlier studies of the dynamics of viscous slabs, thermistors are used to simulate the temperature dependent viscosity in the mechanical model. These are stacked so that heat conduction between contiguous volume elements is also stimulated. To simplify the experiments, the density and elastic modulus are considered to be temperature independent. In many real materials the latter have a much weaker dependence on temperature than the viscosity.

The responses of the slab to abruptly applied boundary velocities and to sinusoidal velocity inputs are reported for a range of ratios of viscosity to elastic modulus (viscoelastic times) and a range of velocity amplitudes. Parameters are described which characterize an analog experiment and identify it with an experiment with a mechanical model. The values of these parameters in a given experiment indicate whether linear or non-linear responses can be expected. They also provide an efficient method for describing the model materials. It is shown that the model material behaves more and more like a liquid as the velocity amplitude is increased. This is in agreement with experience with many real materials. Adaptations of the analog circuit to the study of more general materials and more general experiment geometries are also discussed.

## TUESDAY AFTERNOON

FEBRUARY 1, 1966

### SESSION D, POLYMER FLOW

P. J. Blatz, Chairman

California Institute of Technology, Pasadena, California

#### D-1

2:00-2:30. "Effects of Glass Transition Temperature of Thermoplastics on Sensitivity of Viscosity to Temperature and Diluent Content," R. N. HAWARD, G. WEST and B. WRIGHT\*, The Manchester College of Science and Technology, England.

The low shear rate melt viscosities of polystyrene polypropylene and polyethylene are measured over a range of temperatures and in the presence of various amount of white oil. The results obtained with the three polymers are discussed in relation to their glass transition temperatures using free volume treatments. The effects of temperature and diluent are found to be predicted qualitatively by the "universal" WLF treatment. A more detailed analysis of the results reveals some significant inconsistencies.

\*Shell Chemical Company Ltd.

#### D-2

2:30-3:00. "An Explicit Equation Relating Viscosity and Molecular Weight in Polymers. I. Development of the Theory. II. Application to n-Alkane and Polyethylene Melts," JACK R. KNOX, Avisun Corporation, Marcus Hook, Pennsylvania.

An explicit equation is developed to describe the zero shear viscosity-molecular weight-temperature relationship in polymer melts. The equation is the same as Eyring's basic flow equation for low molecular weight materials,  $\eta = \frac{N_h}{\bar{V}} \exp(-\Delta S/R) \exp(\Delta H/RT)$ . The entropy is expressed in general terms as  $\Delta S = a - b(f(\text{vol}))$  where "a" is a function of the basic flow unit and b (f(vol)) is some function of the entire molecular volume. The entropy gain due to activation of the basic flow unit is expressed as  $a = (n-1)R \ln W$  where "n" is the number of bonds per basic flow unit and "W" is the number of rotational states available to a backbone unit; the molecular volume term is expressed as  $3/2 n^{1/2} \ln \bar{M}_w$ .

The equation does not contain any intermolecular interaction terms such as coupling constants or friction factors, and is shown to apply satisfactorily to both n-alkane and linear polyethylene melts. The fit with experimental data is only for weight average molecular weight, but no concept of a critical molecular weight is required. Application of the equation to branched polyethylenes of known number average molecular weight produces a satisfactory agreement provided that a reasonable value for molecular weight distribution is assumed.

#### D-3

3:00-3:30. "General Relationships for the Flow Activation Energy of Amorphous Polymer Systems," by ROGER S. PORTER and JULIAN F. JOHNSON, Chevron Research Company, Richmond, California.

Apparent flow activation energy for viscosity change with temperature can be evaluated in the non-Newtonian region at either constant shear rate,  $E_s^*$ , or at constant shear stress,  $E_\tau^*$ .  $E_s^*$  decreases with shear approaching a lower limit corresponding to the "power law" region. Relative changes in  $E_s^*$  can be expressed in terms of reduced variables. Absolute change in  $E_s^*$  can be used as a measure of polymer molecular weight distribution.

