

# RHEOLOGY BULLETIN

Publication of the Society of Rheology

Volume 34 No. 1



January, 1965

## SECOND WINTER MEETING OF THE SOCIETY OF RHEOLOGY

MIRAMAR HOTEL-MOTEL,  
SANTA BARBARA, CALIFORNIA

JANUARY 28 AND 29, 1965

*Location.* The motel is on the California Coast in Santa Barbara. Membership in the Society of Rheology is not prerequisite for participation. The West Coast Gordon Conference on Polymers will be held in the same hotel the week days following the Winter Meeting of the Society of Rheology. Dr. Ralph Milkovich, General Tire and Ruber Company, Akron, Ohio, is chairman for the Gordon Conference.

Authors are urged but not required to submit manuscripts to the Transactions. The deadline is January 29 for submitting three manuscripts to Dr. Raymond R. Myers, Chemistry Department, Lehigh University, Bethlehem, Pennsylvania.

*Accommodations and Facilities.* Hotel accommodations may be pursued individually with the Miramar Hotel-Motel. Speakers will be provided with a blackboard and 2-inch by 2-inch and 3 $\frac{1}{4}$  inch by 4 $\frac{1}{4}$  inch slide projectors. If other facilities such as movie projectors are required, contact the local arrangements chairman whose address appears below.

Roger S. Porter, General Chairman, Winter Meeting, California Research Corporation, 576 Standard Avenue, Richmond, California 94802.

Thor Smith, ex-officio, Society of Rheology Executive Committee, Stanford Research Institute, Menlo Park, California.

Charles C. Surland, Local Arrangements, Dept. 4520, Aerojet-General Corporation, P. O. Box 1947, Sacramento 9, California.

Nicholas W. Tschoegl, Stanford Research Institute, Menlo Park, California.

Robert F. Fedors, Jet Propulsion Laboratory, Pasadena, California.

## NOTICE OF ANNUAL MEETING

October 25-27, 1965

The 36th annual meeting of the Society will be held at The Case Institute of Technology, Cleveland, Ohio on October 25-27, 1965.

Correspondence regarding the submission of papers should be conducted with Program Chairman Prager whose address appears below.

## SOCIETY OF RHEOLOGY OFFICERS

1965-1966

### *President*

JAMES T. BERGEN, Armstrong Cork Company, Lancaster, Pa.

### *Vice-president*

ROBERT S. MARVIN, Rheology Section, National Bureau of Standards, Washington 25, D. C.

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RAYMOND R. MYERS, Department of Chemistry, Lehigh University, Bethlehem, Pa.

## Committee Chairmen, 1965

### *Program*

STEPHEN PRAGER, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota.

### *Nominating*

NICHOLAS W. TSCHOEGL, Propellant Science Development, Stanford Research Institute, Menlo Park, California.

### *Membership*

ARMAND F. LEWIS, Stamford Research Laboratories, American Cyanamid Company, Stamford, Conn.

## EXECUTIVE COMMITTEE

This committee is composed of the officers plus Immediate Past Chairman Ferry and two members elected at large: Thor L. Smith, Propellant Research & Development, Stamford Research Institute, Menlo Park, Calif., and Hershel Markovitz, Mellon Institute, Pittsburgh 13, Pa.

## RHEOLOGY BULLETIN

Raymond R. Myers, Editor  
Department of Chemistry  
Lehigh University  
Bethlehem, Pa., 18015

### PROGRAM SECOND WINTER MEETING OF THE SOCIETY OF RHEOLOGY

MIRAMAR HOTEL-MOTEL  
SANTA BARBARA, CALIFORNIA

JANUARY 28 AND 29, 1965

REGISTRATION. 8:00-9:00 p.m. January 27  
8:00-8:45 a.m. January 28

OPENING REMARKS. 8:50 Thursday morning,  
January 28

#### GENERAL SESSIONS.

Chairman: Dr. R. F. Landel

Jet Propulsion Lab, Pasadena, Calif.

A-1

9:00-10:00 INVITED LECTURE: "*Some Conceptual Difficulties in Polymer Rheology*," E. B. BAGLEY, Department of Chemical Engineering, Washington University, St. Louis, Missouri, on loan from Canadian Industries, Limited, McMasterville, P. Q.

In spite of considerable theoretical and experimental advances in the study of polymer rheology over the last decade there seem to be areas where even qualitative explanations of observed phenomena are lacking. It is the purpose of this paper to discuss some of these problems with emphasis on both post-extrusion swelling phenomena and the dependence of the viscoelasticity of polymer melts on molecular structure. Finally, a new procedure (due to B. E. M. Bingham, of Courtaulds North America, Inc., and soon to be published in Part B, Journal of Polymer Science) for calculating a shear rate independent viscosity in ostensibly shear-sensitive material will be discussed.

A-2

10:00-10:30 "*An Equation of State for the Compressibility of Rubbers and Plastics*," P. J. BLATZ, California Institute of Technology, Pasadena, California.

In a previous paper ("*Application of Finite Elastic Theory to the Deformation of Rubbery Materials*") by P. J. Blatz and W. L. Ko, Transactions of the Society of Rheology, Vol. 6, p. 223, 1962), a mechanical equation of state was presented which described the deformation of polyurethane foams in four different

stress fields. In this equation is contained a parameter which plays the role of Poisson's Ratio for large deformation. In the present paper an explanation for the appearance of this parameter is suggested on the basis of an assumed molecular interaction potential. All of Bridgman's data on the compressibilities of rubbers and plastics were plotted according to the form suggested by the equation of state. Excellent straight lines resulted in all cases. Both the bulk moduli and intermolecular repulsion exponents are evaluated.

