THE BINGHAM MEDAL, 1965

Dr. Eugene Guth of the Oakridge National Laboratory, Oakridge Tennessee will receive the Bingham Award for 1965. He is mainly responsible for the kinetic theory of rubber-like elasticity in its present quantitative form. Another important contribution is his work on the extension of the Einstein formula for the viscosity of a suspension of spheres. In addition Dr. Guth for many years led a substantial experimental group who did a great deal to elucidate the mechanical properties of elastomers. The career covers a period of nearly thirty years of sceintific investigation.

SOCIETY OF RHEOLOGY
WINTER MEETING 1966

The Winter Meeting of the Society of Rheology will be held at the U.S. Naval Post Graduate School, Monterey, California, on January 31 through February 2, 1966. This meeting follows the Winter Gordon Conference on Polymers which will be held the preceding week at Santa Barbara, California.

Accommodations are available nearby at the Mark Thomas Inn and reservations may be obtained before January 1, 1966 through Rodney Beyer, United Technology Corporation, P.O. Box 358, Sunnyvale, California. Other motels are available in the surrounding Monterey-Pacific Grove region and reservations may be pursued individually.

Contributed papers are being solicited for oral presentation (30 minutes) and will be considered for publication in the Transactions of the Society. Two copies of a 200-400 abstract are due by November 19, 1965 to D. J. Meier, Shell Development Company, 1400 53rd Street, Emeryville, California.

The program will feature several review talks by outstanding rheologists. Membership in the Society is not a prerequisite for participation.

The Program Committee for this meeting is:

DALE J. MEIER, Chairman, 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.

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

ANNOUNCEMENTS

1. The Annual Conference 1965 of the British Society of Rheology was held at Reading University from September 22-24. In addition to a session on "Rheological Aspects of Aero-space Research" part of the meeting will be devoted to papers dealing with any topic of rheological interest. For information, write D. W. Saunders, Dept. of Materials, College of Aeronautics, Cranfield, Bedford (Aero-space Research), or K. Walters, Dept. of Applied Mathematics, University College of Wales, Aberystwyth (General Session).

2. A symposium on THE DYNAMICS OF FLUIDS AND PLASMAS dedicated to Professor J. M. Burgers has been announced by the Institute for Fluid Dynamics and Applied Mathematics. It will be held on October 6-8, 1965 at the Center of Adult Education, University of Maryland, College Park, Maryland. The purpose of this symposium is to review some of the most recent research in the branches of the dynamics of fluids and plasmas to which Professor Burgers has made valuable contributions.

For information, write: S. I. Pai, Institute for Fluid Dynamics and Applied Mathematics, University of Maryland, College Park, Maryland 20742.

3. A joint symposium on CHEMISTRY AND RHEOLOGY OF WATER SOLUBLE GUMS AND COLLOIDS will be held on March 28, 1966. Papers of medical research interest are particularly welcomed. Preprints of the papers to be delivered will be available before the Symposium and registration forms will be sent out later this year. For information, write B. Warburton, Honorary Secretary, Department of Pharmaceutics, School of Pharmacy, University of London, 29/39 Brunswick Square, London, W.C.I.

4. The Fifth U. S. National Congress of Applied Mechanics will be held at the University of Minnesota from June 14-17, 1966. They have welcomed presentation of appropriate papers published in the Transactions which are not orally presented elsewhere. Request appropriate forms and information on abstracts from: R. Plunkett, Secretary, Vth U. S. National Congress of Applied Mechanics, 117 Aeronautical Engineering Building, University of Minnesota, Minneapolis, Minnesota 55455. Abstracts should carry a footnote stating where the full paper has been or will be published. A firm deadline of January 18, 1966 has been set.

5. A brochure may be obtained on Rheology Courses by addressing The Secretary (Rheology Courses), Battersea College of Technology, Battersea Park Road, London, S.W.II, England. The academic staff comprises twenty-one full-time teachers as well as specialists visiting lecturers. In view of the impending transfer of the College to full university status, the department is running a new undergraduate course, details of which are available on application.

There are postgraduate courses in microwave physics and rheology. Research is carried on in these fields as well as in metal physics, low temperature physics, acoustics, and theoretical nuclear physics.

PROGRAM

36th ANNUAL MEETING OF THE

SOCIETY OF RHEOLOGY

October 25 - 27, 1965

CASE INSTITUTE OF TECHNOLOGY
CLEVELAND, OHIO

MONDAY, OCTOBER 25

SESSION A   *Viscoelastic and Rheo-optical Behavior*
Monday Morning
        Chairman: L. J. Zapas, National Bureau of
                Standards, Washington, D. C.

8:45 A.M.

A1*   A. S. LODGE, Manchester College of Science and
Technology, Manchester, England, *"Constitutive
Equations for Polymer Solutions"*.

        The role of some forms of constitutive equa-
tions as an aid to understanding the main
rheological properties of concentrated polymer
solutions will be discussed. The properties con-
sidered will include the Weissenberg effect,
static and dynamic viscosity, elastic recoil, and
flow birefringence. Some molecular theories will
be referred to.

9:45 A.M.

A2   W. PHILIPPOFF, Esso Research and Engineering
Company, Linden, New Jersey, *"Elasticity in
Steady Flow"*.

        In rheology the use of the concept of elasticity
—or stored energy— or recoverable shear has
been used for some time, but by no means uni-
versally accepted. In this paper the foundations
of the statistical mechanics of polymer solutions
as developed by Kuhn, Rouse and Zimm, to-
gether with numerous others, are reviewed for
the purpose of developing the basic idas of elas-
ticity and birefringence in steady flow and es-
pecially what assumptions and limitations the
present theory has. The quantitative relations
between a number of mathematical theories are
tabulatd and a survey of the experimental re-
sults supporting this point of view is given. The
questions still unsolved are formulated.

        Especially the correlation between viscosity,
flow birefringence, dynamic tests and normal
stress measurements is emphasized.

10:15 A.M.   Break

10:30 A.M.

A3   C. R. SHERTZER[1] and A. B. METZNER, University
of Delaware, Newark, Delaware, *"Stress State
of Elastic Fluids in Viscometric Flow"*.

        Three stress functions which are sufficient to
define the stress-state of an incompressible elastic
fluid in viscometric flow have been measured ex-
perimentally over virtually four decades of shear
rate ranging to 10^5 sec^{-1}. The stress functions
are: the shearing stress, τ; the difference be-
tween extra normal stresses, prevailing in the
direction of flow and the direction of the velo-
city gradient, σ_1; and the difference between
extra normal stresses prevailing in the direction
of the velocity gradient and the neutral direc-
tion, σ_2. The fluid studied was a water solu-
tion containing 0.45 weight percent of a pro-
prietary viscoelastic additive. Supporting data
on the same system at the 0.25% and 0.6%
concentration levels are offered.

        Below shear rates of 10^3 sec^{-1} the functions
were measured in rotational flow using cone-
and-plate and parallel-plate geometries. The in-
tegrated force technique was used for normal
stresses. Above 10^3 sec^{-1} the complete determin-
ation of the stress-state was extended to high
shear rates, unprecedented in the literature, by
measurements of radial and axial stress in capil-
lary flow. To within the scatter of the experi-
mental data, which is analyzed statistically
throughout, the rotational and tube-flow results
agree.

        The relationship $\sigma_1 : \sigma_2 : \tau$ among the values of
the functions is about $10:3:1$ at 10^1 sec^{-1} and
about $50:9:1$ at 10^4 sec^{-1}. Thus the Weissen-
berg hypothesis that $\sigma_2 = 0$, predicted by and
incorporated in some constitutive theories, is
discredited.

        The shortcomings of conventional capillary-
tube viscometry for measuring the shear stress
in elastic fluids at high shear rates are illus-
trated with data. The elastic end-effect is shown
to place conventional shear stress results as much
as 35 percent above the true value as determined
by direct measurement of the pressure gradient
in the region of fully-developed flow.

[1] Present Address: Hercules Powder Company
                        Wilmington, Delaware

11:00 A.M.

