

RHEOLOGY BULLETIN

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ANNUAL WINTER MEETING THE SOCIETY OF RHEOLOGY

MIRAMAR HOTEL - MOTEL
SANTA BARBARA, CALIFORNIA
FEBRUARY 6-8, 1967

Accommodations

For reservations and preregistration send request before January 1, 1967 to M. C. Shen, North American Aviation Science Center, 1049 Camino Dos Rios, Thousand Oaks, California with name, address, affiliation, dates of arrival and departure, and accommodations desired. Single rooms are available at \$10, \$12 or \$16 a day. There are also twin-bedded rooms costing \$8 a person. Give the name of person to share twin room if possible.

Call for Papers

Deadline for abstracts of papers for the Winter Meeting is December 1, 1966. Please confine abstracts to 400 words and send to Chairman of Program Committee:

J. L. White, (Chairman), U. S. Rubber Company, Research Laboratory, Wayne, New Jersey.

A. Eisenberg, Department of Chemistry, University of California, Los Angeles, California.

D. J. Plazek, Mellon Institute, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213.

N. W. Tschoegl, Division of Engineering and Applied Mechanics, California Institute of Technology, Pasadena, California.

THE BINGHAM MEDAL, 1966

Dr. Prince E. Rouse of the Los Alamos Scientific Laboratory has been selected as the 1966 recipient of the Bingham Medal, in recognition of work carried out while he was associated with The Franklin Institute. His theoretical formulation of the problem of the dynamics of polymer chains, published in 1953, provided a physically realistic model whose rheological behavior could be expressed in a simple and useful fashion. His concurrent experimental studies, in collaboration with K. Sittel and E. D. Bailey, provided the first of many confirmations of the essential validity of this model. Most of our present descriptions of the rheological properties of amorphous polymers and polymer solutions have been derived directly from this pioneering work of Rouse.

The Award will be presented at the banquet during our annual meeting to be held at the Traymore Hotel in Atlantic City, October 31 to November 2. John D. Ferry of the University of Wisconsin will introduce Dr. Rouse.

TRAVEL TO ATLANTIC CITY

The best air service to Atlantic City is via Philadelphia, serviced by 11 leading airlines: Allegheny, American, Delta, Eastern, Lufthansa, National, Northeast, Northwest, Pan American, TWA and United. Limousine service delivers conventioners directly to Atlantic City hotels and motels in 65-75 minutes. The service operates several times daily and is increased as demand requires to meet the needs of convention attenders. Make reservations through airline ticket agents or travel agencies, with the Salem Transportation Company or the Yellow Limousine Company at the International Airport - Philadelphia. Limited direct air service to Atlantic City is offered by Allegheny Airlines from Boston, New York City, Pittsburgh and Washington, D. C. Personalized air service is offered by Southern Jersey Airways operating from Bader Field, just five minutes from most hotels.

Train service to the convention site is by connection with the Pennsylvania-Reading Seashore Lines at 30th Street or North Broad Street Stations of the Pennsylvania Railroad in Philadelphia.

Bus schedules prevail for those coming from short distances. Forty daily buses operate from the Port Authority Bus Terminal in New York City. Two companies - Public Service and Lincoln - offer non-stop service from New York to Atlantic City in 2¼ hours, via the Garden State Parkway. From Philadelphia, Public Service operates non-stop service to Atlantic City in 75 minutes.

Motorists traveling from the west may utilize continuous turnpike and expressway systems.

ANNOUNCEMENTS

1. The Ultrasonics Symposium sponsored by the Group on Sonics and Ultrasonics of the IEEE will be held on October 12-15, 1966 at the Statler Hilton Hotel, Cleveland, Ohio. Among the principal topics to be featured are: Industrial Ultrasonics, Phonon Interactions, Medical Ultrasonics, Microwave Devices and Techniques, Materials and Continuum Mechanics and Military Sonics and Ultrasonics.
2. A joint symposium on the Rheology and Texture of Foodstuffs will be held at the School of Pharmacy, University of London, Brunswick Square, London W.C.1 on the 5th and 6th January, 1967.
3. Deformation and Flow in High Polymer Systems was the theme of the British Society of Rheology Conference at Loughborough University of Technology on September 14, 15, and 16, 1966.

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

PROGRAM
37th ANNUAL MEETING
SOCIETY OF RHEOLOGY
Traymore Hotel, Atlantic City, N.J.
October 31 - November 2, 1966

MONDAY, OCTOBER 31, 1966

SESSION A - Monday Morning

Chairman: N. W. TSCHOEGL, California Institute of Technology, Pasadena, California

A-1

8:45 a.m. INVITED LECTURE: "*The Rheology of Metals*",
E. W. HART, General Electric Company, Schenectady,
New York.
Theories of Bulk Viscoelastic Behavior.

A-2

9:45 a.m. "*Physical Aspects of Simplified Constitutive Equations Derived from Irreversible Thermodynamics*," R. A. SCHAPER, Purdue University, Lafayette, Indiana.

Relatively simple constitutive equations for nonlinear viscoelastic media, with and without transient temperature, have been developed by the writer in a series of three papers.^{1,2,3} Specifically, single-integral expressions for multiaxial behavior were derived by combining irreversible thermodynamic principles with assumptions based on actual nonlinear response of unfilled and filled polymers. These equations readily yield, as a special case, nonlinear relaxation moduli wherein strain and time-dependence appear as separate factors; this form has been observed by many investigators for wide ranges of strain, time, and temperature, and is the basis for Halpin's molecular theory of nonlinear viscoelasticity.

This paper deals with physical aspects of these equations in greater detail. Predicted and experimental mechanical behavior is compared using several common uniaxial and biaxial loading histories; good agreement is shown for a wide variety of polymeric materials. Physical significance of the nonlinear material property functions is brought out in this comparison, and it is shown how these functions can be evaluated graphically by using uniaxial and biaxial test data. A sufficient number of tests required to completely characterize an incompressible material is discussed.

Finally, certain comparisons are made between other existing theories of nonlinear constitutive equations and the writer's theory.

¹R. A. Schapery, "Application of Thermodynamics to Thermomechanical, Fracture, and Birefringent Phenomena in Viscoelastic Media," *J. Appl. Phys.*, **35**, 1964, 0pp. 1451-1465.

²R. A. Schapery, "A Theory of Nonlinear Thermoviscoelasticity Based on Irreversible Thermodynamics," *Proc. 5th U. S. Nat. Cong. Appl. Mech.*, June 1966, pp. 511-530.

³R. A. Schapery, "An Engineering Theory of Nonlinear Viscoelasticity with Applications," *Int. J. Solids and Structures*, **2**, July, 1966.

10:15 a.m. Break

A-3

10:30 a.m. "*Nonlinear Viscoelastic Response from the Viewpoint of Kinetic Theory*," J. C. HALPIN, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio.

Modern continuum mechanics has successfully contributed to the theory of nonlinear viscoelastic phenomena through the studies of the restrictions imposed on the permissible forms of constitutive equations by general invariance principles, and by the more special invariance requirements which pertain to the structural symmetries of the material. Although invariance considerations impose serious restrictions on the form an adequate theory must take; the theory still remains undefined and quite arbitrary in nature. In effect the invariance principle defines the criterion by which one may judge whether a proposed constitutive relationship is permissible or not but it does not define the specific structure of the constitutive relationships. The solution of the problem is then undefined unless additional information is obtained from the molecular theories and nonequilibrium thermodynamics and statistical mechanics.

Recently this author has presented an approximate treatment of the problem utilizing the Kinetic Theories of the elastic and viscoelastic response of rubber like solids. The result of this effort was the formulation of a single integral constitutive relationship in which the nonlinearity is introduced through the measure of strain; a nonlinear function of the strain or strain tensor. Extensive experimental data obtained independently by this author and T. L. Smith for simple uniaxial tension have been presented which substantiates the essential characteristics of the deformation function. An additional test of the theory is the execution of multiple step creep and recovery experiments. Experimentation indicates that the single integral approach can predict the response to a variable excitation history. In fact it is possible to predict the increasing and decreasing sides of a stress-strain cycle and as a consequence one obtains a prediction of the energy stored and energy dissipated for the cycle. The theory predicts a proportional relationship of the energy stored or dissipated upon the square of the nonlinear deformation function at the point of maximum extension for the cycle. Experimentation also supports this point. Consequences of this form of linearization, which reduces a nonlinear problem to linear mechanics, shall be discussed.