A-3

10:45-11:15. "*Simple Rheological Models for Surface Areal Deformations*," KAROL J. MYSELS, Department of Chemistry, University of Southern California, Los Angeles, California.

Surface shear viscosity has been studied extensively and its analogy with bulk shear behavior is quite clear. Surface areal (dilatational) rheology on the other hand has been relatively neglected and its analogy to bulk volume rheology is less close or obvious. Yet in fact the importance of the two types of deformations is reversed as one goes from bulk to surface, the areal one being more important and more frequently encountered in surface phenomena. A few examples of this importance are cited, simple models are proposed for several types of experimentally realizable deformations and the corresponding mechanisms discussed in order to clarify the situation. Models for areal rheology seem to be characterized by the need of a new type of element such as a "suspended weight" and differ from those for bulk volume rheology by the frequent presence of this element or of a series dashpot.

A-4

11:15-11:45. "*The Microrheology of Suspensions Flowing Through Tubes*," S. G. MASON, Pulp and Paper Research Institute of Canada, 3420 University Street, Montreal, Canada.

The behaviour of suspensions of rigid and deformable particles of various shapes and dimensions and having a wide range of concentrations flowing through tubes has been studied in considerable detail. The rotational and translational movements, deformations, two-body interactions, radial migration and other aspects of particle behaviour are described for both steady and pulsatile flows. The significance of the phenomena to a number of problems in suspension rheology is discussed.

#### THURSDAY AFTERNOON

JANUARY 28, 1965

#### STEADY FLOW.

Chairman: Dr. D. W. Criddle  
Calif. Research Corp., Richmond

B-1

1:30-2:00. "*Analysis of Flow Properties in Relation to Molecular Parameters for Polymer Melts*," W. H. BAUER, Rensselaer Polytechnic Institute, and E. A.

Collins, B. F. Goodrich Chemical Company, Avon Lake Development Center.

Reported data on polystyrene, polyethylene and polydimethyl siloxanes are contradictory with respect to the shear rate at which the transition from Newtonian to shear-sensitive flow occurs. One set of data implies that the transition occurs at the same lower limiting shear rate and is independent of molecular weight above a critical molecular weight. On the other hand, other data show that above a critical molecular weight the transition occurs at lower rates of shear as the molecular weight increases. The theoretical considerations of Bueche for melt polymer flow appear to predict the latter type of transition behavior. It is proposed that the discrepancies are due to molecular weight distribution and temperature effects and may be affected by methods of obtaining "zero" shear viscosities. Data are presented to support these views.

B-2

2:00-2:30. "Steady State Melt Viscosity of Plasticized Hydrocarbon Elastomers," G. KRAUS and J. T. GRUVER, Phillips Petroleum Company, Bartlesville, Oklahoma.

The steady state melt viscosity of several plasticized hydrocarbon elastomers is shown to be described by a reduced variable treatment which allows superposition of the viscosity-shear rate curve for any polymer containing a diluent on the viscosity curve of the pure polymer. The shift factors which accomplish this superposition may in turn be broken up into two factors: (1) a function of the volume concentration of the diluent alone, which represents the loosening of the entanglement network, and (2) a factor representing the effect of the diluent on segmental friction and chain configuration. The latter is shown to be related to the temperature of measurement and the glass transition temperatures of both polymer and diluent. The relationship developed permit estimates of plasticizer efficacy for any diluent/polymer combination from glass transition and density data alone. Attention is drawn to the seemingly anomalous behavior of certain branched polymers of high molecular weight. These appear to respond to plasticization to an unusually high degree, but only in the low shear range.

B-3

2:30-3:00. "The Flow of a Molten Polymer," T. GILLESPIE, Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan.

The Williamson empirical equation which fits polystyrene melt viscosity data is derived by considering the melt as a dynamic connected system of extensible elements. The theory allows one to trace changes in the number of extensible elements and the relaxation time for the thermal rupture of intermolecular links. For uniform molecular weight samples, the number of

extensible elements per molecule is proportional to the molecular weight. Widening the molecular weight distribution lowers the number of extensible elements per cc. The thermal relaxation time increases rapidly with increasing molecular weight. The effect of fillers on the number of extensible elements and the thermal relaxation time is complex.

B-4

3:00-3:30. "The Role of Entanglements in Polymer Flow Behavior," JACK R. KNOX, Hercules Powder Company.

One interpretation of some recent experimental results on linear polymers strongly suggests that entanglements of polymer molecules do not contribute to the viscous component of the viscoelastic flow behavior of polymer melts and solutions. It is suggested that entanglements contribute only to the elastic component of flow, and an alternate hypothesis (based on the Eyring flow theory) is proposed to explain the break in the  $\log \eta - \log M$  plot.

B-5

3:45-4:15. "Elasticity and Viscosity of Polymer Melts as Related to the Geometry of Polymer Molecules," W. F. BUSSE, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

Standard methods of measuring the elasticity of polymer melts are reviewed, and results of another method of measuring viscoelastic properties of melts are presented. This involved measuring the force required to draw a molten beading and the maximum rate of draw that caused breaking of the filament. For several types of polyethylenes, the maximum draw rate decreased about as the minus three halves power of the melt strength. The effects of irradiation on the melt strength, melt index, and solution viscosity are compared. Polytetrafluorethyene fibrils dispersed in polyethylene greatly increase the melt strength of filaments and the swell of extrudates. The larger "Teflon" fibrils have a corkscrew shape, and they taper off to diameters below the resolving power of the microscope.