A4   R. S. MOORE, Bell Telephone Laboratories, Mur-
ray Hill, New Jersey, *"Models of Spherulite
Deformation, Taking Into Account Changes in
Volume"*.

        A general method for obtaining additional in-
formation on deformation processes in semicry-

* Invited Papers

stalline polymers has been the use of light scattering, birefringence, or X-ray scattering measurements on polymers in a prescribed state of macroscopic deformation. The usual procedure in considering such processes has been to choose a model of spherulite deformation from which the changes in birefringence, X-ray scattering or light scattering are predicted and to compare these with the experimental results. The changes are often described in terms of crystal orientation parameters. These parameters, in turn, are functions of $<\cos^2\theta_i>$, where θ_i is the angle between the ith crystallographic axis and the axis of deformation.

Several models of spherulite deformation have been advanced which have in common the assumptions of affine deformation and no change in volume upon uniaxial deformation.[1-4] In some cases data from experiments at strains up to several hundred per cent were used in comparison with calculated results. It was of interest, therefore, to determine the effect of a change in volume with deformation on the calculated orientation parameters.

The simplest case considered is that for which the fibrils move toward the stress axis without crystal reorientation. For an assumed value of Poisson's ratio to 0.35 it is found that $<\cos^2\theta_b>$ is in error by 3% at 30% strain. (Here the fibril axis is considered the b crystallographic axis.) The error is larger, at higher strains or a further deviation of Poisson's ratio from $\frac{1}{2}$. Calculations of the crystal orientation parameters were carried out for several models of spherulite deformation taking into account the change in volume. These results are presented as well as calculations and experimental results pertaining to the determination of spherulite deformation by low angle photographic light scattering.

REFERENCES

1. Wilchinsky, Z. W., Polymer, *5*, 271 (1964)

2. Sasaguri, K., Hoshino, S., and Stein, R. S., J. Appl. Phys., *35*, 47 (1964)

3. Sasaguri, K., Yamada, R., and Stein, R. S., J. Appl. Phys., *35*, 3188 (1964)

4. Oda, T., Nomura, S., and Kawai, H., J. Polymer Sci., A3, 1993 (1965).

11:30 A.M.

A5   I. M. DANIEL, IIT Research Institute, Chicago, Illinois, *"Mechanical and Optical Characterization of Plasticized Polyvinyl Chloride"*.

Mechanical and birefringent properties of plasticized polyvinyl chloride in the glass transition region were determined by means of quasistatic tests at different temperatures and sinuscidial oscillation tests at room temperature.

In the former method, mechanical creep and photocreep tests were conducted at temperatures ranging from $-80°F$ to $115°F$. The moire method of strain analysis was found well suited for continuous recording of axial and transversal deformation in uniaxial creep tests at these temperatures. Arrays of 300 and 1000 lines per inch were used. In the photocreep tests birefringent measurements were taken at frequent intervals by means of a polariscope inserted in th environmental chamber. Results indicated that Poisson's ratio remains constant and nearly equal to one-half as the temperature decreases. The method of reduced variables (temperature-time equivalence principle) was used to obtain continuous curves for relaxation modulus and stress fringe value corresponding to room temperature and extending over up to 24 decades of time. The resulting curves show a broad transition region for the material. The shift function was plotted versus temperature and was found to be about the same for both mechanical and optical properties.

Short-time (dynamic) properties obtained by the temperature-time equivalence principle were compared with those obtained at room temperature by direct sinusoidial oscillation tests at different frequencies. Uniaxial and simple shear specimens were used in these tests. The complex Young's modulus, shear modulus and complex stress fringe value were determined as functions of frequency. Young's modulus was found to be approximately three times the shear modulus. These complex functions of frequency were converted to a relaxation modulus and stress fringe value as functions of time by means of the Ninomiya-Ferry approximate relationship.

The validity of the temperature-time equivalence principle in this case was proven by the good agreement between these results and those obtained from creep tests at different temperatures.

SESSION B1 *Applied Mechanics*

Monday Afternoon

    Chairman: B. BERNSTEIN, Purdue University, Lafayette, Indiana

2:00 P.M.

B1-1   I. L. HOPKINS, Bell Telephone Laboratories, Murray Hill, New Jersey, *"Comments on the Axially Tensioned, Laterally Vibrating Beam Experiments of Bodner and of Fitzgerald and Woodward"*.

Bodner[1] and Fitzgerald and Woodward[2] have described dynamic tests on beams of aluminum alloy and polytetrafluoroethylene respectively, in which the laterally vibrating bars were subjected

[1] S. R. Bodner, Trans. Soc. of Rheology, *4*, 141, 1960.

[2] E. R. Fitzgerald and A. E. Woodward, Koll-Zeits. *172*, 177, 1960.

to tension by coaxial wires. In both cases, the direct effect of the wires was disregarded. This paper presents an analysis of the wire-bar systems, based on the theories of vibrating bars and strings. The calculations show that a resonance pattern generally resembling that found by Fitzgerald and Woodward should be expected. The correspondence between theory and observation in the Bodner tests is less close; it would appear that the resonant frequencies given by Bodner comprise a sampling of the spectrum rather than a complete list, the reason possibly being that those below some arbitrary level were not observed.

2·30 P.M.

B1-2   J. G. BRODNYAN, Rohm and Haas Research Laboratories, Spring House, Pennsylvania, *"A Critical Evaluation of the Effect of Thermal Feedback in Liquid Flow"*.

In a recent series of articles Gruntfest has obtained numerical solutions of the equations relating the effects of a dissipative process like viscous flow on the observable flow patterns of a heat sensitive material. Gruntfest has implied that non-Newtonian flow is at least partially due to this thermal feedback, and he has demonstrated its significance in the flow of polymer modified oils reported on by Philippoff. This raises the question of how important these effects are in general, i.e., is non-Newtonian flow an experimental artifact.

In this paper the qualitative and quantitative predictions of Gruntfest's analysis are examined. These predictions are then compared to some experimental data obtained with simple fluids, polymer solutions, polymer melts and colloidial dis-

3:00 P.M.

B1-3   I. J. GRUNTFEST and G. E. MUELLER, General Electric Company, Space Technology Center, King of Prussia, Pennsylvania, *"Simulations of Dynamic Viscosity and Viscoelasticity Using Thermistor Circuits"*.

The exothermic nature of viscous processes taken together with the strong dependence of viscosity on temperature can lead to substantial persions. It is shown that non-Newtonian flow usually appears well before the rates of shear at which thermal effects would be noticed. Hence, non-Newtonian flow is not an experimental artifact brought about by the inability to transfer thermal energy away from heat sensitive materials.

non-linearities in the mechanical behavior of materials. Electric analog circuits containing thermistors have been applied to the simulation and study of these effects. In the present work an improved circuit containing operational ampli-

fiers, in the place of inductors, is described. With this device the responses of model materials to sinusoidal shear excitations are studied. Experiments of the type performed in the Fitzgerald-Ferry apparatus for observing the "dynamic" mechanical properties of polymers and of the type using the Mason-Mc Skimin apparatus for the study of liquids are simulated.

It is shown that the departure from linearity must depend on the frequency as well as the amplitude of the excitation. As the frequency is increased, the heating associated with the non-linearity can be expected to lead to cavitation. Regenerative heating effects arise not only because of the temperature dependence of viscosity but also because the depth of penetration of the shear wave decreases as the viscosity decreases. That is, the power density increases with the temperature induced decrease of viscosity.

3:30 P.M.   Break
3:45 P.M.

