

RHEOLOGY BULLETIN

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Erratum: The special issue, dated July 1964, was Vol. 33 No. 3.

THE BINGHAM MEDAL, 1964

Professor Johannes M. Burgers, Research Professor of the University of Maryland will receive the Bingham Award for 1964. He has been making outstanding contributions to our knowledge of the flow of crystalline solids as well as to general rheology for almost thirty years. His contributions to the theory of rheology appeared in the "First and Second Reports on Viscosity and Plasticity" which were published in 1935 and 1938 respectively. In addition to preparing several chapters for these books he edited and supervised the whole project.

His contributions to our understanding of the behavior of imperfections in crystals and of the effect of dislocations in plastic flow are fundamental to the subject and are recognized by the naming of the 'Burgers Circuit' in lattice theory and the 'Burgers Vector' in dislocation theory. He was the first to propose the screw dislocations in contrast to edge dislocations (Burgers dislocations) and in 1939 he developed a dislocation model of grain boundaries. He has more recently written, with his brother, a survey of the subject which is Chapter 6 of Volume 1 of Eirich's 'Rheology.'

Dr. Burgers was born in Arnhem, Netherlands, January 13, 1895. He received a PhD in mathematics and physical science at Leiden in 1918, honorary doctors degrees at the Universite Libre in Brussels in 1948 and in Poitiers, France in 1950. He was professor of aerodynamics and hydrodynamics at the Technical University of Delft, Netherlands, from 1918 to 1955. He has been affiliated with the following societies: American Association for the Advancement of Science, Physical Society, Institute of Aeronautical Science, American Society of Engineering Education, Wilderness Society, Royal Aeronautical Society of Great Britain, Royal Institute of Engineering, Netherlands and the Seismology Society.

The award will be granted during the annual meeting of the Society of Rheology at the Mellon Institute, October 26-28, 1964. The full program, including abstracts is given in this bulletin starting on Page 2.

SOCIETY OF RHEOLOGY WINTER MEETING 1965

Time and Place of Meeting. Thursday and Friday, January 28-29, 1965, at the Miramar Hotel-Motel on

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

Presentation. Two copies of a 100-200 word abstract are due by December 1, 1964, to Mr. Roger S. Porter, address below. No drawings are to be submitted, and symbols should be minimized and fully defined where necessary. Accepted papers will be generally scheduled for 30 minutes including discussion. Abstracts are reviewed by the Program Committee for general content, originality, relevance to Society purposes, and technical character as a basis for acceptance.

Publication. If authors desire, presented papers will be reviewed by the editor for publication in the Transactions of the Society of Rheology. Authors are urged but not required to submit manuscripts to the Transactions. The deadline is January 29 for submitting manuscripts to Professor Raymond R. Myers, Chemistry Department, Lehigh University, Bethlehem, Pennsylvania.

Accommodations and Facilities. Hotel accommodations may be pursued individually or by January 1, 1965, for the Miramar Hotel-Motel through Charles C. Surland, address below.

Speakers will be provided with a blackboard and 2-inch by 2-inch and 3½ inch by 4½ inch slide projectors. If other facilities such as movie projectors are required, the local arrangements chairman, Charles C. Surland, should be notified by January 1, 1965.

ROGER S. PORTER, General Chairman, Winter Meeting.
California Research Corporation, 576 Standard Avenue, Richmond, California 94802.

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

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

NICHOLAS W. TSCHOEGL, Stanford Research Institute, Menlo Park, California.

ROBERT F. FEDORS, Jet Propulsion Laboratory, Pasadena, California.