Consideration of the elasticity and viscosity of polymer melts and solutions, and the geometry of polyethylene molecules suggests that the major part of the melt viscosity and elasticity is due to the "snubbing" or entanglement of long lengths of one molecule around another. The motion of these snubbing points due to the applied strain introduce entropy elasticity in the random coils between these points. The fluidity ( $1/\eta$ ) is a measure of the rate of slippage around these snubbing points. This picture suggests reasonable qualitative explanations of the decrease in viscosity of melts at high shear rate, and of the unstable melt flow through capillary orifices. It also predicts a tendency for fractionation with respect to molecular weight along the radius during extrusion through a capillary.

B-6

4:15-4:45. "A Recording High Shear Viscometer and Measurements Near a Million Seconds<sup>-1</sup>," ROGER S. PORTER, RUDOLPH F. KLAVER, and JULIAN F. JOHNSON, California Research Corporation, Richmond, California.

An improved and recording rotational high shear viscometer has been developed. The instrument employs concentric steel cylinders with unusually narrow and precisely defined shear clearances. Both shear rate and stress are continuously, simultaneously, and independently recorded. Improved cylinders plus other additions have led to accurate viscosity measurements from  $5 \times 10^2$  to  $2 \times 10^6$  seconds<sup>-1</sup>. The temperature range is  $-20^\circ\text{C}$  to  $150^\circ\text{C}$  with a viscosity range which varies inversely with the desired shear rate range for measurement. This shear rate range and upper limit, 2 million seconds<sup>-1</sup>, exceeds previous reported conditions for measurement in defined conditions of homogeneous and isothermal shear field.

Extreme shear viscosity measurements are given for pure liquids and viscosity standards along with other results which represent incisive tests for portions of the rheological theory.

B-7

4:45-5:15. "The Influence of Additional Orientation Mechanisms on the Theory of Streaming Birefringence," GEORGE S. ARGYROPOULOS, Engineering Science Department, California Institute of Technology, Pasadena, California.

The problem of determining the orientation distribution function for rigid particles of arbitrary shape is formulated in a general stochastic approach to consider the influence of any acting orientation mechanism, stochastic or deterministic. The effect of the various orientation mechanisms on the partial differential (Fokker-Planck) equation of the problem is analysed in terms of the drift velocity to vector  $\vec{C}$

and the fluctuating tensor  $\vec{D}$ , and the question of linearity of superposition is examined.

As an application, a particular orientation mechanism acting on rigid ellipsoidal macromolecules in addition to the hydrodynamic and the Brownian effects is considered in Couette flow: a force field in the radial direction  $x$ , varying linearly with  $x$ . It is shown that the effect of an electric field in the radial direction on polarizable ellipsoidal particles is of this nature. The corresponding steady state orientation distribution function is determined to the third order for the case of predominant Brownian influence, and the theory of streaming birefringence of a dilute suspension of rigid ellipsoidal macromolecules in Couette flow is thus generalised: the direction of the isocline and the amount of birefringence are calculated to the second order.

Finally the effect of hydrodynamic interactions be-

tween the ellipsoidal particles and also suspended spheres is examined in terms of a model. It is shown, by considering the energy dissipation, that the effect of the presence of the spheres on the rotational motion of the ellipsoids appears as a reduction of the effective velocity gradient.

#### GENERAL SESSIONS.

Chairman: Dr. N. W. Tschoegl

Stanford Research Institute, Menlo Park, Calif.

C-1

1:30-2:00. "Viscoelastic Behavior of a Filled Elastomer in the Linear and Nonlinear Range," E. LENOE, R. A. HELLER, and A. M. FREUDENTHAL, Department of Chemical Engineering and Engineering Mechanics, Columbia University, New York 27, New York.

The rheological behavior of a filled elastomer (polyurethane rubber and granular potassium chloride) is investigated under long- and short-time torsion, tension and compression over a temperature range from  $-60^\circ\text{F}$  to  $200^\circ\text{F}$ . To represent the observed behavior for moderate stresses, a linear viscoelastic model was developed which represents the test results very well, although in the lower temperature range the non-linearity of response is pronounced even at moderate stresses. Prolonged exposure to high temperature and humidity degraded the rubber-to-filler bond so that the dominant relaxation response is that of a polyurethane rubber foam. Temperature dependence of the relaxation modulus is presented with the aid of the shift function for thermal rheologically simple materials, though such behavior exists only in first approximation at selected strain and temperature levels. Activation energies calculated for initial strain levels of 4.3 and 8.6% suggest that the observed reduction of this energy by doubling the strain might be due to increasing orientation of the elastomer molecules with increasing strain.

C-2

2:00-2:30. "Dependence of Viscosity or Modulus of Highly Filled Polymer Systems on Concentration and Particle Size Distributions," J. S. CHONG, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

Based on the Navier-Stokes equations of motion without inertia terms, an equation for the relative viscosity as a function of solid concentration is derived for monodispersed suspensions. The calculated viscosity is in good agreement with the pertinent existing data up to 50% by volume of solids. At dilute concentrations the theory reduces to the well-known Einstein equation.

An empirical relationship for the dependence of relative viscosity or relative modulus of concentrated suspensions (or of highly filled viscoelastic polymer materials) on solid loading and on particle size distributions is found based on the extensive amount of

published data in literature. The proposed equation has only one constant which may be determined experimentally without performing any viscosity measurement. Based on the above correlation, some possible causes for the variability in the mechanical properties of highly filled polymer systems may be explained. The correlation indicates that at certain feed compositions a small variation in particle size distribution could produce a significant variability in the mechanical properties of final products, while there is a region of feed composition where even large variations in particle size distributions could produce little or no effects on the mechanical properties.