B1.4   A. S. CAKMAK[1], Princeton University, Princeton, New Jersey, and W. W. F. YAU,[2] University of Kentucky, Lexington, Kentucky, *"Time Dependent Concentrated Surface Load Moving With Diminishing Velocity on a Viscoelastic Half-Space#"*

A concentrated force moving on a viscoelastic half-space will result in time dependent displacements. In this paper the effects of the time dependence of the load as well as the variation of its velocity on the resulting displacements are studied. The problem was motivated by the interest of the Air Force in landing aircraft on unprepared sites. The load is considered in two parts and starts at the time the plane has made contact with the runway. The vertical part of the load increases as the velocity of the plane diminishes and the weight is transferred to the ground. The horizontal part of the load results from the braking force and is given as a constant times the normal force. The velocity of the load is the landing velocity of the plane and is considered to be exponentially decaying in nature. As the velocity of the load is considerably less than the velocities of any stress waves that may be generated in the half space, the problem is solved as a quasi-static one.

1. Assistant Professor of Civil Engineering, Member Soc. of Rheology

2. Post Doctoral Research Associate, Dept. of Engineering Mechanics

The solution to the elastic problem is obtained from Love. (1) by changing to a moving coordinate system and replacing the vertical and horizontal forces by their time dependent counterparts.

The viscoelastic behavior of the half space is characterized by the four parameter model for its deviatoric components and its volumetric behavior is taken as elastic.

4:15 P.M.

B1.5 K. ITO, Technical College of Hosei, University, Tokyo, Japan, *"Theoretical and Experimental Studies on Temperature Dependence of the Mechanical Behavior of Polymer Solids by a Creep Recovery Method. Part 2: Penetration of a Steel Ball"*.

A method for measuring the temperature dependence of the mechanical behavior of polymer solids by creep recovery is extended to the penetration of a steel ball. A general theory of linear viscoelasticity under complex stress is analyzed by Laplace transforms and is applied to the Hertz contact problem to calculate the creep recovery during the penetration of a steel ball. In the same manner as in the uniaxial compression method, the temperature dependence of characteristic relaxation times is predicted from experimental recovery vs. temperature curves and compared with the Williams-Landel-Ferry relation.

The Rockwell Number vs. temperature curves obtained during a constant rate of temperature increase in a conventional Rockwell machine, is useful as a simple characterization of various polymer solids. The effect of internal molecular structure on the temperature dependence of mechanical behavior, such as glass transition and flow temperatures, can be demonstrated clearly by this simple method. In addition, the merits of the creep recovery method will be discussed.

4:45 P.M.

B1.6 F. SOLIMAN and M. SHINOZUKA, Allied Chemical Corporation, Morristown, New Jersey, *"The State of Stress and Strain in an Orthotropic Heterogeneous Viscoelastic Cylinder with Burning Inner Boundary"*.

The analysis of stress and strain in an anisotropic heterogeneous linear viscoelastic hollow cylinder with burning inner boundary and subjected to a time dependent internal pressure has been worked out. The assumptions of isothermal conditions and infinitesimal strains are adopted and the conditions are those of a quasi-statio plane strain problem.

The viscoelastic response of the burning cylinder is introduced into the integral constitutive relations by use of a general moduli function $\psi_{ijkl}(r,t)$ of space variable r and time t.

A closed form solution to the general orthotropic heterogeneous problem could not be obtained. However, a numerical approximation to the solution is established that is anticipated to be quite stable. The solution can be reduced to that of a homogeneous orthotropic cylinder. As special cases from the general problem, the solutions of the isotropic compressible cylinder and the isotropic incompressible cylinder can also be derived.

Numerical examples have been worked out to illustrate the influence of the anisotropy, heterogeneity, compressibility and viscosity on the deformation of a burning cylindrical grain in a solid propellant rocket. The results for both short-time and long-time behavior are presented for a relaxation function of a form similar to that obtainable from seven parameter Maxwell model (A.M. Freudenthal, Transactions of the Society of Rheology, Vol. 9, 1965) which has been shown to represent the rheological behavior of a filled elastomer fairly well.

SESSION B2 *Melt and Solution Rheology*

Monday Afternoon

Chairman: S. H. MARON, Case Institute of Technology, Cleveland, Ohio

2:00 P.M.

B2.1 J. E. DUNLEAVY, JR. and S. MIDDLEMAN, University of Rochester, Rochester, New York, *"Correlation of Shear Behavior of Solutions of Polyisobutylene"*.

Viscosity data were obtained at shear rates from <1.0 to 3×10^5 sec.$^{-1}$ for five polyisobutylene samples (viscosity-average molecular weights from 10^4 to 10^6) in toluene at 25°C. The data were in agreement with and extend the range of applicability of a plot of $\eta_r = \eta/\eta_s$ vs. $(cM\eta)^{.68}$ $^{1/2}$ first proposed by M. F. Johnson and Coworkers. The plot is useful for obtaining values of the zero shear viscosity from minimal data $(c, M\eta,$ and $\eta_s)$.

A plot of critical shear rate for the inception of non-Newtonian flow is presented as a function of $cM^{1.1}$. With such a plot it is possible to make a judgment as to whether a given flow situation will require a non-Newtonian analysis.

A reduced plot is given of η/η_0 vs. $\delta\tau_1$, where τ_1 is the molecular parameter in the theory of Bueche. The results are compared with several theories, and with the data of other workers. The results suggest that polydispersity is a signi-

Mr. Dunleavy is with Distillation products Industries, Rochester, New York.

ficant factor unaccounted for in current theories.

Ellis model and power law representations of the reduced plot are presented. It is possible to calculate the parameter of these empirical models from a knowledge of c, M_η, and η_s.

Notation

c = concentration of polymer in solvent
M_η = viscosity average molecular weigth
$\dot{\gamma}$ = shear rate
η = apparent viscosity
η_0 = zero-shear viscosity
η_r = relative viscosity at zero-shear
η_s = viscosity of solvent
$\tau_1 = 12\eta_0 M_\eta / \pi^2 cRT$ = molecular parameter of the theory of Bueche

2:30 P.M.

B2.2 F. RODRIGUEZ, Cornell University, Ithaca, New York, *"Moderately Concentrated Polymer Solutions: Correlation of Flow Data by Simple Models"*.

A mathematical model was proposed recently which appears to correlate the flow curves for several polymers in aqueous solution over a wide range of shear rates and concentrations (Trans. Soc. Rheol. 8, 3 (1964)). New data have been obtained which indicate that the same model is useful in non-aqueous systems as well. In addition, several sets of data from the literature are consistent with the main features of the proposed model. These are the use of relative viscosity, η_r and the rate of energy dissipation (the product of rate of shear, $\dot{\gamma}$, and shear stress, τ) as reducible variables. The reducing parameters are the zero shear viscosity, η_0, and the power input at the inflection point, B. The values of B for each polymer species is a function of molecular weight but independent of concentration. It is estimated by fitting this equation to experimenal data:

$$\frac{\log \eta_r}{\log \eta_0} = 0.68 - 0.32 \; \text{erf} \; \frac{\log (\tau\dot{\gamma}/B)}{2.27\sqrt{2}}$$

where erf (q) is the error function of q. Values of B for several non-aqueous polymer solution systems are reported here.

A comparison is made between the proposed model and other two-parameter flow equations. It is shown that when dealing with real polymer flow curves where concentration is varied, no common model is applicable in which absolute viscosity is explicit in either rate of shear or shear stress alone.

3:00 P.M.

B2.3 J. M. O'REILLY and W. R. HAAF, General Electri Research Laboratory, Schenectady, New York, *"Rheological Properties of Polycarbonate Solutions and Melts"*.

The viscosity of poly (4,4'-dioxy-2,2-diphenyl propane carbonate) has been measured in the melt in a capillary rheometer and a Rheogoniometer. Concentrated solutions (0.1-0.3 volume fraction polymer in tetrachloroethane) were studied in a concentric cylinder viscometer. Molecular weight of the samples ranged from M_W= 12 to 400 x 10^3 and the molecular weight distribution was very nearly the most probable.

The melt viscosity data show Newtonian behavior at shear rates up to 100 sec^{-1} and the Newtonian viscosity is proportional to $M_W^{3.8 \pm 0.2}$ (M_W 12-80 x 10^3). This polymer represents an interesting case of a highly entangled polymer melt which exhibits Newtonian behavior at high shear rates. Some normal stress measurements indicate that P_{11}-P_{22}) is proportional to γ^2 at low shear rates.