A-4

11:00 a.m. "The Exponential Extension-Ratio History," B. BERNSTEIN, Illinois Institute of Technology, Chicago, Illinois, and W. GOLDBERG, Purdue University, Lafayette, Indiana.

According to the elastic fluid theory of Bernstein, Kearsley and Zapas, a knowledge of the responses to single step relaxation provides sufficient information to be able to determine the mechanical properties of an incompressible elastomer. It is further shown that in simple extension the time derivative of the true stress, σ , in the exponential history

$$\lambda(t) = 1 \quad t < 0 \quad (1)$$

$$\lambda(t) = \exp(\eta t) \quad t \leq 0$$

where $\lambda(t)$ is the extension ratio at time t , and η is a constant, is given by $\dot{\sigma}/\eta\lambda = G'(\exp(\eta t), t)$ (2)

where $\lambda = \lambda(t)$ is given by (1), $\dot{\sigma}$ is the time derivative of σ , $G(\lambda, t)$ is the stress measured in single-step stress-relaxation with step λ at time t after the step and G' is the partial derivative of G with respect to λ . According to the theory of Bernstein, Kearsley, and Zapas, then, exponential history provides an alternative way to measure stress-relaxation response. Also, since this measurement involves no discontinuity in deformation, it could be more accurate for short time measurements than stress-relaxation.

Experiments were carried out to check how well (2) correlates exponential data with stress-relaxation data. For polyisobutylene the correlation was very good, but for Goodrich estane and Solithane 113 the correlation was not good at the higher extensions. Reasons for this will be discussed.

A-5

11:30 a.m. "A Fluctuation-Dissipation Theorem Approach to Mechanical Relaxation in Solid Polymers," Y. H. PAO, Bell Telephone Laboratories, Murray Hill, New Jersey,

A general expression has been obtained for the complex dynamic modulus of solid polymers. The approach used is that of the fluctuation-dissipation theorem or equivalently that of Kubo Theory. In this present formulation any of the macroscopic viscoelastic functions can be related to a statistical mechanical time dependent correlation function. Subject to some simplifying assumptions, it is shown that detailed knowledge of the specific heat of the solid suffices to yield information on the frequency and temperature dependences of loss peaks of the solid. This type of formulation also facilitates comparison of mechanical and dielectric relaxation spectra.

MONDAY AFTERNOON

SESSION B1

Chairman: H. MARKOVITZ

Mellon Institute, Pittsburgh, Pennsylvania.

Polymer Solutions

B1-1

2:00 p.m. "On the Molecular Theories of Polymer Solutions," R. E. DEWAMES, W. F. HALL, and M. C. SHEN, North American Aviation Science Center, Thousand Oaks, California.

On the Molecular Theories of Polymer Solutions. R. E. DeWames, W. F. Hall and M. C. Shen, North American Aviation Science Center, Thousand Oaks, California. This paper reports on a review of the basic molecular theories of polymer viscoelasticity and the proper extension of these theories to the continuum limit, including the effects of local changes in the submolecule friction factor. Our first concern is to show the equivalence of the hydrodynamic method of Kirkwood as exemplified by Zimm and the energetic method of Debye, Rouse, and Bueche. The discrepancy between the results of Zimm and Bueche is resolved by including the internal energy of the polymer molecule in Bueche's calculation. The dynamic viscosity and its Fourier transform, the elastic modulus, are obtained for the free-draining and non-free draining cases and the appropriate continuum expressions for these functions are given. Finally, it will be shown that for large hydrodynamic interaction the dynamic viscosity changes markedly with the introduction of small numbers of submolecules having friction factors larger than that of the host.

B1-2

2:30 p.m. "Dynamic Mechanical Properties of Dilute Solutions of Fragmented Helical Deoxyribonucleic Acid; Comparison with Flexible Polymers," H. H. MEYER, W. F. PFEIFFER, JR., L. A. HOLMES, and J. D. FERRY, University of Wisconsin, Madison, Wisconsin.

Calf thymus deoxyribonucleic acid was degraded by high-shear stirring to molecular weights (M) in the range from 1.0 to 3.2×10^6 and purified by chromatography on methylated bovine serum albumin. Dynamic viscoelastic properties of the fragmented products, in aqueous glycerol solutions in the concentration range (c) from 0.003 to 0.01 g./ml., were investigated with the apparatus of Birnboim and Ferry. At values of the product cM higher than 4×10^3 , the frequency dependence of the components of the complex shear modulus, G' and G'' , displayed a plateau region in which $G' < G'' - \omega v_1 \eta_s$, similar to that observed in concentrated solutions of coiling polymers where it is attributed to an entanglement network (ω is radian frequency, v_1 volume fraction of solvent, and η_s solvent viscosity). The width of this plateau region on the logarithmic frequency scale is given by $\Delta = 3.8 (\log cM - 3.56)$. (The same relation applies to earlier measurements on poly- λ -benzyl-L-glutamate in the helical configuration). At lower values of cM , the frequency dependence superficially resembles that predicted by the theory of Zimm for flexible coiled macromolecules. However, fitting to the theory gives highly discrepant values for molecular weights, while fitting the low-frequency end of the dispersion to the theory of Kirkwood and Auer for rigid rods gives reasonable agreement for both molecular weight and rotary diffusion coefficient. It is concluded that the

helical fragments appear as rigid rods in their behavior at very low frequencies, but at higher frequencies reveal substantial flexural flexibility. The behavior of rod-like macromolecules is compared with that of flexible coils, especially with respect to the manifestations of network-like structures.

B1-3

3:00 p.m. "Normal Stresses in the Simple Shear Flow of Concentrated Polymer Solutions", M. C. WILLIAMS, University of California, Berkeley, California.

A molecular theory previously advanced for the description of stress in sheared polymer solutions is reviewed. The general expression for the stress tensor π derived by Fixman is evaluated in an approximate fashion for the case of concentrated solutions by means of an explicit consideration of interpolymer forces. This involves the introduction of an arbitrary but reasonable polymer segment distribution function ν (R) which leads to an intermolecular potential dependent on shear rate $\dot{\nu}$. The pair correlation function $g(r)$ used to compute macroscopic properties is perturbed in terms of Kirkwood's friction coefficient ξ . Three rheological functions, π_{12} , $(\pi_{11} - \pi_{22})$, and $(\pi_{11} - \pi_{33})$, are obtained as functions of $\dot{\nu}$ and are displayed graphically. A unique feature is that the related normal stress difference $(\pi_{22} - \pi_{33})$ is shown to have the same sign as $(\pi_{11} - \pi_{33})$ at low shear, a result in agreement with all experimental data but not predicted by other theories.

A comparison of these functions with two sets of cone-and-plate data (8.0% polyvinyl alcohol in water, and 6.86% polyisobutylene in cetane) shows that shear and normal stress measurements can be simultaneously described at low shear. Values of a time-constant are obtained by the curve-fitting procedure, and are found to be quantitatively reasonable.

3:30 p.m. Break

B1-4

3:45 p.m. "Rheological Properties of Three Solutions, Part I. Non-Newtonian Viscosity, Normal Stresses, and Complex Viscosity," J. D. HUPPLER, L. A. HOLMES, and E. ASHARE, University of Wisconsin, Madison, Wisconsin.