C-3

2:30-3:00. "Thermal Effects In Model Viscoelastic Materials." I. J. GRUNTFEST and S. J. BECKER, General Electric Company, Space Technology Center, King of Prussia, Penna.

As part of general study of the mechanical behavior of materials with temperature dependent properties, simple viscoelastic models are considered. Ideal experiments at constant stress and constant rate of deformation are examined. It is shown that yield and fracture criteria, which are regarded as experimentally determined quantities in the usual theories, appear here as natural consequences of heat production in the material. Rate of strain and size effects are also deduced and a phenomenon resembling strain hardening can develop.

The treatment is independent of, but complementary to, the atomic scale theories of the deformation of solids. The temperature coefficient of viscosity which is introduced into the continuum theory here, is related to the energy of activation for the flow process which is accessible to the atomic scale theory. The appreciation of the temperature field in which motions of the atoms occur could improve the predictions based on dislocation theory.

C-4

3:00-3:30. "Time, Temperature, and Molecular Weight Effects in Environmental Stress Cracking," G. E. FULMER, W. R. Grace and Company, Clarksville, Maryland.

A parametric study was made of the stress relaxation of linear polyethylene in air and a stress cracking environment, Igepal. Breaking time is shown to be a function of reduced variables of time, temperature and molecular weight. Acceleration of tests for failure time can be achieved if the test temperature is raised, since for .96 density P.E. over the range of 50 to 110 degrees centigrade no mechanism change occurs. Stress relaxation measurements are shown to give results similar to the bent strip stress cracking test (ASTM D 1693-60T). This latter test can also be accelerated 80 times for .96 density polyethylene and 1500 times for .95 density polyethylene. A slight modification of the test procedure is required to ob-

tain meaningful results. Some effects of strain, thickness and presoaking are also reported.

C-5

3:45-4:15. "Crazing In Glassy Polymers," ROGER P. KAMBOUR, General Electric Company, Schenectady, New York.

It has been known for several years that crazes in glassy polymers are not cracks but rather thin plate-like regions containing a polymer "filling" which connects with the surrounding bulk polymer and is oriented in the direction of the craze-producing stress. The craze material, however, is of markedly reduced density which accounts for the high reflectivity of the craze. The void content is dispersed on a scale of 100 Å or so and appears to be interconnected. The transition from bulk polymer to fully-developed craze material appears from limited evidence to be rather abrupt, occurring over a distance of 1000 Å or less. Crazes can have remarkably high strengths and yet they act as fracture initiators when polymers fail in a brittle fashion.

C-6

4:15-4:45. "Peel Adhesion: Micro-fracture Mechanics of Interfacial Unbonding of Polymers," D. H. KAELEBLE, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.

A simple and precise means of measuring internal bond stresses in peel is now available. By the use of a newly designed "bond stress analyser" the magnitude and positional distribution of internal normal stresses may be measured during peel. The design theory, construction, and operation of the instrument are reviewed in detail. The influence of the angle of peeling upon the cleavage stress distribution is investigated and analysed. The results, interpreted in terms of present theory of peel adhesion, suggest that the peel test is a valid measure of interfacial adhesion properties only at a peel angle of  $w = \pi$  radian = 180 degrees. The detailed form of the cleavage stress function in the region of boundary fracture indicates that cavitation and orientation processes contribute importantly to high peel strengths in elastomeric adhesive interlayers.

C-7

4:45-5:15. "Tear Phenomena Around Solid Inclusions in Castable Elastomers," A. E. OBERTH and R. S. BRUENNER, Aerojet General Corporation, Sacramento, California.

Adhesion studies on spherical particles imbedded in elastomers have shown that cohesive failure of the binder phase always precedes dewetting. The latter is a sudden and irreversible process resulting in permanent damage to the system. Cohesive failure manifests itself in the formation of a number of small holes near the surface of the filler particle. The stress,  $\sigma$  causing these holes is well defined and

depends only on the elastic modulus,  $E$ , of the binder:  $\sigma = E/2 + C$ . The further propagation of these initial tears depends on the consistency of the boundary layer surrounding the solid inclusion. In case of no modulus gradient or a softer boundary layer, tear propagation leads to the complete separation of the elastomeric binder from the particle. High modulus layers, which are linked to the polymeric matrix by primary chemical bonds, prevent a dewetting. It is shown that the complex response of filled elastomers can be explained in terms of the above results.

GROUP DINNER. THURSDAY EVENING,  
JANUARY 28.

FRIDAY MORNING, JANUARY 29, 1965  
DYNAMIC MECHANICAL MEASUREMENTS  
AND MODELS.

Chairman: Professor R. B. Bird

University of Wisconsin, Madison, Wisconsin.

D-1

8:30-9:30. INVITED LECTURE: "Dynamic Mechanical Properties of Supported Polymers," ARMAND F. LEWIS, American Cyanamid Company, Stamford, Connecticut.

A review of studies on the dynamic mechanical properties of supported polymers reveals that such techniques, although not amendable to direct measurement of dynamic mechanical moduli, extend the applicability of dynamic mechanical methods to many practical systems. It is shown that supported polymer techniques provide a very sensitive tool for following qualitatively the rheological changes which accompany the cure, thermal softening, thermal degradation and solid state reactions of various polymeric (or monomeric) systems. Of particular interest is that these methods can provide information on the complete liquid-to-solid conversion of a curing polymer; this feature, therefore, forms a basis for a rheological criterion of cure of thermosetting polymeric systems. The application of these techniques to several aspects of polymer research will be demonstrated. A critical analysis of the advantages and limitations of these techniques will be made. This appraisal will include results of recent experiments conducted in an effort to correlate these rheological measurements with the chemical processes which govern them.