The concentrated solution studies were undertaken to determine M_C, the critical molecular weight between entanglements and measurements at vol. frac. = 0.1 yielded M_C= 6.0 ± 0.3 x 10^3. This value is in reasonable agreement with recent viscoelastic measurements. Furthermore, if one assumes that there are 12 chain atoms per repeat unit in the chain, then Z_C the number of chain atoms between entanglements is 280. The product $(Z_C/v) \cdot (s^{0\,2}/M)$ is 4.4 x 10^{-15} which is in good agreement with a recent empirical expression suggested by Fox.

The non-Newtonian characteristics of the concentrated solutions can be fitted with the standard Bueche plot and M_R/M_W is approximately 0.6.

3:30 P.M. Break

3:45 P.M.

B2.4 C. J. ALOISIO and S. MATSUOKA, Bell Telephone Laboratories, Murray Hill, New Jersey, and B. MAXWELL, Princeton University, Princeton, New Jersey, *"Measurements of Relaxation Times of a Polyethylene Melt"*.

A device for measuring the elasticity of polymer melts has been designed by one of us (B. Maxwell). The device was used to obtain the relaxation modulus of a linear polyethylene melt. From these data a discrete relaxation spectrum was derived. The range of the obtained spectrum was confirmed to correspond to the terminal zone of the "entanglement plateau" of the spectrum. The limiting dynamic viscosity (as frequency approaches zero) was obtained by integrating the relaxation modulus with respect to time. The viscosity and its activation energy were found to agree closely with the flow viscosity and the flow activation energy, respectively, involved in capillary flow.

4:15 P.M.

B2.5 T. W. HUSEBY, Bell Telephone Laboratories, Murray Hill, New Jersey, *"Application of Pai's Theory of Viscoelastic Fluids to Some Problems in Melt Rheology"*.

Two problems in the flow of viscoelastic fluids are considered. The first problem is an analysis of flow through a tube. In such a simple geometry the analysis is straightforward and conveniently illustrates the manner in which the theory can be applied. Particular emphasis is paid to extracting relations between the relaxation spectrum and the important material properties such as modulus, viscosity, and recoverable strain. Expressions for shear stress and normal stress differences can also be obtained. These relations together with measurements of the relaxation spectrum have been used to analyze the flow behavior of polymer melts.

One result for linear polyethylene is that over a limited range of shear rate, the shear stress bcomes a many-valued function of shear rate. This predicted behavior arises as a natural consequence of the viscoelastic nature of polymers and unifies many previous experimental observations of the behavior of polymer melts at high shear rates. The theory predicts an instability in the flow curve of linear polyethylene. It predicts that this discontinuity occurs at different values depending on whether the shear stress is increasing or decreasing. The recoverable strain is predicted to pass through a maximum and the velocity of a material particle in the unstable region can have a number of values. One interpretation of this would be that the flow can occur as a "stick-slip" process. The effect of hydrostatic pressure on the flow curve is also discussed. All of the results of this analysis have been observed experimentally by others.

The second, more general problem, relates an effort to solve boundary value problems with the theory according to a method outlined by Pao.[1] A numerical solution based on an iterative technique is used to obtain results for flow through a converging cylinder.

[1]Pao, Y. H., *Applied Mechanical Review*, in press

4:45 P.M.

B2.6 J. L. WHITE and A. B. METZNER, University of Delaware, Newark, Delaware, *"Flow of Viscoelastic Polymer Solutions in the Entrance Length of a Capillary Tube or Pipe"*.

In this paper, we give a theoretical analysis of the flow of a viscoelastic fluid, such as a polymer solution, in the entrance region of a tube. The fluid is presumed to be an isotropic viscoelastic medium and to be expressed as an infinite series integral expansion (after Green and Rivlin) in strain. The entrance region may be divided into two sections, one adjacent to the inlet from the reservoir where the viscoelastic material behaves in the manner of an elastic solid and a second further along the tube where the material may be represented as a Rivlin-Erickson fluid. In the latter section of the entrance region, the equations of motion may be integrated in the manner used by von Karman and Schiller for the Navier-Stokes equations. The ideas mentioned above are used to compute the length required to obtain fully developed flow and the end corrections necessary for analyzing capillary experiments. The work described here generalizes the analyses for Newtonian fluids by Schiller and for purely viscous non-Newtonian fluids by Bogue.

* Present Address: U: S. Rubber Company, Research Center, Wayne, New Jersey

TUESDAY, OCTOBER 26

SESSION C1 *Constitutive Equations*

Tuesday Morning

Chairman: J. L. White, U. S. Rubber Co., Wayne, New Jersey

8:45 A.M.

C1-1* D. C. BOGUE, University of Tennessee, Knoxville, Tennessee, *"Constitutive Equations for Engineering Use"*.

A survey of constitutive equations which are explicit enough to be fitted to viscosity, normal stress and recoil data will be made and some discussion of their application to practical problems will be presented. The theories to be discussed will be (1) those of the form of Green-Rivlin or Coleman-Noll second-order theory, (2) those of the form of Oldroyd's theories, (3) Bernstein-Kearsley-Zapas elastic fluid theory, and (4) Pao's theory.

9:45 A.M.   Break

10:00 A.M.

C1.2 Y. H. PAO, Bell Telephone Laboratories, Murray Hill, New Jersey, *"Description of Relaxation Properties of Polymers in Terms of Time Dependent Correlation Functions"*.

It is shown that a description of the viscoelastic properties of polymers may be provided in terms of time dependent correlation functions and that this general approach facilitates discussions of the molecular origins of relaxation spectra.

10:30 A.M.

C1.3 T. W. Spriggs, J. D. Huppler, and R. B. Bird, University of Wisconsin, Madison, Wisconsin, *"An Experimental Appraisal of Viscoelastic Models"*.

More than a dozen constitutive equations for viscoelastic fluids have been tabulated in a uniform notation. Included among these are several very recently published models as well as a new six-constant model for viscoelastic fluids heretofore unpublished.[1]

Representative data, some new and some already published, are used in qualitative and quantitative testing of the equations. The experimental material functions include the viscosity and the primary and secondary normal stress differences in steady shear flow, the complex viscosity in small-amplitude oscillatory motion, and the stress relaxation after steady shearing.

The new data include measurements of non-Newtonian viscosity (including the zero-shear viscosity) and the two normal stress differences for aqueous solutions of carbopol, hydroxyethylcellulose, carboxymethylcellulose, and polyethylene oxide.[2]

Comparisons between the models and the experimental data will be given in the form of a table. In addition the predictions of the models for elongational viscosity, complex normal stress coefficient, and other seldom measured properties are summarized The table indicates which models show promise for future work.

11:00 A.M.

C1.4 M. M. Denn and A. B. Metzner, University of Delaware, Newark, Delaware, *"Elementary Flows of Anisotropic Fluids"*.

A theory of anisotropic fluids proposed by Ericksen is examined with respect to its usefulness as a constitutive equation for describing the properties of real fluids. In viscometric and helical flows the entire flow behavior is described by three material functions of the shear rate, exactly as in the case of simple fluids, and such configurations may not be used either to distinguish between the applicability of the constitutive theories or to determine the functional relations needed for the description of other flows. In time-varying flows an analysis of the motion of a body starting from rest in an infinite sea of the anisotropic fluid indicates that the theory is limited to situations in which the fluid time constant is much less than the characteristic time

of the flow. This is the same limitation as that placed on the use of Rivlin-Ericksen type approximations to simple fluids, and the results lead to the conclusion that for flow situations in which an analysis can be carried out and fluid properties measured, the theory of anisotropic fluids provides no better a description of fluid behavior than less complicated constitutive theories.

11:30 A.M.

C1.5 K. C. Valanis, Iowa State University, Ames, Iowa, *"On the Extension of Classical Irreversible Thermodynamics to Large Viscoelastic Deformations"*.