The shear-dependent viscosity η , the shear-dependent normal stress difference $\tau_{11} - \tau_{22}$, and the frequency dependent complex viscosity have been measured for three solutions:

1. 2% Polyisobutylene in Primol 355
2. 1.5% Dow ET597 in 50-50 glycerine-water
3. Aluminum Soap 7% in decalin (Al-laurante)

The shear-dependent research data extend over about 6 decades, the normal stress data over about $3\frac{1}{2}$ decades, and the frequency dependent data over about $3\frac{1}{2}$ decades. The data used to find the constants in several nonlinear

viscoelastic rheological models, and to evaluate the ability of the models to describe the material functions of the fluids. In particular the Spriggs 4-constant model, the WJFLMB model, and the OWFS model were tested. Although generally satisfactory, all three models give an incorrect slope for the normal stresses in the "power-law region."

Falling spheres were used to measure the zero shear-rate viscosity η_0 ; the Weissenberg Rheogoniometer was used to measure non-Newtonian viscosity, a normal stress difference $\tau_{11} - \tau_{22}$, and the complex viscosity; the Ferranti-Shirley viscometer was used to make additional measurements of the non-Newtonian viscosity; and the Birnboim apparatus (at Professor J. D. Ferry's laboratory) was employed for measuring the complex viscosity.

PART II

Rheological Properties of Three Solutions. Part II. Relaxation and Growth of Shear and Normal Stresses, J. D. HUPPLER*, I. F. MACDONALD, T. W. SPRIGGS, L. A. HOLMES, and R. B. BIRD, University of Wisconsin, Madison, Wisconsin.

The same three solutions used in Part I were used for measuring the stress relaxation after cessation of steady flow and the stress growth at the inception of steady flow (including the "overshoot" phenomenon). Both shear and normal stress behavior were observed. In addition "interrupted flow" (a turret-shaped function for the velocity-gradient) was studied.

The data were used to evaluate the three rheological models mentioned in Part I. These models all make the same predictions for stress relaxation, but differ markedly in their predictions for stress growth. The Spriggs 4-constant model predicts oscillatory behavior, the OWFS model predicts no stress overshoot, and the WJFLMB predicts stress overshoot. The experimental data for the three solutions tested seem to be described best by the WJFLMB model.

*Present address: ESSO Production Research Laboratory
Houston, Texas

B1-5

4:15 p.m. "Relaxation Studies on Polymer Solutions," W. PHILIPPOFF, Esso Research and Engineering Company, Linden, New Jersey.

The emergence of the concept of "recoverable shear s " in the flow of solutions of polymers, or more generally viscoelastic liquids, necessitates a more detailed examination of its measurement in recoil and mechanism.

The influence of the constants of the instrument used on the measured physical properties of the investigated material especially the time-dependent stress-relaxation and recoil are studied. This gives the limits of the time resolution in practical cases. Especially for the Weissenberg rheogoniometer the relaxation measurement in shear gives

a vastly different result than the one in normal stress due to the properties of the instrument. The dependence of the recoil on time at different shear stresses for a 3% solution of a polyisobutylene $M = 15 \times 10^6$ in decalin is studied. The investigation, as is very often the case, is possible only in the strongly non-Newtonian range. Apparently the drop in viscosity from its limiting value η_0 is the main influence in determining the "valid" range of recoil measurements. The recoil-time curve is *not* exponential.

Stress relaxation measurement made by stopping the instrument after steady flow using birefringence on the same solution are performed, showing that the extinction angle χ remains constant during relaxation, the decay being faster than in the recoil experiment. The constancy of χ suggests that normal stresses and shear stresses decay at the same rate. The decay is roughly exponential with time. The viscosity in the calculation of the relaxation time is the lower one under shear conditions, not the "initial viscosity" at low rates of shear.

B1-6

4:45 p.m. "Stress Relaxation Upon Cessation of Steady Flow of Polymer Melts and Solutions," R. A. STRATTON, Mobil Chemical Company, Metuchen, New Jersey.

The accurate measurement of small normal stresses is extremely difficult, while the measurement of shear stress relaxation following cessation of steady flow is relatively simpler and easier. It is shown that from the latter experiment the steady state shear compliance J_e and hence the recoverable shear strain and the first normal stress difference $P_{11} - P_{22}$ can be calculated. Measurements of $P_{11} - P_{22}$ and shear stress relaxation were made with the Weissenberg Rheogoniometer. Results were obtained for dilute solutions of high molecular weight polystyrene and polyisobutylene, silicones, and undiluted monodisperse polystyrene. Very good agreement is obtained between the measured values of $P_{11} - P_{22}$ and those calculated from stress relaxation. Some data calculated from flow birefringence and "recoil" measurements are also compared. It was found that the method works well into the non-Newtonian region if the apparent rather than the zero rate of shear viscosity is used in the equations.

MONDAY AFTERNOON

SESSION B2

Chairman: A. N. GENT, University of Akron, Akron, Ohio.
Filled and Unfilled Elastomers

B2-1

2:00 p.m. "Large Multiaxial Deformation Behavior of a Filled Silicone Rubber," K. C. VALANIS, University of Iowa, Ames, Iowa, and R. F. LANDEL, Jet Propulsion Laboratory, Pasadena, California.

Under conditions of uniaxial and biaxial stress relaxation it has been found that the mechanical response of a filled silicone rubber can be adequately described by the current mathematical theory of large viscoelastic deformation (Refs. 1, 2, 3).

It was further found that three relaxation functions which are independent of the deformation and are proportional to the same function of time are sufficient to describe the state of deformation.

The form of the constitutive relation of this material is in the usual notation

$$\tau_{ij} = \delta_{ij} \int_{-\infty}^t G_1(t-\tau) \frac{\partial C_{kk}}{\partial \tau} d\tau - \int_{-\infty}^t G_2(t-\tau) \frac{\partial C_{ij}}{\partial \tau} d\tau + \int_{-\infty}^t G_3(t-\tau) \left\{ C_{ij}^{-1} \frac{\partial C_{ij}}{\partial \tau} + \frac{1}{C_{ij}} \frac{\partial C_{ij}}{\partial \tau} \right\} d\tau + p(t) C_{ij}^{-1}$$

Under conditions of uniaxial stress the above equation takes the explicit form

$$\frac{t_1}{\lambda_1^2 - \frac{1}{\lambda}} = \left(\frac{t}{30}\right)^{-0.03} \left(5.7 \lambda_1^2 + \frac{100}{\lambda_1} - 40\right)$$

where t_1 is the axial stress per unit deformed area and t denotes time in minutes.

*This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.

**Professor, University of Iowa, Ames, Iowa; Visiting Professor, Polymer Research Section, Jet Propulsion Laboratory, California Institute of Technology, Summer 1966.

References

1. Green, A. E. and Rivlin, R. S., *Arch. Rat. Mech. Anal.* 1, 1 (1957).
2. Coleman, B. D. and Noll, W., *Rev. Mod. Phys.* 33, 239 (1961).
3. Valanis, K. C., Presented at 36th Annual Meeting of the Society of Rheology, October 1965.

B2-2

2:30 p.m. "Deformation and Rupture of an Unfilled Styrene-Butadiene Vulcanizate in Biaxial and Uniaxial Tension," T. L. SMITH, J. A. RINDE, and J. E. FREDERICK, Stanford Research Institute, Menlo Park, California.

Stress-strain and rupture data in biaxial and uniaxial tension were obtained on an unfilled styrene-butadiene vulcanizate at extension rates between 0.02 and 20 inches per minute at 25, 35, 50, 70, and 90°C. Thin - wall cylindrical specimens were stretched in the axial direction while gas pressure inside a specimen was regulated to maintain constant its original outside diameter and thus to obtain a pure shear deformation on the outside surface. From the tests, the stress σ_1 and the extension ratio λ_1 in the axial direction were obtained along with the circumferential stress σ_2 . Uniaxial tests were made on rings cut from the gage section of a cylindrical specimen.