D-2

9:30-10:30. INVITED LECTURE: "The Rheology of Synthetic Polymer Latices," JOHN G. BRODNYAN, Rohm and Haas Research Laboratories, Springhouse, Pennsylvania.

There have been a number of unresolved problems in latex rheology; for example, what causes shear-sensitive flow and what is the correct functional form

of the dependence of viscosity upon dispersion concentration. Some recent work has gone a long way toward clarifying many of these problems, and this review is an attempt to summarize the present state of our knowledge.

Apparently Mooney's formula describes the dependence of viscosity on concentration, provided an effective volume fraction and the correct maximum packing fraction are used. The effective volume fraction is an additive combination of the polymer volume fraction and the volume excluded to other particles by the coulombic repulsive forces of the double layer. Shear-sensitive behavior appears when the effect of volume goes above a certain value; that is, it appears to be a crowding phenomenon.

D-3

10:45-11:15. "The Theory of the Gamma Transition in Polyethylene and Related Polymers," T. F. SCHATZKI, Shell Development Company, Emeryville, California.

The literature on dynamic mechanical loss measurements in polyethylene and related polymers will be reviewed. It will be shown that it is necessary in the case of the 160°K loss peak in polyethylene to postulate a molecular mechanism involving hindered internal rotation in hydrocarbon chains. This model, which was described by us in J. Poly. Sci. 57, 496 (1962) will be supplemented by more recent results from the literature and from our measurements. A number of predictions regarding activation energies and the types of loss peaks to be expected will be made on the basis of our model and compared with experiment.

D-4

11:15-11:45. "The Transient Response of a Viscoelastic Torsional Pendulum," ALEXANDER S. ELDER, U. S. Army Ballistic Research Laboratories, Aberdeen Proving Ground, Maryland.

The pendulum consists of a circular viscoelastic rod fixed at one end and attached to a disc at the other end. The disc, initially at rest, is subjected to a step function of torque. The subsequent motion is analyzed in terms of normal modes and normal coordinates. The characteristic numbers associated with the modes depend only on the moments of inertia of the rod and disc, and not on the mechanical properties of the rod. The normal coordinates are solutions of integro-differential equations of the Volterra type. These equations have been solved by means of the Laplace transform.

The torsional motion of a mechanical system consisting of a viscoelastic rod, a disc, and an elastic spring is also considered. The Sturm-Liouville method used in the preceding analysis is not effective. A separable solution with  $\exp(st)$  as the time-dependent factor is assumed. A formal solution in terms of a contour integral is obtained.

The relation between the calculated results and the observed motions of a torsional pendulum is discussed.

D-5

11:45-12:15. "A Thermistor Model for Non-Linear Viscous and Viscoelastic Materials," I. J. GRUNTFEST, General Electric Company, Space Technology Center, King of Prussia, Pennsylvania.

The physical and mathematical similarity of the resistance-temperature relation in thermistors to the viscosity-temperature relation in typical liquids makes it possible to simulate the essential non-linearity of the flow of Newtonian liquids by the use of an electric analog. Simple measurements of current and voltage take the place of detailed computation. Circuits containing a thermistor and capacitor simulate non-linear viscoelastic materials.

The behavior of the analogs agrees with available analytical results. In addition, it duplicates experimentally observed temperature effects and apparent departures from Newtonian behavior in liquids as well as necking, yield, fracture, creep, strain hardening and stick-slip effects in solids. This electric analog literally simulates the mechanical system. In contrast, the widely discussed simulation of linear viscoelasticity by electric networks is figurative. That is, there, the well developed mathematics of linear circuits was applied to the mechanical system. The new simulation is effective over wide ranges of stress, strain and time even with a single thermistor.

FRIDAY AFTERNOON,

JANUARY 29, 1965

POLYMER FLOW AND NORMAL STRESS.

Chairman: Dr. Dale Meier  
El Cerrito, California

E-1

1:30-2:00. "Flow of Viscoelastic Fluids in the Entrance Region of Parallel-Plate Channels," J. L. WHITE, U.S. Rubber Company Research Center, Wayne, New Jersey and A. B. METZNER, University of Delaware, Newark, Delaware.

An analysis of flow in the entrance region of parallel-plate channels or dies is presented for the several purposes of using "end effect" measurements for evaluation of material properties, for gaining a better understanding of the flow characteristics in such geometries as are of industrial importance and of gaining insight into the properties of viscoelastic fluids in accelerating (non-viscometric) flow fields. The analysis employs the usual simplifying assumptions and the integral momentum method of boundary layer theory.

The predicted increase in the length of the entrance region with the increasing values of the Reynolds and Weissenberg numbers is at least in qualitative

agreement with the known behavior of polymeric systems and, in the limiting case of Newtonian behavior, reduces to the usual solution for those fluids. The implications of these results insofar as constitutive equations suitable for description of non-viscometric flows is discussed.

E-2

2:00-2:30. "Three Parameter Correlations of Complex Flow Phenomena," R. BYRON BIRD, Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin.

Data from complicated flow systems involving viscoelastic materials can be interpreted by using analyses based on the determination of three parameters from shear-sensitive viscosity curves. The three constants are: the zero-shear viscosity  $\eta_0$ , a characteristic time  $\lambda$ , and a dimensionless quantity  $\alpha$  which describes the "power-law" behavior of the shear-sensitive viscosity at high shear rates. The applicability of the method to seven experimental systems is summarized including turbulent tube flow, laminar annular flow, flow in a packed column, flow in a converging channel, flow in an oscillating manometer, and flow around spheres. It is further suggested how shear-sensitive viscosity measurements might be used to predict the elongational viscosity using the same three constants.