Although the theory of irreversible thermodynamics has been with us for some time, its application in the derivation of constitutive equations of viscoelastic materials has so far been limited to deformations that constitute small excursions from an equilibrium state.

To examine the reasons, we recall some concepts that pay a central role in the development of the theory irreversible thermodynamics; (a) the "hidden coordinates;" these were given the physical interpretation of "molecular configurations;" (b) Gibb's relation; this is a statement to the fact that in a closed system and for small excursions from an equilibrium state, the entropy is a function of the internal energy and the thermodynamic coordinates; (these consist simply of the components of an appropriate strain tensor and the "hidden" coordinates); Onsanger's relations; these constitute linear relations between the "forces" and "fluxes," with certain assumed symmetries of the coefficients.

It is evident that as far as large viscoelastic deformations are concerned one would have difficulty in arguing a case, even for slow motions, that Onsanger's relations might still hold. However the assumption that is most difficult to justify, in the light of the currently held interpretation of the hidden coordinates, is Gibb's relation. For, since the deformation of a viscoelastic material is a dissipative process, one would expect that the entropy would depend on the entire history of the deformation and of the "molecular configurations" and not simply on their current values; unless the "molecular configurations" are themselves functionals of the history of deformation! It is thus apparent that the classical theory of irreversible thermodynamics, in its present state, is not immediately applicable to large viscoelastic deformations.

The paper extends the theory to the large deformation of viscoelastic materials with recently slow history. The "hidden" coordinates are shown to be functionals of the deformation history and a modified form of Onsanger's relations is shown

[1]T. W. Spriggs, Ph.D. Thesis, University of Wisconsin (1965)

[2]J. D. Huppler, Ph.D. Thesis, University of Wisconsin (1965)

to exist, with symmetries that are derived from analytical considerations. Thus Gibb's relation is shown to be applicable to dissipative processes that belong to the class of large viscoelastic deformations.

Fading memory is not introduced in an ad hoc fashion but becomes a consequence of: (a) the fact that in the equilibrium configuration the stress state is a function of the equilibrium deformation and (b) the Clausius-Duhem inequality.

Thus for general viscoelastic materials, under large deformation but recently slow history, it is shown that the Piola stress tensor π_{ij} is given by the relation

$$\pi_{ij} = 2 \frac{\partial \mathcal{F}}{\partial C_{ij}} + \int_{-\infty}^{\xi} \psi_{ijk} (\xi - \xi' | C_{rs}) \frac{\partial C_{kl}}{\partial \xi'} d\xi' \quad (1)$$

where F is the specific Free Energy and ξ is a "reduced" time given by the relation

$$\xi = \int_0^{\tau} \frac{\frac{+}{A}(C_{ij})}{B(C_{ij})} d\tau \quad (2)$$

A and B being functions of the deformation. More specific forms of eq. (1) for isotropic materials are also given.

SESSION C2   *Heterogeneous Systems*

Tuesday Morning
    Chairman: L. E. Nielsen, Monsanto Co., St. Louis, Missouri

10:00 A.M.

C2.1   R. F. LANDEL and R. F. FEDORS, California Institute of Technology, Pasadena, California, *"Failure Criteria and the Reduced Tensile Failure Envelope for Composite Systems*"*.

Our previous studies have shown that for amorphous rubbers the high temperature portion of tensile failure envelopes can be reduced to a single master curve if the data are normalized to a hypothetical standard state of unit crosslink density and a standard reference temperature. In order to test the applicability of the reduced variable principle to composite systems, the ultimate properties of a number of such systems have been examined. These included a polyurethane propellant with varied crosslink density but fixed oxidizer concentration and Schwarzl's polyurethane binder of fixed crosslink

density but filled with NaCl at various concentrations, particle sizes, size distributions. To show that the results are unaffected by the modulus of the filler, various data in the literature on polyurethane and latex foams were also reduced. The variables in the foams included the crosslink density, of the type crosslinker (tri-vs. tetrafunctional), the phenyl and urethane group concentration, the type of the isocyanate, and (over a small range) the density. When the crosslink density is not known explicitly and the modulus is used as a reducing parameter, the value used must be, as expected, that of the binder and not that of the system. The reduction to a single master curve for each type of composite was successful in all cases. However, for the systems discussed, the reduced envelopes for the hard and soft fillers do not agree with the master reduced envelope for gum rubbers because the strain in the composite is not the strain in the elastomer portion of the composite. An application of the reduced failure envelope to aging studies is indicated.

10:30 A.M.

C2.2   A. BRANDT[1] and G. BUGLIARELLO, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, *"Concentration Redistribution Phenomena in the Shear Flow of Monolayers of Suspended Particles"*.

The full range of phenomena occuring in the flow of suspensions remains still unexplored. This paper describes phenomena observed in a neutrally buoyant suspension consisting of a single layer of spherical particles, flowing through a 220 cm long rectangular channel of high aspect ratio (1:16) with its minor dimension (1:58) 1.6 times larger than the particles' diameter. The flow was investigated over a range of particle Reynolds numbers between 101 and 407, and of concentrations between 1.7 and 4.8.

Concentration distributions obtained from a detailed analysis of direct photographic observations show the existance of four consecutive regions as the suspension moves down the channel:

a) An initial region, close to the channel entrance, characterized by essentially uniform particle distribution.

b) A region in which the particles move away from the wall forming a particle-free layer next to it. The core containing the particles does not have a uniform concentration

distribution but exhibits marked concentration peaks at its outer margin.

c) A region in which the core has narrowed, the peaks have merged and the concentration has become uniform.

d) A region of instability characterized by the onset of waves in the configuration of the core, followed, as the flow progresses downstream, by a breaking up of the core and by the formation of groups of particles separated by axial gaps of suspending liquid.

The transitions between these four regions are not sharply bounded, each region evolving gradually into the next. The process is accelerated by increases in flow velocity, and decelerated by increases in concentration.

The phenomena point to the existence of a hydrodynamic force leading to the formation of the core, and of concentration-dependent particle interactions opposing such a formation and leading to the onset of instabilities.

Other rheological implications of the phenomena are discussed, including the relation of the concentration redistribution pattern to the bulk energy losses of the flow. One of the most significant aspects is that while in the absence of particles the inlet length is short, with the particles the flow fails to achieve a uniform state, and is characterized by an inlet length extending from the channel entrance to the point where instabilities set in.

[1] current address:

11:00 A.M.

C2.3 H. LEEMING and T. W. GILLIS, Lockheed Propulsion Company, Redlands, California, *"The Rheology of Highly-Filled Solid Propellants"*.

Rheological properties of highly-filled cured and uncured solid propellant systems depend strongly on the particulate properties of the solid fillers.

In the uncured condition, a solid propellant is regarded as a dispersion of rigid particles in a viscous fluid. The uniformity of spatial dispersion of the particles is shown to be sensitive to the particle-size distribution. The best dispersion is obtained with a randomly oriented, log. normal distribution of particle sizes (a "random" distribution).

A random distribution can be obtained from combinations of groups of particles with individually normal or skewed distributions.

Cured solid propellants containing 70 percent or greater volumetric filler exhibit significant small-strain nonlinearities in response and low ultimate elongations. It is shown that response

linearity and ultimate properties of highly-filled propellants are improved by using a random particle-size distribution of the filler. Deviations from this type of distribution cause more complex stress-strain response, apparently because of particle agglomeration. Under load, the agglomerates are thought to dewet, producing irreversible nonlinearities. Volumetric shrinkage of the binder is also shown to be important in regulating the extent of small strain nonlinearity at a given solids loading.

Shear and normal stress data for PBAA and PBAN propellants are presented and discussed.

11:30 A.M.

C2.4 R. L. KONDNER and J. B. FORREST, Northwestern University, Evanston, Illinois, *"Dynamic Compression of Clay Under an Explosive Pulse"*.