RHEOLOGY BULLETIN

Raymond R. Myers, Editor

Department of Chemistry

Lehigh University

Bethlehem, Pa., 18015

PROGRAM

35th ANNUAL MEETING OF THE SOCIETY OF RHEOLOGY

October 26-28, 1964

MELLON INSTITUTE,
PITTSBURGH, PENNSYLVANIA

MONDAY, OCTOBER 26

10:00 a.m.-12:15 p.m. SESSION A—

Melt Flow

Auditorium

Chairman: Mr. Robert F. Westover

"A Molecular Mechanism For Polymer Extrudate Swelling," T. W. HUSEBY and C. G. GOGOS*, Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

Various continuum theories of viscoelastic materials have predicted that extrudates issuing from a die will swell, and this phenomenon is well known experimentally. One such continuum theory has been formulated by Pao in terms of relaxation times which can be evaluated independently in other tests. Since relaxation times are qualitatively understood in terms of molecular mechanisms, the swelling of extrudates can be given a molecular interpretation. We have found that the phenomenon originates from entanglement and those molecular motions characterized by relaxation times in the terminal zone of the viscoelastic spectrum.

Extrudate swelling has been associated also with the capacity of materials to store energy. Since stored energy is also related to relaxation times, there must exist a functional relation between stored energy and swelling. For this same reason there must also exist a relation between swelling and recoverable strain. We have also presented in this paper some data concerning this latter relation.

* Princeton University, Princeton, New Jersey

"Steady State Melt Flow Behavior of Polyethylene Blends," NOBUYUKI NAKAJIMA and PATRICK S. L. WONG, W. R. Grace and Co., Clifton, N. J.

The steady state melt flow behavior covering six decades of shear rate was studied for various types of polyethylene and their blends. Two instruments were used. The Kepes cone and plate consistometer measures viscosities at low shear rate at the range from 10^{-3} to 1 sec^{-1} . High shear data were obtained from a

gas driven capillary viscometer. The shear stress at capillary wall was calculated by the method proposed by Bagley and the shear rate at the wall was obtained after Rabinowitsch. A special effort was made to observe the change in low shear flow behavior of a resin due to an addition of gels, high ends or low ends of molecular weight distribution. Addition of low ends up to 20 percent does not alter the "shape" of the viscosity shear rate flow curve appreciably. But with an addition of high ends, the "shape" of the flow curve changes considerably. With an addition of gels, the flow curve at low shear rises rapidly as shear rate decreases. An inflection was observed followed by a "tail-up" at low shear range.

"The Effect of Pressure Losses in the Barrel on Capillary Flow Measurements," A. P. METZGER and J. R. KNOX

Melt flow data obtained from capillaries having constant length-to-diameter ratios, but different diameters, do not lie on a single curve. At constant shear rate the apparent viscosity decreases with capillary diameter. This diameter effect has been interpreted by some investigators as an indication of slippage along the capillary wall. This paper presents data which demonstrate that, if corrections are made for pressure drop in the rheometer barrel, the flow curves coincide. Although it has been recognized that pressure losses in the barrel can have a significant influence on melt index values, it has usually been assumed that they are negligible in high shear measurements. However, if reliable flow curves are to be obtained, the barrel losses can not be ignored. Furthermore, the value of losses can be used to calculate the shear stress in the barrel and thus extend the range of the measurements.

"Polymer Melt Flow Behavior in the Barrel of a Capillary Rheometer," N. P. COOK, F. J. FURNO and F. R. EIRICH*, Marbon Chemical, Washington, W. Va.

A study was made of the flow patterns in a capillary rheometer barrel to determine if there were any phenomena which might affect viscosity determinations. The rheometer barrel was loaded with layers of several different colors of the same plastic. Various percentages of the initial charge were extruded through the capillary using normal techniques at various shear rates and temperatures. At the end of each test, the material remaining in the barrel was frozen and removed as a plug. The plugs were then sectioned and a flow diagram was constructed by measuring the colored layers.

Although the expected laminar flow was observed, upward flow at the wall and channeling at the center were also evident. These phenomena were noted even when only a small portion of the charge had been extruded through the capillary. The paper presents these findings in detail, picturing the flow patterns observed and illustrating the effects of temperature and shear rate.