A justification of the method is given in terms of several non-linear viscoelastic models. It is shown how the characteristic time  $\lambda$ , easily obtained from a standard shear-sensitive viscosity measurement, is related to various other time constants suggested previously.<sup>[1-3]</sup> The importance of comparing the characteristic time of the fluid with the characteristic time of the flow system is emphasized.

[1] M. C. Williams and R. B. Bird, *Physics of Fluids*, 5, 1126 (1962).

[2] T. W. Spriggs and R. B. Bird, *Ind. Eng. Chem. Fund.*, to be published.

[3] C. Truesdell, *Phys. Fluids*, 7, 1134 (1964).

E-3

2:30-3:00. "Laminar Converging Flow of Dilute Polymer Solutions in Conical Sections," JOHN L. SUTTERBY, University of Wisconsin, Madison, Wisconsin (now with the Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio).

The test fluids were three aqueous solutions of Natrosol 250 H hydroxyethyl cellulose. Their nominal concentrations were 0.3%, 0.5%, and 0.7%. Viscosity data for each solution were fitted with a generalized Newtonian viscosity model which properly describes the zero-shear viscosity.

There were two conical sections. The vertex angles of the two sections were approximately 14° and 21°. Flow rate versus pressure drop data were taken for each Natrosol solution in each conical section. Approximate expressions relating flow rate and pres-

sure drop were derived for the limiting cases of very low and very high flow rates. The low flow rate asymptote was of form

$$\text{pressure drop} = \text{function of (flow rate, geometry, viscosity model parameters)} \quad (1)$$

The high flow rate asymptote was of form

$$\text{pressure drop} = \text{function of (flow rate, geometry, fluid density)} \quad (2)$$

Equations (1) and (2) were in excellent agreement with the data at low and high flow rates. The sum of equations (1) and (2) was in good agreement with data over the *entire range* of flow rates. This superposition expression in no way accounts for normal stresses or time-dependent viscoelastic effects. Its success in describing the data implies that these phenomena were not important. For engineering purposes generalized Newtonian viscosity models will probably be adequate for characterizing the flow of dilute polymer solutions in conical sections.

E-4

3:00-3:30. "Non-Newtonian Flow Through Porous Media," T. J. SADOWSKI and R. BYRON BIRD, Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin.

In a study of the flow of shear-sensitive fluids through porous media, fourteen different aqueous solutions of polyethylene glycol, polyvinyl alcohol, and hydroxyethyl-cellulose were investigated. The shear-sensitive viscosities of these fluids were characterized by the three-parameter Ellis model. The application of an Ellis fluid to a capillary model of a porous medium led to a generalized Darcy law in which the Newtonian viscosity is replaced by an effective viscosity

$$\frac{1}{\eta} = \frac{1}{\eta_0} \left\{ 1 + \left( \frac{4}{3+\alpha} \right) \left( \frac{\tau_{Rh}}{\tau_{1/2}} \right)^{\alpha-1} \right\}$$

where

$$\tau_{Rh} = \frac{1}{6} \left( \frac{D}{1-\epsilon} \right) \frac{\Delta P}{L}$$

The particle diameter is  $D_p$ , the bed porosity is  $\epsilon$ , the pressure gradient is  $\Delta P/L$ , and the fluid parameters are  $\eta_0$ ,  $\alpha$ , and  $\tau_{1/2}$ .

Two different types of flow behavior were observed: (1) When the volumetric flow rates were held constant, the results were both steady and reversible. The flow data for low and medium molecular weight polymer solutions were successfully correlated by the generalized Darcy law. An additional dependence on the dimensionless group  $(v_0 \eta_0 / D_p \tau_{1/2})$  was noted for high molecular weight solutions. Here  $v_0$  is the "filter velocity" and  $\eta_0 / \tau_{1/2}$  represents a characteristic "relaxation" time. (2) When the bearing

pressure was held constant, the results were both unsteady and irreversible. In this case, polymer adsorption and gel formation were believed to have occurred throughout the bed.

E-5

3:45-4:15. "A Four-Constant Model for Viscoelastic Fluids," THOMAS W. SPRIGGS, Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin.

A nonlinear extension of the generalized Maxwell model is proposed as a constitutive equation for viscoelastic fluids. This paper is a continuation of work started in reference [1]. Expressions for complex-viscosity, oscillatory normal stresses, viscosity and two normal stress differences are given in terms of four parameters. Comparison is made with M. C. Williams [2] complex-viscosity data for 1.46% polyethylene oxide in water and with Williams' normal stress and non-Newtonian viscosity data for 1.54% hydroxyethylcellulose in water. The viscosity function from the proposed model agrees with the Ellis model [3] in the regions of high and low shear rate. The expressions for the oscillatory shear stresses and normal stresses agree with those derived from a special case of the Coleman and Noll [4] theory of second-order viscoelasticity.

[1] T. W. Spriggs and R. B. Bird, IEC Fundamentals to be published.

[2] M. C. Williams, Ph.D. Thesis, University of Wisconsin (1964).

[3] R. B. Bird, Kagaku Kagaku, 28, 405 (1964).

[4] B. D. Coleman and W. Noll, Rev. Md. Phys., 33, 239 (1961).

E-6

4:15-4:45. "Experimental Determination of the Second Normal Stress Difference for Aqueous Polymer Solutions," JOHN D. HUPPLER, Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin.