The dynamic stress-strain-time response of a clay in compression is studied using a high speed explosive pulse type of apparatus. The rise times of the applied stress pulses are the order of magnitude of 0.2 milliseconds and the entire test durations are approximately 3.0 milliseconds. Response properties of clays under such rapid loading are important in studies of free-field motion and protective construction as related to nuclear blast loading. The results also may be of interest in dynamic studies of other composite materials. Various aspects of the design, construction, and operation of the device are presented. Dynamic loading is obtained by firing a Springfield 30-06 cartridge into a combustion chamber. The high pressure developed drives a piston downward compressing the test specimen. Measurements include forces at the top and bottom of the test specimen, deformation of the specimen, and acceleration as well as velocity of the upper platen. Test results are presented for a wide range of consistencies expressed in terms of moisture content. The dynamic stress-strain response can be represented in terms of a hyperbolic expression. Stress wave propagation velocities obtained from time lag measurements are discussed.

SESSION D *Polymer Processing*

Tuesday Afternoon
    Chairman: D. H. Kaelble, Minnesota Mining and Manufacturing Co., St. Paul, Minnesota

2:00 P.M.

D1* J. T. BERGEN, Armstrong Cork Company, Lancaster, Pennsylvania, *"Rheological Factors in the Mixing of Plactics Compounds"*.

In the course of converting a polymeric material into a technologically useful form, the

polymer is often subjected to a mixing process. The object of the mixing process is to achieve a uniform spatial distribution of the several components throughout the mass. Thus, several polymers may be mixed with one another, or solids and liquids — such as pigments, fillers, chemicals and plasticizers — may be incorporated into the polymer. The questions of technological importance are: what is the effect of the variables in the mixing process on the physical and chemical properties on the resultant compounded polymer, and what physical and rheological factors lead to an optimum mixing process for the compound being considered?

This paper reviews present theories on the description of "goodness" of mixing and on the processes by which such a mixture is achieved. The application of the results of these theories to several commonly-used mixing machines is exemplified in order to illustrate their use in choosing a mixing system and in evaluating the quality of the mixture. Limitations on present theories in describing the mixing of actual polymeric compounds are shown to be related in good part to basic problems in rheology that have yet to be solved.

Further, an important aspect of mixing involves the role of molecular diffusion in achieving a dispersion of liquid plasticizers in polymeric materials. There is little discussion on this topic in the literature (1) and in particular one finds almost no data on diffusion of plasticizers in polymers under conditions obtaining in actual mixing processes. Likewise, the thermodynamics of solution equilibrium has only recently been discussed in relation to the mixing processes (2). The significant effect of these factors on the mixing process and the resultant compounded plastic is pointed out, calling attention to the need for further study of these basic physical characteristics in this respect.

(1) Mohr, W. D. p. 3 in "Processing of Thermoplastic Materials" ed. by E. C. Bernhardt. Reinhold, N. Y. (1959)

(2) Moore, W. R. Plastics Inst. Trans. & J. 32, 247-251 (1964)

3:00 P.M.

D2   H. P. SCHREIBER, S. H. STOREY, and E. B. BAGLEY[1], Canadian Industries Ltd., McMasterville, Quebec, Canada, *"Molecular Fractionation in the Flow of Polymeric Fluids"*.

The concept of molecular fractionation during the capillary flow of polydisperse thermoplastics, previously rationalized on thermodynamic grounds, has been examined theoretically using simple kinetic theory of liquids. Two crude models have been derived which predict a molecular weight decrease near the polymer/wall interface. A decay in the degree of extrudate swelling with increasing die length is also predicted, each of the models giving equations relating the decay rate with die dimensions and extrusion shear rate.

Experimental data for high pressure polyethylenes indicate some shortcomings in the theory but both models fit swelling data well, and appreciably better than an empirical equation of exponential decay. Polyethylene data give further evidence for molecular fractionation, in that surface sections of a high pressure polyethylene and a blend of linear polyethylenes, both with wide molecular weight distributions, have appreciably lower molecular weights than whole extrudates. The magnitude of this effect increases with increasing die length. However, no significant molecular weight effect was detected in a fractionated linear polyethylene. Similarly swelling ratio decay is much greater for the broad molecular weight distribution samples than for the fractionated material. The results suggest that molecular fractionation in capillary flow is an important contributing cause to the difference in die length variation of melt viscosity and melt elasticity.

(1) Present Address: Department of Chemical Engineering, Washington University, St. Louis, Missouri, U.S.A.

3:30 P.M.

D3   N. NAKAJIMA and M. SHIDA, W. R. Grace and Company, Clifton, New Jersey, *"Viscoelastic Behavior of Polyethylene in Capillary Flow Expressed with Three Material Functions"*.

It was shown that three material functions are required to relate various phenomena in the capillary flow of polyethylene. The material functions are steady state viscosity, η, shear modulus, G, and a modulus associated with the normal stress phenomenon, G_N. The phenomena examined are the entrance pressure loss, laminar flow through a capillary, memory decay in the flow and extrudate swelling. The experimental observations were, besides the relationship between shear stress and shear rate, the complete recovery of extrudate swelling, Sw, as a function of shear rate and the length to diameter ratio, (L/D), of the capillary. From the value of Sw, the recoverable strain in the flow, γ, was estimated. In turn the value of γ was used to calculate the stored energy, W, which was assumed to be directly related to the normal stress phenomenon. The decay of the energy, W, with apparent time of flow, ta, was found to obey the first order rate equation. From this, apparent relaxation time of the decay, λ_N was evaluated. Assuming that the decayed energy dissipates by the steady state viscous response, the modulus

G_a^N was calculated as (λ_a^N / η_a). From the limiting value of recoverable strain at infinite time of flow, γ_∞, the apparent shear modulus, G_a, was evaluated as (τ_R / γ_∞), where τ_R is the shear stress at the capillary wall. It was found that G_a^N was about one decade smaller than G_a at a given shear rate, but there was no simple relationship between them. The relaxation time of the normal stress behavior, λ_a^N, was found to be, in general, larger than the relaxation time of shear flow, $\lambda_a = (\eta_a / G_a)$. This is in agreement with the observation by Benhow and Howells[1]. An approximate correction was applied to G_a and the corresponding value at the capillary wall, G, was estimated. The G values at all shear rates, $\dot\gamma$, of the observations were comparable in magnitude, but smaller than the dynamic storage modulus, G', obtained by a torsion pendulum, when the values were compared at corresponding frequencies, ω. The difference increased with $\dot\gamma$ (or ω). Considering the large deformation in the capillary flow, this difference is reasonable. The elastic response in the flow is non-linear and the modulus decreases with the increase of deformation. From the recoverable strain at zero time, γ_0, the elastic stored energy at the entrance, W_0, was calculated. The "Couette correction", n, calculated from W and the entrance pressure loss, i.e. $\Delta P - W_0 = 2\tau_R \cdot n$, was found to be constant in the shear rate range examined. The energy balance of the capillary flow was calculated.

[1] Benbow, J. J. and E. R. Howells, Polymer 2, 429 (1961).

4:00 P.M. Break

4:15 P.M.

Society of Rheology Business Meeting.

Tuesday Evening

Banquet and Presentation of Bingham Medal.

WEDNESDAY, OCTOBER 27

SESSION E   *Dynamic Behavior and Flow*

Wednesday Morning

Chairman: Y. H. Pao, Bell Telephone Laboratories, Murray Hill, New Jersey

8:45 A.M.

E1* T. A. LITOVITZ, Catholic University of America, Washington, D. C., *"Viscoelastic Properties of Non-Polymeric Liquids"*.

9:45 A.M.

E2 W. PHILIPPOFF, Esso Research and Engineering Company, Linden, New Jersey, *"Vibrational Measurements with Large Amplitudes"*.

In rheology, vibrational measurements (dynamic tests) have usually been performed at low shear amplitudes, of the order of a few % in shear, when "linear viscoelastic theory" is demonstrably valid. Under these conditions, the viscosity and elasticity are dependent on frequency, f, but independent of amplitude, a. The present paper reports on measurements with considerably larger shear amplitudes than used heretofore—up to $\pm 700\%$ in shear at variable frequencies, together with tests in steady-state in the same geometry: a concentric cylinder viscometer.