* Brooklyn Polytechnic Institute

10:00 a.m.-12:14 p.m. SESSION B—

Thermodynamics and Constitutive Relations: I.
Conference Room

Chairman: Dr. Louis J. Zapas

"Elasticity in the Thermodynamics of Perfect Elastic Fluids," B. BERNSTEIN, E. A. KEARSLEY and L. J. ZAPAS, National Bureau of Standards, Washington, D. C.

The theory of perfect elastic fluids deals with the non-equilibrium thermodynamics of a visco-elastic material under finite deformations. A feature of the theory which expresses the fluid nature of the material is that local thermodynamic equilibrium cannot prevail when shear stresses are present. A principle of time-temperature superposition is part of the theory. Consistency with the second law of thermodynamics follows from fading memory and positive heat conductivity. Temperature increases when work is done on the material and decreases when work is done by the material adiabatically and isochorically. The theory seems to be in agreement with viscosity-temperature data and with experimental results on simple extension with different histories.

It is shown that a perfect elastic fluid behaves as an elastic material with a strain energy whose form depends on past history. At any instant one may define force-free configurations of a volume of the material. These force-free configurations are those which for given entropy make the internal energy stationary or for given temperature make the free energy stationary. In general the force-free configurations vary with time. This is consistent with the phenomenon of time-dependent recovery.

"On the Thermodynamics of Materials with Gradually Fading Memory," BERNARD D. COLEMAN, Mellon Institute, Pittsburgh, Pa.

This paper is concerned with the thermodynamics of materials for which the specific Helmholtz free energy, the stress tensor, the specific entropy, and the heat flux vector each depend on the history of the deformation gradient, the history of the temperature, and the present value of the temperature gradient. A theory starting with such general constitutive assumptions is certainly compatible with the principle of equipresence. Assuming only that the functionals in the constitutive equations have the smoothness properties required by the principle of fading memory, necessary and sufficient conditions are found for the functionals to be compatible with the second law. Among the consequences of the second law is an algorithm which enables one to calculate the stress and the entropy when the free energy functional is known. It also follows from the second law that although the heat flux can depend on the temperature gradient, the free energy, stress, and entropy cannot. This last conclusion is, however, very sensitive to the smoothness postulates behind the principle of fading memory.

"Shocks and Acceleration Waves in Materials with Memory," BERNARD D. COLEMAN, Mellon Institute, Pittsburgh, Pa. and MORTON E. GUTIN, Brown University, Providence, R. I.

We present here a one dimensional theory of wave propagation in materials obeying the general non-linear constitutive assumptions laid down in the previous paper "On the Thermodynamics of Materials with Gradually Fading Memory." Assuming that the constitutive functionals have the smoothness properties required by the principle of fading memory, and making use of the restrictions which thermodynamics places on those functionals, explicit formulae are derived for the velocity of shocks and acceleration waves. These formulae generalize the known expressions for elastic materials. We also obtain a generalization of the Hugoniot equation and show that even when there are memory effects the instantaneous jump in the entropy across a shock is third order in the shock strength. Using the fact that the Clausius-Duhem inequality requires that the jump in entropy be positive, we find convexity conditions on the stress-functional for the existence of shocks.

"Thermodynamics and the Possibility of Long Range Interaction in Elastic Materials," MORTON E. GURTIN, Brown University

In this paper we consider materials for which the stress, the internal energy, the heat flux, and the temperature at a given point depend on the present configuration of the body as well as the present entropy distribution over the entire body. We prove that constitutive equations of this type are compatible with the first two laws of thermodynamics only if they reduce to the constitutive assumption of a simple material.

1:45-5:00 p.m. SESSION C—

Dynamic Viscosity Auditorium
Chairman: Dr. T. G. Fox

"The Dynamic Melt Viscosity of Polyolefins," BRYCE MAXWELL and R. P. CHARTOFF, Princeton University, Princeton, N.J.