All cylindrical specimens broke cleanly and perpendicular to the stretch direction. By applying time-temperature superposition to rupture data from both biaxial and uni-

axial tests, composite plots were obtained which show the marked dependence of σ_{1b} , σ_{2b} , and λ_{1b} (from biaxial tests) and of σ_b and λ_b (from uniaxial tests) on the reduced strain rate $\dot{\lambda}^a T$. At all— except possibly the largest— values of $\dot{\lambda}^a T$, the ultimate extension ratios in biaxial and uniaxial tension were sensibly identical whereas σ_b was intermediate between σ_{2b} and σ_{1b} .

The stress-strain data were slightly time-dependent at each temperature. One-minute biaxial data at all temperatures gave single curves on plots of $\log 3\sigma_1/F(1)$ and $\log 3\sigma_2/F(1)$ vs $\log(\lambda_1 - 1)$, where $F(1)$ is the 1-minute modulus from uniaxial data. Data from the curves were used to evaluate $3W_1/F(1)$ and $3W_2/F(1)$ where W_1 and W_2 are analogous to the strain-energy gradients, in equilibrium theory, with respect to the strain invariants I_1 and I_2 . For λ_1 less than about 2.2 ($I_1 = 6.0$), $3W_1/F(1)$ is a constant and only slightly dependent on λ_1 at higher extensions (up to $\lambda_1 = 3.0$); $3W_2/F(1)$ is a strongly decreasing function of λ_1 . Subject to reasonable assumptions, uniaxial data were computed from W_1 and W_2 and found to agree closely with experimental values.

B2-3

2:30 p.m. "Thermoelastic Behavior of Natural Rubber,"

M. C. SHEN, and D. A. McQUARRIE, North American Aviation Science Center, Thousand Oaks, California, and JULIUS L. JACKSON*, Howard University, Washington, D.C.

The Elliott-Lippmann anisotropy factor, which is useful in calculating the internal energy contribution to stress, is derived in terms of current statistical theory of rubber elasticity. The final equation is identical to that of Khansanovich and Flory. The new derivation, however, offers greater insight into the physical basis of the equation for the anisotropy factor and will facilitate subsequent discussion of the experimental results on the thermoelastic behavior of natural rubber. Stress-temperature measurements were carried out up to the elongation ratio, α , of 2.0. An automatic stress-relaxometer was constructed for this purpose which can be completely enclosed in a controlled environment. Experiments were so conducted as to minimize possible chemical effects and non-equilibrium conditions. Relative internal energy contribution to stress, f_e/f , is calculated as a function of α in terms of statistical and thermodynamic theories. Both of these yield similar results. It is shown that in the region of low strains ($1.0 < \alpha < 1.5$), f_e/f decreases rapidly with increasing α , but appears to remain constant at $1.5 < \alpha < 2.0$. This observation is not in agreement with the prediction of the current statistical theory of rubber elasticity, which stipulates that the energy effects are intramolecular and independent of deformation. Implications of these findings are discussed. It is suggested that perhaps at low strains the intermolecular interactions are large in comparison with intramolecular energies, but become relatively insignificant at higher elongation ratios. The temperature coefficient of unperturbed chain dimensions is also calculated from thermoelastic data. It only constant in the region $1.5 < \alpha < 2.0$.

*Visiting Scientist, North American Aviation Science Center, 1965.

3:30 p.m. Break

B2-4

3:45 p.m. "Dynamic Studies of a Composity Viscoelastic Material,"* M. G. SHARMA, Pennsylvania State University, University Park, Pennsylvania.

This paper is concerned with a study on the dynamic mechanical behavior of rubberlike material filled with spherical particles of finely divided aluminum of prescribed volume concentrations, in a frequency range of 100 to 2000 cycles per second. An apparatus that is developed for the determination of the dynamic mechanical behavior of soft rubberlike materials in the above frequency range, is described. The specimen, in the form of a rod is supported horizontally in the apparatus and is subjected to a longitudinal vibration at one end by sending an alternating current through a coil (fixed to the specimen end) operating in a magnetic field. The vibration is picked up at the other end by an identical magnet and coil system. By operating the rods at various resonant frequencies, it is possible to evaluate storage and loss moduli for the material at several resonant frequencies. The apparatus is provided with a thermal cabinet to study the effect of temperature on the dynamic mechanical behavior.

A theory that considers composite rubber system as made up of an elastic substance (aluminum) randomly disposed in a matrix of a viscoelastic substance (rubberlike material) has been developed. The theory predicts the dynamic behavior of the material in terms of static creep properties of constituent materials for uniaxial and volumetric compression loading and volume concentration of the filler in the rubber matrix. Comparison of the theoretically predicted values with the experimental results has been found to be reasonably good. Finally, the paper discusses the influence of temperature and filler concentrations on the dynamic mechanical behavior.

*This investigation is a part of the research project sponsored by the Army Research Office, Durham, N. C., under project No. 20010501B700.

B2-5

4:15 p.m. "Dynamic Shear Behavior of a Polyurethane Propellant," N. W. TSCHOEGL,* California Institute of Technology, Pasadena, California, and T. L. SMITH, Stanford Research Institute, Menlo Park, California.

The dynamic moduli of a polyurethane propellant were determined at 11 temperatures between -40 and 60°C and at as many as 14 frequencies between 0.064 and 24.5 cps at each temperature. Tests were made on conventionally bonded specimens 1.25 inches in diameter and 0.50 inch thick. The data were corrected to a shear strain amplitude of 0.01. Both the G' and G'' data at the different temperatures could be precisely superposed to give composite curves which show the dynamic moduli at frequencies in the range $-2.0 < \log \omega a_T < 9.6$, where ω is the circular frequency in radians per second. Values of the shift factor a_T obtained by superposing the G' and G'' data were sensibly identical and corresponded to those predicted by

the WLF equation. Over the frequency and temperature ranges covered, the storage modulus increased from about 1.4×10^7 dynes/cm² (205psi) to 1.4×10^9 dynes/cm² (20,500 psi), the latter value being less than the expected glassy modulus by a factor of 8 to 10. The mechanical loss tangent had a shallow maximum at $\log \omega a_T = -1.2$; above $\log \omega a_T = 6.0$, it decreased rapidly with increasing frequency. In the range $-2 < \log \omega a_T < 6$, the loss tangent varied only $\pm 12\%$ above the mean value in this frequency range.

*Present address: California Institute of Technology, Pasadena, California.

B2-6

4:45 p.m. "The Influence of Vacuole Formation on the Response and Failure of Solid Propellants," R. J. FARRIS, Aerojet-General Corporation, Sacramento, California.

The mechanical response and failure of solid propellants are shown to be related to the formation and growth of vacuoles which cause strain dilatation in these materials. A simple statistical interpretation of the dilatation-strain behavior has been used to assess both the cumulative and instantaneous frequencies of vacuole formation with strain. This provides a method for describing analytically the initiation and extent of microscopic failures which govern the non-linear stress-strain response and ultimate failure of this type of material. Stress-strain and dilatation-strain data taken under various conditions of superimposed pressure shows that the strong effect of superimposed hydrostatic pressure on propellant behavior is the result of suppressed vacuole formation.

MONDAY EVENING

9:00 p.m. Film Showing

"Rheological Behavior of Fluids," H. MARKOVITZ, Mellon Institute, Pittsburgh, Pennsylvania.

"Secondary Flow," E. S. TAYLOR, Massachusetts Institute of Technology, Cambridge, Massachusetts.

"Deformation of Continuous Media," J. LUMLEY, Pennsylvania State University, University Park, Pennsylvania.

TUESDAY, NOVEMBER 1

SESSION C - Tuesday Morning

Chairman: L. NIELSEN, Monsanto Company, St. Louis, Missouri.

Invited Lecture

8:45 a.m. "The Rheology of Inorganic Glasses," M. GOLDSTEIN, Yeshiva University, New York, New York.

General Session

C2

9:45 a.m. "Distribution of Relaxation Times and Annealing of B.S.C. Glass," P. B. MACEDO and A. NAPOLITANO, National Bureau of Standards, Washington, D. C.