For many linear amorphous polymers, it has been shown that  $E_\tau^*$  is independent of stress over the full range for shear stress data. This conclusion appears to hold for solutions as well as undiluted polymer.

Each linear amorphous polymer exhibits a constant, characteristic  $E_\tau^*$  at high temperature and at high polymer molecular weight. These characteristic values for  $E_\tau^*$  have been related to the chemical composition and structure of individual polymer coils.  $E_\tau^*$  increases as a regular function of the molar volume of pendant groups along the polymer chain. A general relation has also been developed between  $E_\tau^*$  and the steric or conformational factor  $\sigma$ . For polyolefins,  $E_\tau^*$  also increases regularly with the molar volume per monomer unit and with the mean square displacement length per chain unit.

D-4

3:45-4:15. "Flow Behavior of Liquid Carboxyl-Polybutadiene and Butadiene-Acrylonitrile Copolymers," by RICHARD J. BOYCE, WALTER H. BAUER, Rensselaer Polytechnic Institute, EDWARD A. COLLINS, B. F. Goodrich Chemical Company, Avon Lake Development Center.

The flow behavior of some low molecular weight polymers was studied as a function of shear rate, shear stress and temperature. The polymers included polybutadienes, random carboxyl and carboxyl terminated polybutadienes, carboxyl terminated butadiene-acrylonitrile and acrylonitrile-butadiene copolymers.

Measurements were made in the temperature range 3.8 to 73°C. A cone and plate viscometer and pressure capillary viscometer were used to cover the shear rate range 1 to 10<sup>5</sup> sec<sup>-1</sup>. Measurements were carried out with various capillary radius to length ratios.  $\bar{M}_w$  and  $\bar{M}_n$  values were calculated from molecular weight distribution data obtained by Gel Permeation chromatography. Limiting viscosity numbers were also determined.

In the range of shear rates studied, all polymers showed a limiting viscosity at low rates of shear and a region of shear rate thinning. The log viscosity-log shear rate flow curves for each sample at the various temperatures were superimposable by linear shifts. Energies of activation calculated according to the method of Fox and Loshaek were found to have values characteristic of the molecular structure. Normal stresses developed in capillary flow as measured by entrance effects showed dependence on structure and molecular weight. Flow results were compared with the Bueche-Harding experimental standard curve and the Bueche theoretical curve.

The presence of polar groups in the polymer chain increased the energy of activation and the relative magnitude of the viscosity. The log viscosity-log shear rate flow curves for all the samples at any constant temperature were superimposable by linear shifts in two distinct classes according to differences in molecular weight distribution.

D-5

4:15-4:45. "Stable and Unstable Flow in Polymer Melts," by T. W. HUSEBY, Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.

Previous investigations<sup>1</sup> of the capillary flow of polymer melts have been carried out using the continuum theory of Y. H. Pao.<sup>2</sup> These studies have utilized relaxation spectra, portions of which are experimentally determined according to a method described by Aloisio, Matsuoka, and Maxwell.<sup>3</sup> For linear polyethylene several results concerning the flow behavior and the onset of an instability have been predicted and also have been observed experimentally.

Presented here is a quantitative comparison between experimental results and some of the previous reported predictions for well characterized linear polyethylenes. One result is that the predicted shear stresses are of the

correct order of magnitude although somewhat lower than the experimental values. The agreement is examined and discussed in some detail.

<sup>1</sup>Huseby, T. W., paper presented to 36th Annual Meeting, Society of Rheology, October 1965.

<sup>2</sup>Pao, Y. H., *J. Poly. Sci.*, 61, 413 (1962); *Polymer Letters* 2, 437 (1964).

<sup>3</sup>Aloisio, C. J., S. Matsuoka, B. Maxwell, paper presented to 36th Annual Meeting, Society of Rheology, October 1965.

## WEDNESDAY MORNING

FEBRUARY 2, 1966

### SESSION E, GENERAL SESSION

S. Prager, Chairman

University of Minnesota, Minneapolis, Minnesota

E-1

9:00-10:00. INVITED LECTURE: "Ionic Forces in Polymers," by A. EISENBERG, Department of Chemistry, University of California, Los Angeles, California.