A method has been developed for measuring three orthogonal forces in a polymer melt subjected to shear. Data will be presented showing the relationship of these forces to shear rate for a series of polyolefins.

It has been found possible to measure the out-of-phase or viscous force while varying the shear rate in two different independent manners: (1) by varying the time scale of applying a given magnitude of shear deformation, (2) by varying the magnitude of shear deformation for a given time scale of application. Method number one results in the usual non-linear relationship between shear stress and shear rate for polymer melts. Method number two results in a linear relationship between shear stress and shear rate thus making it possible to determine a single

value of the coefficient of viscosity for any given time scale of application of shear strain. By varying the time scale of strain application, it has been found possible to measure polymer melt viscosities from essentially the zero shear rate viscosity to the disentangled viscosity.

"Polyethylene Melt Viscosity—Shear Rate-Temperature Superposition," ROBERT A. MENDELSON, Research Department, Plastics Division, Monsanto Company, Texas City, Texas

The steady-state melt viscosity of polyethylene has been studied for a series of samples of both high density and low density material over a broad range of temperature and of shear rate. In the case of low density polyethylene the samples covered a wide range of molecular weight distributions. Melt viscosity measurements were made using a capillary extrusion rheometer and a capillary with $L/D=66.7$, for which it was demonstrated that end corrections were negligible. Over a four decade shear rate range and temperature from 120°C to 300°C a shear rate-temperature superposition was applicable using arbitrary reference temperatures. A single set of shift factors for a given reference temperature was general for all low density polyethylene samples regardless of molecular weight distribution, and a second set was general for all of the high density polyethylenes. For low density polyethylene the exponent, or "activation energy", was 11.3 kcal/mole, while for high density polyethylene it was 6.3 kcal/mole.

"Yield-Stress Master Curves for Various Polymers Below Their Glass Transition Temperatures," JEROME J. LOHR, Ames Research Center, Moffett Field, California

Yield-stress master curves are presented for poly-(methyl methacrylate), polystyrene, polyvinyl chloride and mylar. Tensile yield stress measurements were carried out at strain rates varying from 0.003 to 300 min⁻¹ and temperatures varying from 15°C above T_g , the glass transition temperature, to $T_g - 125^\circ\text{C}$. The yield (or, in the brittle range, failure) stresses have been shifted to construct a yield-stress master curve in a manner similar in concept to that of the stress-relaxation master curve. These master curves cover from 12 to 18 decades of shifted strain rate. The master curve for each material has a characteristic slope which leads to a simple equation relating yield stress to strain rate and temperature and is applicable for temperatures from T_g to $T_g - 100^\circ\text{C}$. The temperature-dependent shift factors, a_T , of each material were determined for both yield stress and stress relaxation over the subject temperature range. Comparison of these results shows that in the ductile range of each material the shape of the a_T curves obtained from yield stress and stress relaxation measurements is essentially identical; however, the curves diverge in the temperature range where the material fails in a brittle manner. A tentative explanation for this phenomenon is offered.

"Viscoelastic Properties of Monodisperse Polystyrene," A. V. TOBOLSKY, J. J. AKLONIS and G. AKOVALI, Princeton University, Princeton, N.J.

The viscoelastic properties of five monodisperse polymer samples of polystyrene ranging in molecular weight between 80,000 and 270,000 were studied and accurate values of η_t , J_e , τ_m and E_m were obtained. It is shown that the dependence on molecular weight of these quantities is very different from that predicted by the Rouse-Bueche Theory or by the Ferry Landel Williams modification of this theory.