The relation between time-temperature dependence of strain (annealing) and frequency dependence of modulus is considered. Spinner and Napolitano have compared two glasses of identical composition and index of refraction (density) one in equilibrium, and the second in a non-equilibrium state by their behavior upon further annealing. It is shown that the time dependence of the strain in these experiments is linear and permits the calculation of the distribution of relaxation times. Topological and mechanical models for the distribution are investigated. A topological model is found which not only explains the temperature dependence of viscosity, but also the resistivity experiments of Ritland. In doing so Tool's fictive temperature is extended to two parameters, which can explain both equilibrium and non-equilibrium glasses. The temperature dependence of the viscosity is due to a true activation energy rather than a free volume or configuration entropy effect. The stress (thermal) strain experiment gives a distribution many decades narrower than the stress (pressure) strain work previously done in the relaxation region by Kurkjian. Since no pressure was applied no "delayed elastic relaxation" takes place in the thermal experiment. Thus, there is the added advantage of only measuring the structural distribution of relaxation times.

This analysis is applied to a borosilicate crown glass, and it is found that $\tau_2/\tau_1 \approx 8$ (Gaussian $b = .6$). This narrow distribution indicates that the flow in this material is monomeric rather than polymeric ($10^3 < \tau_2/\tau_1 \leq 10^6$). The monomeric nature of silicate glasses has been postulated by Bockris et. al from zero frequency compressibility measurements at high temperatures, but was questioned when Westman proved that phosphate glasses are polymeric. The present work together with Macedo and Litovitz distribution of relaxation times in B_2O_3 indicates that the iceberg picture of Bockris is correct for the borates and silicates. The ratio of the average volume to average shear relaxation time is found to be ≈ 2 , in good agreement with other associated liquids.

10:15 a.m. Break

C3

10:30 a.m. "Viscoelastic Properties of Polydimethylsiloxanes," J. M. O'REILLY and W. M. PREST, Jr., General Electric Research and Development Center, Schenectady, New York.

The dynamic viscosity $\eta'(\omega)$ and dynamic modulus $G'(\omega)$ of polydimethylsiloxanes with viscosity average molecular weights, M_v , between 5×10^4 and 1×10^6 have been measured at frequencies between 0.1 and 30 cps at temperatures from 25-200°C. These measurements, rotational viscosity and normal stresses were made using cone-plate geometry on a Rheogoniometer. The zero shear

viscosity, η_0 , is proportional to $M_v^{3.4}$ indicating that the molecular weight of all these samples is above the entanglement molecular weight of this polymer. A scale factor $m = 1.6$ can be used to superimpose $\eta'(\omega)$ and $\eta'(\dot{\gamma})$ and m is independent of molecular weight and temperature. Normal stresses are proportional to $\dot{\gamma}^{1.5}$ at low shear rates and parallel the behavior of $G'(\omega)$. Continuum theories predict that $P_{11}-P_{22}(\dot{\gamma})/2\dot{\gamma}^2 = G'(\omega)/\omega^2$ and we find $P_{11}-P_{22}(\dot{\gamma})/2 \simeq G'(\omega)$ when $\omega = \dot{\gamma}$. There is a definite relation between $P_{11}-P_{22}(\dot{\gamma})$ and $G'(\omega)$ which is independent of molecular weight and temperature.

Dynamic viscosity and rigidity can be examined in light of molecular theories which predict that relaxation times are directly proportional to η_0 and molecular weight and inversely proportional to temperature. Relaxation times determined from $\eta'(\omega)$ and $G'(\omega)$ for silicones are dependent only on viscosity and *not* on molecular weight. The effect of temperature on the relaxation time, other than through the viscosity is small. $\eta'(\omega)$ and $G'(\omega)$ for different molecular weights and temperature can be superimposed onto a master curve if the reduced frequency is taken as $\eta_0\omega$. The master curve has the general characteristics predicted by molecular theories such as Rouse's.

C4

11:00 a.m. "Secondary Transitions of Poly(Methyl Methacrylate) and Their Activation Energies as Determined by Shear and Tensile Creep Compliance Measurements," E. V. THOMPSON, American Cyanamid Company, Stamford, Connecticut.

The activation energy of the so-called β process of poly(methyl methacrylate) has been determined by numerous methods including shear creep and stress relaxation measurements and is found to be about 18-20 kcal/mole. However, insufficient creep data exists to clearly define other secondary transitions in this polymer. Since a possible γ process has been detected by high frequency experiments at about -30°C and numerous workers have found a transition in the $25-70^\circ\text{C}$ range using various dilatometric techniques, it is of interest to extend the temperature range of the creep measurements in an effort to locate these other transitions.

C5

11:30 a.m. "The Temperature and Molecular Weight Dependence of the Viscoelastic Behavior of Polystyrene," D. J. PLAZEK and V. M. O'ROURKE, Mellon Institute, Pittsburgh, Pennsylvania.

The viscoelastic creep and creep recovery behavior of anionically polymerized polystyrene is being investigated as a function of molecular weight. A torsional apparatus which employs a magnetic bearing and induced torques on the moving element, the rotor, is the principal tool being used. The recoverable compliance is being measured from glassy levels at relative short times out to steady state levels at relative long times where possible. Some

measurements have been made below the glass temperature where isothermal volume contraction can be observed with the concomitant shift of the retardation spectrum to longer times.

The molecular weight dependence of the steady state compliance is being determined and that of the viscosity is being established beyond the range previously measured. To date three unexpected observations have been made: 1) the steady state compliance appears to have a temperature dependence that is greater than expected and in the opposite sense than the rubberlike entropic response found in crosslinked systems; 2) the "entanglement plateau" is not clearly established unless the molecular weight is about 5×10^5 or higher; 3) the behavior in the region of glassy response appears to show a slight molecular weight dependence.

TUESDAY AFTERNOON

SESSION D

Chairman: J. C. BRODNYAN, Rohm and Haas Company, Springhouse, Pennsylvania.

General Session

2:00 p.m. "General Solutions in the Hydrostatic Theory of Liquid Crystals," J. L. ERICKSEN, Johns Hopkins University, Baltimore, Maryland.

A primary function of a hydrostatic theory of liquid crystals is to predict orientation patterns which occur in these fluids. Certain patterns are universal, being possible for arbitrary forms of the stored energy function. Our purpose is to characterize these. It turns out that there are three types of such patterns, one of which is frequently observed.

D2

2:30 p.m. "Linear Free Energy Effects in the Poly(vinyl Chloride)-ester System from Creep Compliance, Melt and Solution Viscosity Techniques," R. J. HAMMOND and E. M. SMOLEY, Armstrong Cork Company, Lancaster, Pennsylvania.

Current literature indicates that considerable effort is being made to relate the rheological behavior of various materials to molecular mechanisms of flow. Implicit in the viscoelastic spectra of various substances is the molecular configuration and motion that gives shape to the stress relaxation or creep compliance curves. In dilute solutions or concentrated melts at higher temperatures flow curves give indications of molecular arrangements present causing deviation from some previously defined rheological standard. Research on high polymers has generally taken the course of investigations into pure one component or two component solvent-polymer systems. Experimental evidence obtained can thus be used for purely phenomenological, molecular or general processing application depending on the objectives of the program. In research on poly(vinyl chloride) melts, complications arise

due to the presence of necessary impurities (thermal stabilizers and secondary plasticizers). While it is possible to describe the flow properties of these melts and solutions by suitable empirical equations, it is difficult to predict beyond any gross qualitative aspect what general chemical or physical property will result from small changes in the basic formulation. It is, therefore, quite impossible to explore the rheological behavior of poly(vinyl chloride) without understanding and evaluating the magnitude of the effect of these added substances. Our primary considerations here are directed at understanding the nature of the interaction of ester-type plasticizers with poly(vinyl chloride) and its model, 1,3-dichloropropane compliance, dilute solution and melt viscosity characteristics. The method employed represents a departure from conventional thought in that the rheological behavior has been successfully correlated to both Hammett and Taft substituent constants as implied in Eyring's concept of absolute reaction rates. While changes in interaction free energies and enthalpies evolve simply and naturally from this technique, the significant conclusion obtained from these data is that the generally accepted "hydrogen-bonding" interaction hypothesis of poly(vinyl chloride) with esters is clearly absent.