Ionic forces in polymers have recently received considerable attention from several laboratories. These studies were, by and large, limited to organic materials, which, unfortunately, can acquire only a relatively low ionic character before becoming quite unmanageable. Inorganic systems exist, however, in which every repeat unit can be ionized and in which the counterion can be varied at will; a wide range of studies is therefore possible.

Here, several studies of an anionic phosphorus-oxygen polymer are reported. The work includes studies of the following:

- a) The effect of ionic forces on the glass transition. It is shown that  $T_g$  can be varied by over 500°C depending on the degree of ionization and the counterion. One single equation accounts for the effects observed.
- b) Molecular weight dependence of the viscoelastic properties. Attention is paid particularly to the low molecular weight region (<10,000), and the variation of the relaxation behavior is studied in detail.
- c) Counterion dependence of the viscoelastic properties. Keeping the backbone identical, the relaxation properties are studied in detail and the effects on the spectra discussed.
- d) Simultaneous multiple relaxation mechanisms. If traces of  $\text{La}^{+++}$  are incorporated in the polymer in place of  $\text{Na}^+$ , it is possible to observe both normal diffusional flow and bond interchange simultaneously. This, and other examples will be discussed phenomenologically, and methods described for the quantitative separation of the contributions of these two relaxation mechanisms.

It is believed that most of the findings of this study are applicable, at least in part, to organic polymers.

The financial assistance of the Office of Naval Research is gratefully acknowledged.

E-2

10:00-10:30. "Particle Motions in Sheared Suspensions XIX Viscoelastic Media," A. KARNIS and S. G. MASON, Physical Chemistry Division, Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, Montreal, Canada.

The behaviour of rigid and deformable particles suspended in viscoelastic fluids undergoing slow Couette and Poiseuille flows was studied experimentally. In tube flow the particles migrated from the wall to a limiting radial position at which the velocity gradient was effectively zero; in Couette flow between concentric rotating cylinders migration occurred towards the outer cylinder wall. The rotations of rigid rods and discs were similar to those in newtonian liquids, except for a steady drift in orbit constant to asymptotic values which in newtonian liquids correspond to minimum energy dissipation. Two-body collisions of rigid uniform spheres were unsymmetrical and irreversible. The deformation and burst of newtonian liquid drops were as in newtonian suspending liquids of comparable suspending phase viscosity, except for the alignment angle of the drop at zero deformation.

E-3

10:45-11:15. "The Biophysics of an Anatomical Discovery in the Arterial System," HARRY LOBEL, Physics Department, Independent School District, Council Bluffs, Iowa.

The human arterial system is normally free from turbulence. However, a change in bodily activity, such as suddenly rising from a sitting position or running from a standing position, results in turbulence at the points of arterial bifurcation. This lasts only for a fraction of a second, being very brief in athletes; in certain diseases, persistent turbulence may accompany bodily stress. Examination of healthy arteries led to the discovery of several features for the prevention of turbulence. One feature is the structure and design of the mouths of arteries branching from the aorta. These areas are funnel-shaped and have diameters three to five times the diameter of the branch; they point upstream like Pitot tubes. On microscopic examination, some are found to contain muscle fibers; on artificial stimulation, the renal artery of the dog for example, is seen to adjust its contour to streamline varying flows of blood. Work with models, indicates that these structures act as impedance couplings between the large aorta and the smaller branches. When the contour of the funnel corresponds with the acceleration of blood, stress is at a minimum; malfunction results in hypertensive pressure, reflected waves, and turbulence.

E-4

11:15-11:45. "Rheological Behavior of a Filled Epoxy," E. M. LENOE and C. J. MARTIN, Avco Corporation, Wilmington, Massachusetts.

The results of a series of isothermal compression and torsional relaxation tests for temperatures from  $-65^{\circ}\text{F}$  to  $+160^{\circ}\text{F}$ , for several strain levels, are presented for the filled epoxy. By utilizing different specimen geometries, the effect of edge conditions in observed mechanical response is studied. The influence of the specimen boundary restraints, as well as the effect of strain level on thermal

activation energy is considered. Master relaxation curves, formed by applying the time-temperature principle (WLF equation) are compared to the relaxation response observed on a high speed testing machine.