"On Liquids, Polymers, and Time-temperature Superposition," D. O. MILES, G. C. KNOLLMAN, A. S. HAMAMOTO, and G. C. NORSTROM, Lockheed Research Laboratories, Palo Alto, California

Studies on pure liquids can yield results of considerable significance to polymer physics. The simplicity of a liquid (in displaying no measurable entropy behavior, for example) and its narrower distribution of relaxation times relative to a polymer signifies that the relaxation process can be studied more conveniently in a liquid than in a polymer. The relaxation mechanism in liquids is presently regarded as an energy storage process, whereas in polymers it is partly an energy storage process and partly an entropy effect. Dynamic shear moduli data are presented for both representative liquids and polymers to illustrate the similarities in the respective relaxation processes. It is shown that insofar as relaxation behavior is concerned, the liquid state may be viewed as a special case of the polymer state. As an illustration of a contribution to polymer physics derived from studies in the liquid state, we propose a modification of the familiar time-temperature superposition routine such that dynamic data can be treated in a more realistic fashion than heretofore. The aforementioned liquid and polymer data are utilized to demonstrate the modified approach. Finally, some possibilities are discussed for obtaining additional insight regarding the relationships existing between polymer and liquid states.

"Time-Dependence of Recovery Mechanisms in Amorphous Polymers," P. S. THEOCARIS, Pennsylvania State University, State College, Pa., and CHR. HADJI-JOSEPH, Athens National Technical University, Athens, Greece

Transient recovery tests in simple tension were performed in a series of cross-linked high polymers in pure and plasticized states. These tests followed either a creep or a stress-relaxation type of loading. The mechanical and optical characteristic functions of the materials were determined. Different times of loading were applied corresponding to a state of transient compliance and relaxation modulus.

Strain and birefringence curves versus log time for various loading steps and time periods showed that

recovery from normal stresses over prolonged periods of time followed a logarithmic law independently of the previous history of loading. The linearity of variation of the relative retardation and of the strain with time was established and the influence of plasticizer was determined.

1:45-5:00 p.m. SESSION D—

General Papers

Conference Room

Chairman: Dr. I. M. Krieger

"Cold-Drawing of Glassy Polymers," S. L. COOPER¹, W. WHITNEY², N. S. SCHNEIDER¹, R. D. ANDREWS², S. J. KURTZ¹ and G. LANGFORD³, Massachusetts Institute of Technology, Cambridge, Mass.

¹Dept. of Chemical Engineering; ²Textile Division, Dept. of Mechanical Engineering; ³Dept. of Metallurgy.

Polystyrene, although normally a brittle polymer, will show necking and drawing when tensile specimens are extended at constant strain rate, provided the polymer has been pre-oriented (by stretching above the glass transition temperature, and quickly quenching to freeze in the oriented state). Pre-orientation makes cold-drawing possible for this polymer by raising the tensile strength to a value higher than the yield stress at which necking can initiate. The drawing of polystyrene has been studied at a single fixed strain rate as a function of temperature (from room temperature to 90°C) and degree of pre-orientation, using birefringence as an index of the degree of orientation. As orientation increases progressively from zero, samples show brittle fracture, ductile fracture, and finally steady-state drawing. The draw ratio, or extension produced in the drawing process, shows a marked decrease from roughly 200% to 40% as the pre-orientation increases. This behavior would be compatible with the concept of a potential degree of extensibility of the molecular chains which is partially used up by the pre-orientation. Drawing produces an increase of birefringence, and the birefringence of drawn samples is roughly constant, independent of the initial pre-orientation and draw ratio.

Poly(methyl methacrylate) will neck and draw in tensile experiments in certain ranges of temperature and strain rate. No pre-orientation is required, in contrast to polystyrene. The yield stress and steady-state drawing stress are both dependent on strain rate and temperature: the values increase with increasing strain rate, and show a linear decrease with temperature which extrapolates to zero stress at about the glass transition temperature of the polymer. This same behavior is observed for polystyrene. The effect of molecular weight on the drawing behavior has been investigated over a six-fold range (viscosity average MW = 200,000 to 1,200,000); the drawing behavior shows no dependence on molecular weight. The effect of cross-linking has also been investigated and again no effect is seen except for a slight shift vs. temperature which would correspond to an increase of a few degrees in the glass transition temperature.