An axial annular flow device has been utilized to determine the second normal stress difference  $\pi_{22} - \pi_{33}$  where the velocity field is  $v_1 = v_1(x_2)$  for several aqueous polymer solutions. When an appropriate trial function is chosen, approximate values of  $\pi_{22} - \pi_{33}$  can be determined by numerically integrating the radial component of the equation of motion; to do this one needs a viscosity curve and data on the axial pressure gradient versus the radial pressure difference between inner and outer walls of the annulus. In this analysis values of  $\pi_{22} - \pi_{33}$  were obtained by assuming that a non-linear Maxwell model recently proposed by T. W. Spriggs [1] adequately describes  $\pi_{22} - \pi_{33}$ . Three of the model parameters were determined from the viscosity curve, the fourth from a best fit analysis of the annular flow normal stress data.

The annular test section and a micromanometer (designed by J. L. Sutterby [2]) for measuring radial pressure differences as small as two dynes/cm<sup>2</sup>, are described. Experimental data and approximate curves



of  $\pi_{22}-\pi_{33}$  are presented for several aqueous solutions of hydroxyethyl cellulose, carboxy methyl cellulose, guar gum, and polyethylene oxide. These curves indicate that this normal stress difference, while not zero, is considerably smaller than the first normal stress difference,  $\pi_{11}-\pi_{33}$ , for the solutions studied.

- [1] T. W. Spriggs, Submitted to Chemical Engineering Science.  
[2] J. L. Sutterby, Ph.D. Thesis, University of Wisconsin (1964)

#### E-7

4:45-5:15. "A Pitot Tube Method for Measuring The First Normal Stress Difference and Its Influence on Laminar Velocity Profile Determination," J. G. SAVINS, Socony Mobil Oil Company, Inc., Field Research Laboratory, Dallas Texas.

A method is described for determining the first normal stress difference ( $P_{11}-P_{22}$ )\* at low shear rates from measurements of point value dynamic pressures with a pitot tube under the steady laminar conditions of Poiseuille flow. The method is free of assumed relationships between shear rate and shear stress. It permits ( $P_{11}-P_{22}$ ) measurements over a shear rate range comparable to that encountered in the torsional and circular flow methods; hence it should prove useful in providing data for evaluating constitutive equations. In contrast, the capillary jet methods, which also have their origin in Poiseuille flow are restricted to measurements of ( $P_{11}-P_{22}$ ) at shear rates greater than  $10^3 \text{ sec}^{-1}$ . An example is cited to show that the presence of this normal stress difference can, in theory, produce a significant aberration in the local velocities which an observer would compute from the conventional formulae. Thus the interpretation of velocity profile measurements is complicated because of normal and shear stress contributions. However, this analysis provides a method for extracting the ( $P_{11}-P_{22}$ ) component from the measurements.

\* The convention followed is that the  $P_{11}$  component is parallel to the streamlines while the  $P_{22}$  component is normal to the shearing surfaces.

#### VISCOELASTICITY AND CREEP.

Chairman: Professor P. J. Blatz  
Calif. Institute of Technology, Pasadena

#### F-1

1:30-2:00. "An Apparatus for Biaxial Stress-Relaxation Measurements of Rubberlike Materials Under Large, Combined Torsion and Tension," G. W. BECKER, Resident Research Associate, 1963-64 from the Physikalisch-Technische Bundesanstalt, Braunschweig, Germany and J. M. KENDALL, SR., P. A. CARUTHERS, R. F. LANDEL, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

An apparatus has been developed for biaxial stress relaxation measurements of rods of rubberlike material under axial strains of  $-25\%$  to  $+60\%$  and rotations of  $0$  to  $300^\circ$ . The apparatus is designed so that the rotation and extension are independent of each other, and therefore any combination within these ranges may be studied. The deformations are

applied simultaneously and in less than 0.5 seconds. The resulting torsional and axial forces are measured by standard tensile load cells, the former depending on a force acting over a one-inch mechanical moment arm. Two specimen sizes have been used to date: 10 cm. long and 3 cm. in diameter, for tests at low and intermediate rotation and elongations; 2 cm. long by 1 cm. in diameter for intermediate and high deformations. Some illustrative results for unfilled natural rubber will be presented and compared with similar results obtained with the Becker and Landel<sup>1</sup> biaxial sheet relaxometer.

<sup>1</sup>"An Apparatus for the Biaxial Stress Relaxation Measurements of Rubberlike Materials under Large Deformations," Becker, G. W., and Landel, R. F., presented at the March 1964 meeting of the Division of High Polymer Physics, American Physical Society, Pittsburgh, Pa.

#### F-2

2:00-2:30. "Typical Lubricating Greases as Linear Viscoelastic Materials," DEAN W. CRIDDLE, California Research Corporation, Richmond, California.

This paper is an experimental study of rheological properties of typical lubricating greases. Viscosity-shear rate relations are compared for steady-state shear and for transient shear conditions of stress relaxation and creep. In steady-state shear, the systems are shear-sensitive, but under transient shear conditions, they were linear viscoelastic for strains approaching their ultimate yield strain. The linear viscoelastic nature of two greases was confirmed by studies of the dampening of a torsion pendulum for small strains. A sodium soap grease is shown to be linear viscoelastic by an analysis of creep data from the literature. Recognition of the wide range of strains for linear viscoelastic behavior simplifies the study of the flow and deformation of greases.