Due to the inherent large materials properties variations encountered in this production material, a numerical technique is applied in order to characterize the viscoelastic behavior of the epoxy. The general integral operator forms of constitutive equations for the linear isothermal theory of viscoelasticity are considered. Laplace transform techniques are utilized to obtain the well known relations between the seven viscoelastic functions. Inversion of these relations, leads to the standard linear Volterra integral equation of the second kind, which is solved by numerical means. The IBM 7094 digital computer program is used to calculate the equivalent viscoelastic "Poisson's ratio," and uniaxial and deviatoric creep compliance directly from observed deviatoric and uniaxial relaxation moduli. The numerical technique allows the rheologist to make the best theoretical estimate of mechanical behavior by utilizing various combinations of upper and lower bounds of the experimentally observed moduli. This is of particular importance in this instance due to the large experimental error and the fact that the uniaxial data is probably more reliable than the torsion relaxation observations.

E-5

11:45-12:15. "Mechanical Behavior of Plastic Composites," E. M. LENOE, D. W. OPLINGER, C. L. THEBERGE and G. N. WASSIL, Avco Corporation, Lowell, Massachusetts.

Three reinforced plastic composite materials are considered in this research. Tensile, compressive, shear and thermal expansion properties are presented for the temperature range  $-65^{\circ}\text{F}$  to  $400^{\circ}\text{F}$  for a graphite cloth phenolic laminate and for room temperature response of a silica tape reinforced phenolic resin system. Comparison of theoretical and observed uniaxial and shear moduli, "Poisson's" ratios, thermal expansion coefficients and ultimate uniaxial strengths for various angles to the laminations demonstrates that these materials may be characterized as transversely isotropic media.

Damping behavior of the silica tape phenolic composite is also presented as a function of reinforcement orientation. Influence of strain rate on tensile response and the results of static (failure in 2 to 3 seconds) and dynamic (failures in a few milli seconds) quarter-point simple beam tests are discussed. Preliminary results of time-at-temperature studies, performed by applying radio frequency heating techniques are illustrated. On the basis of these data, regions of applicability of continuum mechanics concepts of anisotropic elasticity theory are discussed.

Room temperature mechanical behavior of a unique three dimensionally reinforced epoxy resin system developed at Avco/RAD was investigated by tension, compression, torsion and thermal expansion experiments. The data suggests the validity of an orthotropic stress-strain response and points out the characteristic failure behavior of the orthogonally reinforced "S" glass fiber epoxy composite.



WEDNESDAY AFTERNOON

FEBRUARY 2, 1966

SESSION F, HETEROPHASE MATERIALS

T. F. Schatzke, Chairman

Shell Development Company, Emeryville, California

F-1

1:30-2:00. "On the Rheological Response of a Soil Column Under Dynamic Loading," J. O. McCUTCHEON, S. B. SAVAGE, R. N. YONG, McGill University, Montreal, Canada.

This paper is concerned primarily with experimental studies on the response of a soil column under uniaxial loading, applying varied forcing functions developed through three different test techniques. Lateral motions of the soil column are constrained through the use of a sheath consisting of a rubber-encased steel-coiled spring. Thus only axial deformations are allowed if the spring modulus is chosen as very small.

Load systems are described in terms of rise time to peak load; short rise times being obtained by a shock tube, and long rise times by an impulsive hydraulic loaders. In addition, a variable forcing function with square, triangular and sinusoidal wave inputs is obtained with an oscillating load plate. By measuring accelerations and displacements in addition to input parameters, material constants may be determined based on linear visco-elasticity.

Under certain conditions, soil may be considered as a visco-elastic material, and thus allows use of theories developed in visco-elasticity for examination of stress-strain time phenomena. However, because of the multiphase nature of the material, i.e. soil solids, water and air, linear idealization for simplicity in analysis may not often be realistic. Additionally, the study investigates methods whereby non-linear behaviour may be examined further.