D3

3:00 p.m. "Rheology of Aluminum Dilaurate in Toluene," F. H. GASKINS, U. S. Army Edgewood Arsenal, Maryland, J. C. BRODNYAN, Rohm and Haas Company, Springhouse, Pennsylvania, and W. PHILIPPOFF, Esso Research and Engineering Company, Linden, New Jersey.

The stress-optical properties of aluminum dilaurate-toluene solutions were investigated over a wide range in shear rates, D . Flow curves of 1, 2 and 3 weight-percent of the aluminum soap dispersed in toluene displayed the type of behavior previously reported by Weber and Bauer⁽¹⁾: i.e., Newtonian behavior at low shear rates, pronounced shear thinning at D greater than 10^{-2} sec⁻¹ and dependence of apparent shear stress, ζ , on length-to-radius ratio, L/R , of the capillary tubes used at high shear rates.

Flow birefringence behavior was similar. For example, at low shear rates the degree of birefringence, $\Delta\eta$, increased in proportion to D and the extinction angle, χ , was nearly 45° . Above a critical shear rate, $\Delta\eta$ increased overproportionally, finally leveling out at a high value. Simultaneously, χ decreased equally rapidly to about 1° . Despite these dramatic changes in dependence of τ , $\Delta\eta$ and χ on D , the stress optical coefficient remained constant over the entire range of variables.

Elastic recoverable shear strains, or simply "recoverable shears", s , were calculated from the variance of τ with L/R . These were found to be in good agreement with data obtained from normal stress measurements in a Weissenberg Rheogoniometer. At low shear stress s increased linearly with τ . Above a critical shear stress the recoverable shear increased rapidly with small increases

in τ , finally leveling off at a value of approximately 300 shear units and remaining constant with additional increases in shear stress. This behavior is similar to that observed with polyethylene in the region where melt fracture occurs. In these experiments, however, the transition takes place in a rotational instrument under continuous shear in which no "entrance effects" can be postulated as causing melt fracture.

During the progress of this investigation it was ascertained that the rotational viscometer could be used to determine elasticity in aluminum soap solutions under dynamic conditions. Quantitative evaluation of the results produced data which correlated with dynamic test data obtained by a variety of techniques. The authors believe that this is a unique and novel method for measuring the dynamic rheological properties of viscoelastic materials.

3:30 p.m. Break

D4

3:45 p.m. "Elastomer Processing and Application of Rheological Fundamentals," J. L. WHITE and N. TOKITA, U. S. Rubber Company Research Center, Wayne, New Jersey.

A rational analysis of elastomer processing in a rubber mechanical goods plant is described. The various phases of processing are divided into unit operations. The theory of non-linear isotropic viscoelasticity is then applied to these unit operations and characteristic dimensionless groups derived. From the above analysis the most important rheological properties to be specified are the relaxation modulus, laminar shear viscosity and a tearing energy. The significance of the maximum relaxation time is discussed.

The limitations and asymptotic nature of the Rivlin-Ericksen and second order fluid theories are described in this development. The reason for the Coleman-Duffin-Mizel paradox are noted.

The paper is concluded by a study of the behavior of raw rubber on a two roll mill. The differences in behavior between natural rubber, emulsion butadiene-styrene copolymer and the newer Ziegler and butyl lithium stereo elastomers are discussed.

TUESDAY EVENING

Society of Rheology Business Meeting

Banquet and Presentation of Bingham Medal

WEDNESDAY, NOVEMBER 2

SESSION E

Chairman: R. F. LANDEL, Jet Propulsion Laboratory, Pasadena, California.

Invited Lecture

E1

8:45 a.m. "Rheological Problems in the Earth Sciences,"
B. KAMB, California Institute of Technology, Pasadena,
California.

Flow Behavior

E2

9:45 a.m. "Deformational Behavior of Viscoelastic Materials
in Processes Defined by Small Time Constants," A. B.
METZNER and M. JOHNSON, University of Delaware,
Newark, Delaware.

It may be shown analytically that in the asymptotic limit of very rapidly changing deformation rates materials ordinarily considered to be fluids may take on the characteristics of elastic solids. For example the stresses become dependent upon total deformation, not on deformation rate. These conclusions follow simply from either the Oldroyd or the Green-Rivlin approximations to material behavior.

The essential part of the presentation of this paper consists of a short motion picture filmed at 1,000 - 5,000 frames per second, in which the response of a low viscosity fluid suddenly deformed by impacting a blunt object upon it is observed. One notes a large (6" - 12" in radius) conical sheet of fluid is formed, moves outward rapidly and then returns to nearly its initial configuration. The duration of this elastic recoil experiment is approximately 10 milliseconds. Some considerations on the use of this experimental technique for obtaining material parameters quantitatively, which may then be used to characterize the material behavior in other high Deborah number experiments, are included.

10:15 a.m. Break

E3

10:30 a.m. "Oscillatory Flow of Suspensions Through Tubes,"
M. TAKANO and S. G. MASON, McGill University, and
Pulp and Paper Research Institute of Canada, Montreal,
Canada.

The translation, rotation and radial migration of neutrally buoyant rigid spheres, rods and discs, as well as the deformation and radial migration of fluid drops suspended in Newtonian liquids undergoing oscillatory and pulsatile flows through circular tubes were studied.

The axial displacements of small spheres, rods and discs in oscillatory flow were generally in agreement with the theory of Womersley for homogeneous fluids, and in pulsatile flow could be predicted by superposition of the oscillatory and the steady flows. The rotations of the cylindrical particles were in accord with the theory based on slow steady flow when the fluctuating velocity-gradient was used. When the particles were very close to the wall, however, both translational and rotational slip were observed as in steady flow.

The oscillating deformation and orientation of liquid drops of low viscosity agreed with a theory derived from that for steady flow. When the drop viscosity was increased, however, the deformation lagged the velocity-gradient due to dissipation of energy in dilatational flow inside the drop.

Rigid spheres drifted radially to equilibrium positions determined by Womersley's dimensionless parameter α and the relative size b/R of the particle to the tube radius, the migration velocity being a function of α , b/R and the radial position. In pulsatile flow, the migration velocity near the wall increased and the equilibrium position shifted inwards at low values of α .

Cylindrical particles exhibited not only radial migration but also a drift in orbit constant with the long axis of a rod and the faces of a disc becoming oriented in the planes passing through the tube axis as found in steady flow at high Reynolds numbers. The migration velocity depended on the orientation of the cylinder axis in addition to the parameters for spheres.

Fluid drops also migrated radially in oscillatory flow. When the drop viscosity was very low, the drop migrated to the tube axis, but when it was high, the drop migrated more or less like a rigid sphere.

With concentrated suspensions, the velocity profile, the amplitude and phase of the oscillating pressure-gradient and the power dissipated per unit length of the tube were influenced by radial migration of particles. The velocity profile of concentrated suspensions became blunted as the particle-free layer developed near the wall. The power dissipated for oscillatory motions of rigid sphere suspensions generally decreased with time after passing through a maximum value. The power dissipated in fluid drop suspensions decreased as a definite drop-free zone developed near the wall.

The relevance of some of these phenomena, which will be illustrated by a cine film, to several problems in suspension rheology will be discussed.

Projection facilities required: 16 mm. cine film (silent)
35 mm. slides

E4

11:00 a.m. "Quantitative Relationship Between Steady-State Flow Curve and Molecular Weight Distribution of Polyethylene," N. NAKAJIMA, Allied Chemical Corporation, Morris Township, New Jersey.