#### F-3

2:30-3:00. "Viscoelastic Properties of Lithium Perchlorate Solutions in Poly (Propylene Oxide)," J. MOACANIN and E. CUDDIHY, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Solutions of lithium perchlorate (LP) in poly-(Propylene oxide) exhibit marked negative volumes of mixing which are due to strong interactions between lithium and the polyether oxygens. Non-ideal behavior for LP solutions in low molecular weight ethers was also observed by other workers. For our studies, poly(ethylene oxide) (mol. wt. 2000) solutions containing up to 25 wt.% LP were characterized by dilatometric, modulus, and damping constant curves over a temperature range between  $-80$  and  $80^\circ\text{C}$ . For the mechanical property measurements the solutions were supported on cellulose pads. The gradual volume contraction with increasing LP content resulted in a gradual rise in the glass-transition temperature  $T_g$  from  $-70^\circ\text{C}$  for the pure polyether to  $40^\circ\text{C}$  for the 25 wt.% solution. The  $T_g$  shifts

were paralleled by shifts in both the inflection temperature in the modulus curve and the peak in the damping constant curve, but neither the modulus nor the damping curves could be superposed by allowing  $T_g$  changes, suggesting marked changes in the distribution of relaxation times.

F-4

3:00-3:30. "Combined Stress Creep Experiments on a Non-Linear Viscoelastic Material to Determine the Kernel Functions for a Multiple Integral Representation of Creep," K. ONARAN, Research Associate, Brown University (presently Assistant Doctor, Malzeme Laboratuar, Istanbul Teknik Universite, Istanbul, Turkey), and W. N. FINDLEY, Professor of Engineering, Brown University, Providence, Rhode Island.

A multiple integral functional relationship has been employed as a constitutive equation for non-linear creep of viscoelastic material under combined stress. The kernel functions of this representation for first, second and third order stress terms have been determined from tests on a single tubular specimen of polyvinyl chloride copolymer. Tests needed to determine kernel functions adequate to describe multi-axial creep under constant stress were found to be three pure tension tests at different stress levels, three pure torsion tests at different stress levels and two combined tension-torsion tests.

Experiments include twenty tests under various combinations of tension and torsion on the same specimen. The use of only one specimen was made possible by the fact that following two hours of creep the recovery in 4 days was almost complete. Agreement between the multiple integral representation and experimental results was very satisfactory. Agreement with a hyperbolic sine representation of stress dependence was less satisfactory owing in part to the fact that the synergistic effect of tension plus torsion in the non-linear range was not accounted for.

F-5

3:45-4:15. "Control of Plastic Flow to Increase the Creep Strength of High Temperature Alloys," MUKUL K. MUKHERJEE, Midwest Research Institute, Kansas City, Missouri.

The fundamental concept of the creep phenomenon in metallic materials has been discussed from the lattice structural point of view. A mechanism to increase the creep strength of high temperature alloys has been proposed by utilizing the degree of short range order of these alloys accompanied by the resistance to the movement of dislocations which is

offered by the inclusions dispersed in the alloys.

The creep strength  $\sigma_{\dot{\epsilon},t}$  is expressed as

$$\sigma_{\dot{\epsilon},t} \approx f(S, \Lambda^{-1})$$

where  $\dot{\epsilon}$  = creep rate

t = time

S = degree of short range order

$\Lambda$  = distance between two adjacent inclusions

F-6

4:15-4:45. "Viscoelastic Response of a Cohesive Soil in the Frequency Domain," ROBERT L. KONDNER, Associate Professor of Civil Engineering, The Technological Institute, Northwestern University, Evanston, Illinois, and MICHAEL M. K. HO, formerly Research Assistant, Northwestern University, currently Assistant Professor of Civil Engineering, University of Manitoba, Winnipeg, Canada.

Energy storage and energy dissipation characteristics of a cohesive soil, which are important considerations in earthquake phenomena, machine foundation design and soil-structure interaction under dynamic loading, are studied in the frequency domain using strain-controlled vibratory uniaxial compression. The soil response is expressed in terms of the storage, loss, and complex moduli as well as the loss tangent. Dynamic stress-strain amplitude response is nonlinear even at small values of dynamic strain. Storage and complex moduli decrease with increased dynamic strain amplitude. The energy dissipation is dependent on moisture content, frequency, and dynamic strain amplitude. Loss tangent values determined by the direct method are compared with those obtained by transformation of stress relaxation test data. Effects of concentration (moisture content) are presented in terms of a non-dimensional dynamic stress-strength parameter using the ultimate compressive strength in uniaxial compression as a consistency index.

F-7

4:45-5:15. "Low Frequency Ultrasonic Wave Propagation Characteristics of Solid Propellants," G. J. KOSTYRKO and R. E. LEE, Aerojet General Corporation, Sacramento, California.

A stress wave propagation technique utilizing low-frequency burst continuous ultrasonic signals is discussed. The frequency range covered is 66 KC to 350 KC. Piezoelectric ceramic discs are used for sending and receiving transducers. The attenuation

which is much lower in this frequency range than at 1-10mc is used as a measure of mechanical properties. Changes in signal transmission during cure of solid propellant are shown. A good correlation between the ultrasonic signal transmitted and standard tensile properties such as modulus and elongation at break seems to exist. Such a correlation was obtained for

highly filled polybutadiene solid propellant formulations with different glass transition temperatures. This "sonic" test method seems feasible for in-situ determination of cure and mechanical properties of solid propellants and other polymers. Other potentials of this stress wave propagation technique are pointed out.

## ANNOUNCEMENT

RHEOLOGY SYMPOSIUM

AT

ASME: APPLIED MECHANICS

FLUID MECHANICS JOINT CONFERENCE

June 7-9, 1965 in

WASHINGTON, D. C.

The aim of the Symposium is to disseminate information concerning recent activities and advances in the field of Rheology. Works in such areas as the general non-linear continuum mechanics of visco-elastic and oriented materials, hypo-elasticity, plasticity dislocations, experimental and theoretical researches in visco-elastic vibrations, shear flows of simple fluids, plastic flow, flow of suspensions, medical aspects of Rheology, etc. will be covered.

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# Happy New Year

Editor