After due calibration, Newtonian liquids gave the same viscosity in sinusoidal vibration as in steady-state over the whole frequency and amplitude range. At low frequencies viscoelastic liquids also behaved similarly: the properties were independent of a and f. At higher frequencies, however, the results were markedly dependent on a and f—giving rise to distorted ellipses—or causing higher harmonics to appear in the force-time curve.

Correlations of these results with the ones in steady-state are performed. The materials used were solutions of polyisobutylene of different molecular weights in different hydrocarbon solvents including an oil of 150 cp and tetralin of 2 cp.

10:15 A.M. Break

10:30 A.M.

E3 W. McCOMIS, S. CHARM, Tufts University Medical School, Boston, Massachusetts, and G. KURLAND, Harvard Medical School, Boston, Massachusetts, *"Pulsing Blood Flow in Capillary Tubes"*.

The energy losses of pulsing blood flow was studied in capillary tubes ranging from 72μ to 2000μ. The frequency of the pulse varied from 35 to 120 cycles per minute. It was found that there were no differences in energy loss between steady and pulsing flow when the time average pressure is used in calculation of velocities. Pulsing flow is laminar when its energy losses are comparable to losses at steady flow. However, turbulence is induced at a lower Reynolds Number than in steady flow.

11:00 A.M.

E4 E. W. MERRILL, H. SHIN, H. S. MICKLEY, and K. A. SMITH, Massachusetts Institute of Technology, Cambridge, Massachusetts, *"Reduction of Drag in Turbulence by Dilute Polymer Solutions"*.

The reduction of drag, in non-laminar flows, by the presence of random coiling macromolecules was studied using two kinds of polymers

differing significantly in chain flexibility: poly-ethylene oxide (PEO), the more flexible, and polyisobutylene (PIB). A concentric cylinder apparatus was used to generate the flows, which above the laminar regime were Taylor vortex flow or fully turbulent flow, depending respect-ively on whether the inner or the outer cylinder was rotated, the other cylinder being stationary.

It was found that, within either homologous polymer series, the ability of macromolecules to reduce drag increased drastically with in-creasing molecular weight. It was further found that there existed an optimurm concentration for any polymer species at which the observed drag reduction reached a maximum. PEO was found to be a better drag reducing agent than PIB, when the comparison was made either at the same molecular weight or at the same num-ber of segments in the main chain. Based on experimental observations, the most important macromolecular parameters associated with drag reduction are believed to be: (1) number of segments in the main chain, (2) the intramole-cular expansion factor α, and (3) the parameter σ, the ratio of the rms end-to-end distance under theta solvent conditions to the rms end-to-end distance for fixed valence bond angles with no rotational restrictions.

Alternative mechanisms by which drag may be reduced are considered: (1) anisotropic viscos-ity, (2) sequestration of solvent within the ma-cromolecules, and (3) viscoelastic interaction of the macromolecules with turbulent eddies.

11:30 A.M.

E5   J. A. WHEELER, JR., Esso Production Research Laboratory, Houston, Texas, and E. H. WISSLER, University of Texas, Austin, Texas, *"Steady Flow of Non-Newtonian Fluids in a Square Duct"*.

The steady flow of an incompressible Stokesian fluid through a tube of uniform square cross section was investigated theoretically. Numerical solutions for the complete equations of motion and the continuity equation were obtained for rectilinear and for non-rectilinear flow through a square duct for Reynolds numbers as large as 215. The numerical methods which were devel-oped can be used, at least in principle, to obtain solutions for any realistic Stokesian model.

An optical time-of-flight device was developed for measuring local velocities in fluid systems. Small particles carried by the fluid were observed at two points on a fluid streamline by a photo-multiplier which activated an electronic timer. The 95% confidence limit for the magnitude of velocities measured with the device was esti-mated to be $\pm$ 1.6% for velocities between 0.1 ft/sec and 10.0 ft/sec. The uncertainty in the direction of the velocity vector was less than four degrees.

The device was used to measure local, longi-tudinal velocities in aqueous solutions of sodium-carboxmethylcellulose flowing through a duct with a cross section 1.5 in. square. The observed velocities were compared with velocities pre-dicted on the basis of cone and plate viscometer data with the assumption that the cross viscosity, or viscous normal stress coefficient of the Stok-esian model, was zero. The pattern of the devi-ations between the observed and predicted velo-cities indicated that secondary flow of too small a magnitude to measure directly with the time-of-flight device did occur. Observation of an injected dye filament also indicated that second-ary flow of small magnitude did occur.

SESSION F   *Creep and Relaxation*

Wednesday Afternoon

Chairman: I. L. Hopkins, Bell Telephone Labor-atories, Murray Hill, New Jersey

2:00 P.M.

F1   A. S. SAN MIGUEL and R. F. LANDEL, California Institute of Technology, Pasadena, California, *"Some Experimental Observations on the Stored Energy Function for Small Values of Strain Invariants"*.

In order to evaluate the stored energy func-tion, W, for elastomeric materials, at least bi-axial experiments must be made. Two of the biaxial testers developed at the Jet Propulsion Laboratory are an inflated cylinder device and a biaxial sheet tester. Some preliminary experi-mental results obtained with these two devices at small values of strain invariants are presented for a polyurethane elastomer. These results are analyzed without making the assumption that the elastomer is incompressible, a fact which modifies the analysis of multiaxial or large-strain behavior. The results from the biaxial sheet tester are consistent with those obtained from an inflated cylinder of the same material, though experimental difficulties prevent a de-tailed comparison. Nevertheless both series of experiments show that all three terms, $\partial W/\partial I_i$, where I_i are the three strain invariants, de-pend strongly on the invariants. Moreover, $\delta W/\delta I_2$ is negative, in agreement with theoretical expectations. Thus the form of W in the region where $I_i < 4$ is very complex.

F2   P. H. DeHoff, Jr. and G. Lianis, Purdue University, Lafayette, Indiana, *"Experimental Studies on Finite Linear Viscoelasticity"*.

In recent years there has been considerable research in the theoretical development of constitutive equations for non-linear behavior of viscoelastic materials. These constitutive equations are generally formulated either in the form of functions of the rates of deformation [1] or as herditary functionals of the history of deformation. [2], [3]. In either approach, however, the explicit development of a general constitutive equation for non-linear behavior will, of necessity, involve a large number of material functions.

Since the application of the general non-linear theory to the solution of boundary value problems will require the knowledge of these material functions, it seems appropriate that approximations to the general theory should be sought. One important approximate theory was proposed by COLEMAN and NOLL [4] for simple viscoelastic materials with fading memory under slow motions. This theory, which the authors called "finite linear viscoelasticity," contains, for isotropic materials, 12 transient material functions and 3 steady-state coefficients.

LIANIS [5] recognized the inherent difficulty of designing the necessary experiments required to evaluate 15 material coefficients and has thus proposd a further simplification to COLEMAN & NOLL'S theory. Based on existing experimental data, he suggested an approximate equation for incompressible materials containing only 4 relaxation functions and 3 steady-state coefficients in order to describe the behavior of some polymers subjected to large strains. The purpose of the present investigation is to verify and extend Lianis' suggestion and to experimentally determine the form of these material functions.

The experimental program consisted of a series of isothermal uniaxial stress relaxation tests for various deformations ranging from approximately 10% to 210% strain. In addition, one test of 10% uniaxial strain superposed on 100% strain was required in conjunction with the relaxation tests. Two different types of materials were used and results are presented for both. For one material (Estane polyurethane) it was found that Lianis' approximate theory fit the experimental data quite satisfactorily. However, for the second material (Ethylene propylene rubber), it was found that a more general approximation was required to fit the experimental data.

One of the features of the experimental program is the accurate control of the temperature and the motion and stability of the hydraulic piston, so that reliable results under large strains (up to 210%) can be obtained even for short times of the order of 0.3-0.4 seconds.