F-2

2:00-2:30. "Microrheology of Two-Phase Systems," D. R. Axelrad, McGill University, Montreal, Canada.

Previous investigations of the flow of two-phase systems consisting of an elastic phase embedded in a fluid matrix dealt with the formulation of a thermodynamic strain-time function.

It was shown on basis of irreversible thermodynamics that the isothermal stress-deformation relation of such systems is of the same mathematical form as the relation obtained from a simple rheological model.

The present paper however is concerned with the description of the response of the system to a constant input of stress in terms of micromechanics. Hence the microstructure of the two-phase material is taken into consideration by defining micro stresses and strains acting on a subregion of supermolecular dimensions of a material specimen. It is then attempted to formulate the response characteristics of the two-phase system by using the correlation theory of random processes for the condition of arbitrary small deviations from linearity, i.e., for small deviations from the thermodynamic equilibrium.

F-3

2:30-3:00. "On Some Concepts of Yield Functions for Heterogeneous Media," D. R. AXELRAD and R. N. YONG, McGill University, Montreal, Canada.

Some concepts of yielding for a heterogeneous medium are examined in the light of experimental results derived from studies on a saturated clay. In saturated clays, the two phases present are water and mineral particles, and hence may be considered in terms of the dispersion of solids in a fluid matrix.

Accelerated creep tests utilizing a multi-loading process provided results for the general relationship between cumulative strain and applied stress for test specimens under various conditions of lateral restraint. Thus:

$$\epsilon = \alpha t^w < e >^m \text{ in } h \beta \sigma$$

where  $\alpha$ ,  $n$ ,  $m$ , and  $\beta$  are experimentally determined constants, and  $t$  represents time. The geometrical parameter given in terms of the volume fraction  $< e >$  has been found to be related to particle spacing and density.

Considering the particles as super-molecular, the problem of yield may be examined in terms of micro-inhomogeneities. Thus the characteristics of the states of stress within the test specimens can be visualized as being random quantities of space and time. Comparisons between the micro and macro analyses are examined in terms of the experimentally derived results—e.g. the generalized relationship between cumulative stress and applied stress.

F-4

3:15-3:45. "Difficulties Encountered in Ultrasonic Measurement of Mechanical Properties of Solid Propellants and Other Composite Materials Containing Microvoids," G. J. KOSTYRKO and C. C. SURLAND, Aerojet-General Corporation, Sacramento, California.

When low frequency ultrasound waves are used to measure mechanical properties of solids the velocity and attenuation of these waves yield real and imaginary components of complex modulus. During the aging of some composite solid propellant formulations the transmission of sound waves is attenuated in the material in the course of aging. At some point in time during aging transmission is attenuated below measurable levels. This is shown to be related to the formation of gas filled bubbles in the material which constitute only a small fraction of the volume. This occurs without appreciable change in other commonly measured physical properties of the material. Experimental techniques utilizing simultaneous measurement of quasi-static compressibility and ultrasonic measurement of velocity and attenuation under pressure are described and discussed. Sonic transmission is correlated with included gas bubbles in solid propellants having up to 2% void gas filled microregions.

Experimental results on large blocks of material show that when the included void is compressed to essentially zero volume fraction by external pressure, after some delay, transmission increases until an equilibrium value is reached. This equilibrium value is very nearly that obtained for the transmission of the material before thermal aging was initiated. This delay is attributed to the diffusion of the

compressed gases in the bubble into the surrounding polymer, or liquification of the gas in the bubble, or both. These mechanisms either reduce the large impedance mismatch at the original solid interfaces of the void, or reduce the amount of surface and improve ultrasound transmission. The large increase in attenuation of ultrasound waves observed in solid propellants during elevated temperature storage is shown to be primarily caused by the formation of gas filled microvoids, presumably formed from chemical reactions of the propellant ingredients. Without recognizing this effect, such results of ultrasonic attenuation might be erroneously ascribed to large changes in the imaginary component of complex modulus.