Mechanical response of matter arises from various mechanical elements which compose the matter. One of the most important features of the element is its size. At the lower temperature and/or the higher frequency, the responding elements are smaller. On the other hand, the response of the larger elements can be observed at the higher temperature and/or the lower frequency. If an appropriate condition is chosen, then, the responding elements can be made to coincide with the dimension of polymer chain. In other words, a quantitative, though relative, information on the molecular weight distribution

can be obtained from the mechanical measurement. For thermoplastic materials, such condition can be obtained in the melt, steady-state flow behavior, where the shear rate is analogous to the frequency. Examples of such studies were shown with linear polyethylene (1) and polypropylene (2). A logical extension of the study is to discover the quantitative relation between the flow curve and the fractionation data. Such a relationship was derived, using four commercial samples and two synthetic blends of polyethylene. These six resins represent a wide variety of the commercial material. The molecular weight distribution thus calculated from the flow curve is in good agreement with the fractionation data (3) within the accuracy of the latter measurement. Therefore, it is possible to calculate the molecular weight distribution from the flow curve. The applicability of the method, however, is limited to the single peaked, smooth but not necessarily symmetric distribution. The present study provides some insight into the molecular mode of the response. It is dependent not only on the chain length but also on the medium, where the chain is placed. This is quite analogous to the environmental effect in the spectroscopic measurement. In the case of the mechanical measurement, however, the interaction with the environment is much more significant. Classically, this was interpreted as an entanglement of chains. At the high shear rate, where the polymeric chain as a whole can no longer respond as a mechanical unit, only the segmental motion is permitted. Namely, the polymer exhibits a rubbery response. This behavior was also traditionally interpreted as the chain entanglement.

(1) NAKAJIMA, N. and P. S. L. WONG, *Trans. Soc. Rheol.*, 9:13 (1965).

(2) NAKAJIMA, N. and P. S. L. WONG, *J. Appl. Polymer Sci.*, 9, 3141 (1965).

(3) NAKAJIMA, N., *J. Polymer Sci.*, Part A-2, 5, 101 (1966).

E5

11:30 a.m. "A Relationship between Molecular Weight Distribution and Non-Newtonian Flow for Polyisobutenes," R. S. PORTER, M. J. R. CANTOW, and J. F. JOHNSON, Chevron Research Corporation, Richmond, California.

In recent years it has been demonstrated widely that relationships do exist between molecular weight distribution and the non-Newtonian flow of linear amorphous polymers. Variations in distribution cause marked deviations from general reduced variable curves for non-Newtonian flow. This conclusion means that reduced variables must involve more than a single molecular weight average. This complexity has been evaluated in this study by equating shear relaxation spectra for polymer solutions to their respective molecular weight distributions. Molecular weight distributions have been generated by column fractionation, measured by gel permeation chromatography, and expressed in terms of their standard deviations. The distributions, expressed in the common form of M_w/M_n , ranged from 3.07 to 1.01. The procedure has been successfully applied to non-Newtonian flow curves for concen-

trated solutions of polyisobutenes. This new relationship may be suitable for expressing the non-Newtonian flow of other linear amorphous polymers. A general approach of this type is of value for predicting and tailoring the flow properties of polymers.

WEDNESDAY AFTERNOON

SESSION F1

Chairman: R. S. PORTER, University of Massachusetts, Amherst, Massachusetts.

Flow Behavior

F1-1

2:00 p.m. "Steady Flow and Dynamic Oscillatory Experiments on Polymer Melts," L. L. BLEYLER, JR., and T. W. HUSEBY, Bell Telephone Laboratories, Murray Hill, New Jersey.

We present here a correlation scheme for the behavior of bulk polymer melts in steady flow and dynamic oscillatory experiments. The correlation is not limited to low shear rates, but is theoretically valid for all frequencies and shear rates. Basis for the scheme derives from Pao's theory for viscoelastic liquids. The result, $s = (2 \cot \delta) \omega = K$, where s is recoverable shear strain and $\cot \delta = \frac{G'(\omega)}{G''(\omega)}$ (reciprocal of the loss factor), is easily derived and provides the key to the correlation. The remaining results are

$$\eta(K) = \left\{ \eta'(\omega) [1 + 2 \cot^2 \delta] \right\} \omega = K$$

$$G(K) = \left\{ G'(\omega) [1 + \frac{1}{2} \tan^2 \delta] \right\} \omega = K$$

$$\tau_{12}(K) = \left\{ G''(\omega) [1 + 2 \cot^2 \delta] \right\} \omega = K$$

$$P_{11}(K) - P_{22}(K) = \left\{ 2G'(\omega) [1 + 2 \cot^2 \delta] \right\} \omega = K$$

where the quantities have their usual meaning. Thus the steady flow shear viscosity is expected to equal or exceed the dynamic viscosity at all frequencies and shear rates. Similarly, the correlation predicts that G exceeds or equals G' over the entire frequency range. At low shear rates, τ_{12} should correlate with G'' and the first normal stress difference is given by $2G'$.

Experimental results are shown and compared to predicted behavior. Steady flow experiments were performed in a capillary rheometer and dynamic results were obtained using a Maxwell Orthogonal Rheometer.

F1-2

2:30 p.m. "Velocity Profiles of a Non-Newtonian Fluid in Helical Flow," D. R. REA and W. R. SCHOWALTER, Princeton University, Princeton, New Jersey.

Flow behavior of a 3 percent solution of polyisobutylene (Vistanex L-100) dissolved in Decalin was studied in helical flow at 25° C. Helical flow was generated by simultaneously

imposing an axial pressure gradient and a rotational torque on the fluid as it passed through a $\frac{1}{2}$ inch gap between concentric cylinders which were 18 inches long. The inner and outer cylinders had nominal diameters of 3 and 4 inches, respectively. A flow visualization technique was developed which permitted quantitative measurement of velocity profiles in the helical flow field. Light was scattered to a camera-microscope assembly from minute tracer particles (approximately 5-micron bubbles) located in the test fluid. From the resulting photographs both direction and magnitude of the velocity vector could be determined as a function of position in the flow field.

Results indicate that the correspondence between helical flow and Poiseuille flow which is predicted for simple fluids in viscometric flows is in fact observed to a close approximation. One concludes that the spatial variation in direction of flow which exists in helical flow does not have an important effect on the flow of the polyisobutylene solution under conditions studied in these experiments, a result consistent with the theory of simple fluids.

Velocity profile measurements at two axial positions in the helical flow field indicated that a fully developed velocity profile was readily established.

A supplementary result is the perfection for non-Newtonian flows of a versatile optical technique that permits measurement of velocity profiles without disturbance of the flow field.

F1-3

3:00 p.m. "Parallel Plane Rotational Viscometer," I. M. KRIEGER and M. WOODS, Case Institute of Technology, Cleveland, Ohio.

The distribution of shear rate and shear stress is analyzed for the steady shear motion of a non-Newtonian fluid between rotating parallel planes. A relationship similar to that obtained by Weissenberg for the capillary viscometer is obtained, permitting the true viscosity to be calculated from the apparent viscosity. Confirming experimental data are presented.

3:30 p.m. Break

F1-4

3:45 p.m. "Behavior of Suspended Matter in Rapidly Accelerating Viscoelastic Fluids - The Uebler Effect," A. B. METZNER, University of Delaware, Newark, Delaware.

The observation that large bubbles entrained in accelerating viscoelastic fluids may suddenly stop and remain stationary for long periods of time, though imbedded in a region of high fluid velocities, is noted and described. An analysis of this phenomenon, termed the Uebler effect, shows that it may be expected to occur with all particulate matter provided that the continuum field fluid is accelerating sufficiently rapidly to generate high stresses as a result of fluid stretching, and provided these stresses change sufficiently rapidly in the direction of the velocity vector in the flow field.

F1-5

4:15 p.m. "Taylor Instability in Elastic Fluids," C. DUGAN and M. M. DENN, University of Delaware, Newark, Delaware.

An experimental determination of the hydrodynamic stability of elastic fluids in laminar flow between rotating concentric cylinders was carried out. As predicted by analyses for second order fluids, the critical Taylor Number for the onset of instability was below that of a Newtonian fluid of the same apparent viscosity. The quantitative agreement between theory and experiment was sufficiently good to suggest the use of stability measurements as a means of estimating normal stresses in elastic fluids, particularly dilute solutions of interest in drag reduction studies.