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2. GREEN, A. E., R. S. RIVLIN and A. J. M. SPENCER, Arch. Rat. Mech. Anal., *3*, 83 (1959)

3. NOLL, W., Arch. Rat. Mech. Anal., *2*, 197, (1958)

4. COLEMAN, B. D. and W. NOLL, Reviews of Modern Physics, *33*, 239 (1961)

5. LIANIS, G., Purdue University Report A&ES 63-11 (1963)

F3   D. J. Plazek, Mellon Institute, Pittsburgh, Pennsylvania, *"Creep Compliance of Some Natural and Polybutadiene Rubbers"*.

Creep compliance measurements on natural and polybutadiene rubbers have been carried out at temperatures between 0° and 80°C. The stress relaxation behavior of four similarly prepared samples of natural rubber, which were crosslinked with dicumyl peroxide to varying degrees, have been investigated previously by Thirion and Chasset. Complex shear compliance measurements on such samples were also made by Ferry, Mancke, Maekawa, Ōyanag, and Dickie. The measured curves obtained in this study are reduced to 30°C and the resulting temperature dependence is discussed. Crystallization was encountered at the lowest temperatures and a limited amount of thermal degradation at the highest temperatures and longest times. The change in creep compliance as a function of time, which in the region of behavior measured is attributed to the adjustment or migration of the entanglements present in the rubber precursor, becomes less severe as the crosslink density increases. However, no equilibrium compliance is reached for any of the samples studied.

The creep response of a randomly crosslinked narrow molecular weight distribution polybutadiene sample is compared with an endlinked rubber. The original molecular weights were 220,000 and 5500, respectively. In spite of the fact that the endlinked rubber has a somewhat higher effective crosslink density, as indicated by swelling measurements, the level of the compliance measured is greater than that for the

more conventional rubber, indicating that fewer entanglements are present in the endlinked material.

The response of the crosslinked rubbers is compared to that of uncrosslinked similar polymers. Densities of the samples have been measured using the flotation technique and thermal expansion coefficients have been determined by dirct measurement with a traveling microscope. Swelling indices in benzene were also determined.

3:30 P.M.   Break

3:45 P.M.

F4   J. F. WILSON and N. K. WILSON[1], U. S. Steel Corporation Research Center, Monroeville, Pennsylvania, *"Kinetics of Stress Relaxation in Metals"*.

To predict the mathematical form of the material function describing the average relaxation stress in a single-step, uniaxial experiment, Tobolsky and Eyring[1] have relied on absolute reaction rate theory, which has evolved in various forms to help explain many rate phenomena observed in metals[2-4]. Combined with the theory of elasticity, the resulting equations are shown to be identical to the classical Maxwell model and to the empirical logarithmic form in limiting cases for stress relaxation in solids. Without reference to the specific details of the localized flow, these equations are found to correlate uniaxial data for many types of steels, copper, aluminum, magnesium, and lead for various temperatures and stress levels. In all of the data is found one characteristic controlling reaction, and in some cases a secondary reaction dependent upon the level of the uniaxial prestress. For non-aging metals, the data fit equations in which the relaxation stress approaches zero asymptotically in time. A simple modification of the rate equations is made so that an age-hardening metal can approach a non-zero stress during relaxation. Prestress is used as a controlling variable in correlating data for uniaxial stress-relaxation. Apparent heats and entropies of activation are calculated for Inconel and copper at elevated temperatures. For nearly all metals, the apparent free energy of activation for the controlling raction in the relaxation process decreases slightly as the prestress is increased.

After consideraton of several theories and an analysis of a large amount of uniaxial data for the stress relaxation of metals, it is concluded that absolute reaction rate theory adequately describes these data. Although the specific microscopic mechanism or mechanisms giving rise to the phenomena are not considered, the analysis does make it possible to calculate apparent values for activation volume and free energy.

These values may lead to greater understanding of the microscopic processes of stress relaxation. Critical experiments on the microscopic scale are needed to determine the exact nature of the localized flow processes.

1. Tobolsky, A., and H. Eyring, J. Chem. Phys. *11*, 125 (1943).

2. Fredrickson, J. W., and H. Eyring, Metals Technology, (AIME), *15*, (1948).

3. Cagle, F. W., and H. Eyring, J. Appl. Phys., *22*, 771 (1951)

4. Hahn, S. J., T. Ree, and H. Eyring, in V. D. Frechette, ed., "Non-Newtonian Relaxation in Amorphous Solids, "Wiley and Sons, N. Y. p. 297, 1960.

[1]Carnegie Institute of Technology, Department of Chemistry

4:15 P.M.

F5   R. E. ROBERTSON, General Electric Research Laboratory, Schenectady, New York, *"The Plasticity of Glassy Polymers"*.

The tremendous increase in polymer mobility that occurs in drawing a glassy polymer is ascribable to the following three causes: the shear component of the applied tensile stress, the expansive component of the applied stress, or the temperature rise produced by the work of plastic deformation. Of the three, how the shear stress can enhance the polymer mobility is probably the least understood. And yet, in the typical cold-drawing experiment at moderate rates of strain, the effect of the shear stress is dominant.

In the present paper, we will try to show how the shear stress can enhance the polymer mobility by, essentially, considering the effect of the shear stress field on those bonds or molecular arrangements that form in the polymer on lowering the temperature from melt and which can be said to cause the molecular immobility or glassiness of the polymer. For concreteness, though, we assume that the molecular immobility is due only to intramolecular forces that cause long, rigid polymer segments. Although a simplification, this model is realistic for many polymers including, apparently, such polar substances as polyacrylonitrile.

Our approach is to calculate the increase in the total number of flexed bonds as a shear stress field is applied to groups of polymer backbone atoms. The general effect of the shear stress is to relocate the flexed bonds, to give them a more favorable orientation with respect to the stress field, without significantly changing the total number of flexed bonds. But because bond-

flexing is so much more rapid than bond-unflexing, the total number of flexed bonds does go through a maximum in the relocation process. Indeed, from the work of Kovacs in the kinetics of volume expansion vs volume dilation, for example, it seems that at the maximum we can assume that the equilibrium number of flexed bonds that are favorably oriented with respect to the shear stress are competely formed but that none of the unfavorably-oriented flexed bonds are destroyed. By assigning a temperature to the maximum number of flexed bonds (the temperature at which this number would be the equilibrium number) we can assign an activation free energy for plasticity from the WLF equation, for example. Then, using Eyring's plasticity equation with this activation energy and with the pre-exponential factor chosen so that the equation agrees with the traditionally defined viscosity at the glass transition temperature, we have calculated the shear strain rate for polystyrene and polymethacrylate as a function of the temperature and the shear component of the applied stress. We find that the calculated rates agree well with the respective strain rates from tensile yield experiments.

4:45 P.M.

F6   S. UENO, T. OUE, H. YAMAZAKI, Mitsubishi Edogawa Chemical Company, Osaka, Japan, and K. ITO, Technical College of Hosei University, Tokyo, Japan, "Rheological Study on Cold and Warm Proecssing of Polycarbonate".

Retentivity in processing of polycarbonate is experimentally explored in uniaxial compression for cold and warm processing ability. "Solvent Method" polycarbonate "Iupilon" is used as test specimen. The strain recovery of a compressive test specimen worked at various processing temperatures is measured by free annealing at temperatures higher than the processing temperature. Worked specimens are strain-recovered completely by annealing at a temperature higher than the glass transition temperature, though polycarbonate has excellent cold

processing ability and is strain-frozen solidly at temperatures below the glass transition temperature.

A new "Modified Erichsen" testing apparatus is proposed for measuring temperature dependence of processing ability of sheet plastics in comparison with cold and warm processing of polycarbonate sheet. A sheet heated uniformly in a chamber is penetrated by a solid punch at a constant rate of stroke, and the penetration depth at fracture is measured. The processing ability of polycarbonate sheet (1 mm. thickness) is gradually improved with temperature rise up to the glass transition temperature.

Strain recovery in Erichsen test specimens is measured in the same way as in uniaxial compression. The results obtained under combined stresses, such as Erichsen bulging, are similar to those in uniaxial compression.