F-5

3:45-4:15. "Compressibility of Elastomers with Crystalline Fillers and Microvoid Inhomogeneities Related to Various Empirical Equations of State for Liquids and Solids," C. C. SURLAND, Aerojet-General Corporation, Sacramento, California.

Two basically different methods for determining the quasi static hydrostatic compressibility of highly filled elastomers are described briefly. One of these, a uniaxial compliance method, is shown to be useful only with composites that deform isotropically. The other method is volumetric and depends upon the measurement of the combined compliance of the test material and a confining fluid.

Experimental results will be presented which illustrate that volumetric methods must be used to obtain compressibility data for composites which deform anisotropically under applied pressure. Empirical equations of state for various confining fluids are described and discussed. These are shown to be useful and necessary for making accurate determination of the volumetric compressibility of elastomers and filled elastomers.

The effect of included void on the compressibility of elastomers and composites is discussed. Various theories for void compression are enumerated and discussed and compared with experimental PV data for voided composites.

(Continued from Page 1)

7. Stephen Prager reported the program for Cleveland consisted of forty-two pages, 38 contributed and 4 invited lectures.
8. The membership chairman Armand Lewis reported via the Secretary-Treasurer that 35 new members were obtained this year.
9. R. S. Marvin reported that Prof. Stockmayer had agreed to present the Bingham Medal to Eugene Guth, but that Stockmayer was ill and might not make it. In that case, R. S. Marvin will do the honors.
10. R. S. Marvin collected the necessary information to nominate J. D. Ferry for the National Medal of Science and sent the information to the selection committee.
11. I. M. Krieger reported on the local arrangements and pointed out that attendance of 300 members would seriously strain Case Institute. A banquet will be held Tuesday evening. An attempt to hold an instrument exhibit fell through because some of the companies complained of inadequate notification. Krieger suggested that an instrument exhibit to be held in 1966 should be started now.
12. Dale Meier reported arrangements for the Monterey meeting were proceeding satisfactorily. A discussion ensued about the advisability of separate accounts to run meetings. The Secretary will check with Mr. Waterfall at AIP about liability of the Society.
13. No information had been received on the Fifth International Congress to be held in Japan. T. L. Smith suggested charter flight could be arranged to Japan for the Congress.
14. J. Brodnyan local arrangements chairman for Atlantic City asked about publicity. The Secretary will check with Mr. Kone of AIP.
15. The 1967 meeting will be held in Washington, D.C. probably at the Sheraton Hotel, Oct. 23-25.
16. A request from the National Referral Center for Science and Technology of the Library of Congress for cooperation of the Society via individual members was not considered applicable to the Society functions.
17. A request from Sectional Committee ZII on Petroleum Products and Lubricants to cooperate and appoint a representative from the Society was not considered an appropriate function of the Society at present.

John C. Miller  
Secretary-Treasurer

## ANNOUNCEMENTS

1. The Fluids Engineering Division of the ASME and the Society of Rheology will co-sponsor a symposium entitled "Biomedical Fluid Flow." The Chairman, R. J. Nickerson is located at the Stevens Institute of Technology in Hoboken, New Jersey. The Biomedical Fluid Flow Symposium is a special feature of the meeting which will have other sessions in fluid mechanics. Both permanent interest papers and short, current interest papers will be covered. George Rudinger of the Cornell Aeronautical Laboratory will present a survey paper on "Flow and Elastic Tubes." The dates are April 25 through 27, 1966 in Denver, Colorado. Further information will be supplied by the ASME.

2. J. Mandel, president of the French Society of Rheology announced that the French group will resume publication of the "Notebook" which contains a text of their conferences.

3. The "First International Conference on Hemorrheology" will be held under the auspices of the University of Iceland from July 10 through 16, 1966. Arrangements to attend should be made as soon as possible through the Icelandic Government Tourist Bureau in Reykjavik. A. L. Copley, Hemorrhage and Thrombosis Research Laboratories, Veterans Administration Hospital, East Orange, New Jersey is Chairman of the Scientific Organizing Committee and can supply information.