SESSION F2

Chairman: J. L. WHITE, U. S. Rubber Tire Company, Detroit Michigan.

General Session

F2-1

2:00 p.m. "Fatigue Under Complicated Load Histories. Law of Cumulative Damage," D. C. PREVORSEK and M. L. BROOKS, Central Research Laboratory, Allied Chemical Corporation, Morristown, New Jersey.

The applicability of Miner's law of cumulative damage to predict lifetimes in experiments involving complex load histories is examined. Lifetimes estimated by $\sum \frac{t_i}{(t_b)_i} = 1$ are compared with those calculated by the expression for the time to rupture derived by Prevorsek and Lyons assuming that the time to rupture can be approximated by the time to form an unstable crack. For experiments in which the loading conditions became increasingly severe with time, lifetimes predicted by Miner's law are longer than those calculated from the rate of crack propagation, the opposite being found for experiments in which the loading conditions become decreasingly severe with time. Experimental data on hand are in agreement with these findings. Effects of changes in the structural parameters ρ , E and ΔF^* and of variations in the experimental conditions on the accuracy of the lifetime estimates are discussed.

F2-2

2:30 p.m. "Failure of 0.95 Density Polyethylene Under Constant Load in Aggressive Stress-Cracking Environments," G. E. FULMER, W. R. GRACE and Company, Clarksville, Maryland.

The creep failure of polyethylene in Igepal CO 630 was measured as functions of temperature and molecular weight. Boltzman kinetics are found applicable to creep curves if failure mechanism changes are accommodated. Reduced variable treatment of the data gives a master creep failure curve with the same shift factors used for

the failure envelope. To describe the failure, both a master creep curve and a failure envelope are required. A reduced multivariant force variable which depends on the failure mechanisms is necessary. Three distinct failure mechanisms were observed; ductile, elastic, and brittle. Eyring kinetic theory can be useful in the analysis of the failure data.

F2-3

3:00 p.m. "The Dynamic Response of Periodically Deformed Non-Newtonian Fluid Films," C. WACHMANN, D. E. DOUGHERTY, and C. H. T. PAN, Mechanical Technology Incorporated, Latham, New York.

Analysis has shown that a squeeze film of a non-Newtonian fluid possessing a shear dependent viscosity would show a time average superambient or subambient pressure when subjected to a transverse skew periodic deformation. The magnitude of this effect depended on the fluid consistency and the degree of deviation from the Newtonian regime and on the skewness of the deformation. Elastic properties did not contribute to this net pressure effect and determined only the rapidity with which the transients would disappear.

The squeeze film analyzed was formed between two semi-infinite flat parallel plates moving 180° out of phase with respect to each other. One complete cycle of film deformation consisted therefore of a compression stroke and a return stroke.

A pseudoplastic fluid showed a net subambient pressure when the compression stroke was less than one half period, and a net superambient pressure when more than one half period. A dilatant fluid showed the reverse effects. No net super- or subambient pressures were indicated if the deformation was symmetric. Newtonian fluids showed none of these effects.

The implications of the super- or subambient pressure responses are that a net load support or a net suction can be achieved when a non-Newtonian fluid film is deformed in a skew periodic fashion.

Analysis proceeded as a solution of the equations of conservation of mass and of conservation of linear momentum subject to the appropriate boundary conditions. The visco-elastic fluid was represented by a Maxwell model with a "power-law" viscosity and a single relaxation time λ .

The mathematics was made more tractable by order-of-magnitude simplifications which, however, imposed some restrictions on squeeze film deformations and flow rates. The instantaneous plate loading $W(t)$ could be represented by the integral-differential equation

$$W(t) + \frac{1}{\lambda} W(t) = \frac{1}{\lambda} F(t)$$

The forcing function $F(t)$ had integral form and contained the values of squeeze film geometry, fluid consistency and flow behavior index. By Fourier analysis the time average plate loading was determined. Actual values of \bar{W} for

chosen film geometries were determined for five non-Newtonian fluids.

Potential applications of the above analysis may be in the study of bearings, mechanical isolators, valveless pumps and other mechanical devices and biomechanical phenomena.

3:30 p.m. Break

F2-4

3:45 p.m. "Responses of Model Materials to Impact," I. J. GRUNTFEST, General Electric Company, Space Technology Center, King of Prussia, Pennsylvania.

As part of a continuing exploration of the mechanical behavior of materials which have temperature dependent properties, the effect of a hammer blow on a small sample of model viscoelastic material is considered. In this situation, the duration of the experiment is long compared with the time required for stress equilibrium to develop and short in comparison with the thermal relaxation time of the sample. The analysis shows how a material which responds in an almost perfectly elastic manner to a light blow can respond in a viscous manner to a heavy blow. It also suggests that a homogeneous continuum with properties that would make it acceptable as a structural material must be brittle. This result may contribute to the understanding of the important relationship between microstructure and ductility.

The hammer experiment involves relatively high strain rates which vary continuously during the deformation. In earlier work, the constant deformation rate case was studied. The latter situation is difficult to produce in the laboratory in the range of rates of interest here and is likely to arise in practice.

F2-5

4:15 p.m. "Linear Viscoelasticity and Flow in Lipstick," R. A. WALL and G. F. DASHER, Clairol Research Laboratories, Stamford, Connecticut.

An apparatus is described for measuring the shear creep compliance and recovery of lipsticks in the shear strain region of up to 0.06. Shear stresses applied to the lipsticks are of the order of 10^3 dynes/cm². Creep and recovery cycles studied are identical in length and range up to about 3×10^5 sec. Some representative commercial lipsticks are studied and it is found that, as would be expected, there are easily measured differences in the compliance behavior. The object of the study is to obtain basic rheological parameters for correlation with product performance characteristics as described by consumer test panels.

The creep and recovery cycles for stresses below the limit of linear stress - instantaneous strain relationship may be described by the behavior of a series Maxwell-Voigt model combination. The time course of the experimental creep and recovery curves are described by the theoretical relationships using a single set of four model parameters for all stresses below the above mentioned limit.

The viscosity corresponding to the dashpot in the Maxwell element (derived from the small strain creep compliance data) is compared with the apparent viscosity at large strains (measured at higher shear rates in a plate and cone rheometer). It is found that in the plate and cone rheometer the apparent viscosity is about seven orders of magnitude lower than the Maxwell dashpot viscosity, however, the shear rate in the plate and cone system is seven orders of magnitude higher than in the

creep experiment. The outcome of this analysis is the conclusion that for the lipsticks studied, the shear stress opposing irrecoverable deformation (print-out) over seven orders of magnitude of shear rate and going from very small to very large strains, is roughly (within a factor of 3) constant. The somewhat lower shear stress observed in the plate and cone measurement could very easily be due to high shear rate work softening produced in the operation of placing the sample in the instrument.

CHARTER FLIGHT TO JAPAN 1968

The Fifth International Congress on Rheology is scheduled for October 7-11, 1968 in Kyoto, Japan. The Society is exploring possibilities for one or more charter flights to Japan to coincide with this Congress. Because tentative arrangements with an airline should be made about 18 months in advance, it will be helpful if those who have a potential

interest would furnish the information requested below prior to November 15, 1966. As the sponsoring organization will not necessarily be the Society of Rheology, please bring this announcement to the attention of your associates and friends who may not be members of the Society.

Name _____

Affiliation _____

Street Address _____

City, State _____

My wife will probably accompany me: Yes ___ No ___

I prefer a 3-week trip: Yes ___ No ___

I prefer a 4-week trip: Yes ___ No ___

I would prefer to leave from: New York ___;

Washington, D.C. ___; Chicago ___; West Coast ___.

I am a member of: Society of Rheology ___; another society affiliated with the American Institute of Physics ___; a technical society outside the American Institute of Physics ___.

Please mail above to Thor L. Smith, Stanford Research Institute, Menlo Park, California, 94025.