The phenomenon of cold-drawing is sometimes described as a process of "solid state flow." However the lack of dependence on molecular weight or cross-linking clearly indicates that this "flow" cannot be of the type observed in the molten polymer, involving cooperative motions of molecular segments.

"Flow of Power-Law Fluids in Rectangular Ducts," STANLEY MIDDLEMAN, University of Rochester, Rochester, N.Y.

The equations governing pressure flow and drag flow of the power law fluid in channels of rectangular cross section have been solved. Application is made to the calculation of wall effects and die characteristics for screw extruders. It is shown that the Newtonian wall corrections usually used in extruder calculations can lead to considerable error for markedly non-Newtonian melts in deep flighted screws.

"The Stretching of a Viscous Tube Over a Conical Mandrel," R. A. WESSLING and T. ALFREY, JR., Plastics Department Research Laboratory, The Dow Chemical Company, Midland, Michigan

The deformation of a cylindrical viscous membrane, by stretching it over a conical mandrel, has been analyzed. The material is assumed to be an incompressible Newtonian fluid with sufficient tensile strength to support the membrane stresses. The analysis is carried out for a steady-state stretching operation in which the motion of the tube is opposed by sliding friction.

The problem is developed in terms of a material velocity field; strain rates are written as functions of the instantaneous velocity gradient. The stress relations for a Newtonian fluid combined with the equation of equilibrium lead to a non-linear differential equation for the velocity as a function of the radial coordinate. Boundary conditions are fixed by specifying the initial and final velocities.

Analytical solutions are obtained for the case of constant friction coefficient and an exponential dependence of viscosity on radial distance. The conditions for membrane stability (no buckling) and for uniform stretching are established.

The pattern of biaxial stretching calculated from this analysis is strongly dependent on the boundary conditions as well as the viscosity and friction. The results, using an equivalent set of variables and boundary conditions, are compared to the elastic solution which was given in a previous communication. (Paper presented at the Winter Meeting, Soc. of Rheology (1964).)

"Instability in the Flow of Synthetic Latex Dispersions," JOHN G. BRODNYAN and E. LLOYD KELLEY, The Rohm and Haas Research Laboratories, Spring House, Pennsylvania

In the work reported here the transition from laminar to turbulent flow was investigated as a

function of volume fraction of the dispersed phase for a number of synthetic latices. Since two instruments, a conicylindrical viscometer and a high-pressure capillary viscometer, were used and the Reynolds number depends strongly on the geometry of the instrument, a normalized Reynolds number was used to compare the data.

It was found that the use of a dispersion viscosity gives a Reynolds number which decreases with increasing volume fraction. However, if one uses the viscosity of the continuous medium, i.e., water, the Reynolds number increases by a factor of about three. This result is very similar to some results reported on the laminar-to-turbulent transition for solutions of poly(acrylic acid) in water.

"Randomly Distributed Rough Particles In Concentrated Suspensions," T. W. GILLIS, Lockheed Propulsion Company, Redlands, California

Variational methods have recently been successfully used to obtain the bounds of the apparent viscosity η^* of a suspension of solid particles in a liquid medium of viscosity η , where the particulate geometry is random.¹ Experimental confirmation of this technique is somewhat hampered however by the non-Gaussian nature of most particulate materials obtained by comminution.

A practical method of obtaining randomly distributed systems by combining skewed (non-Gaussian) distributions is demonstrated.

The apparent viscosities of concentrated suspensions of several random and skewed combinations are compared. The suspensions tested were: Ammonium perchlorate—PBAN; Aluminum—PBAN; Ammonium perchlorate—Aluminum—PBAN. (PBAN refers to polybutadiene-acrylonitrile.) Solids volume fractions ranged from 0.528 to 0.700. The particles ranged in size from 2.5μ to 325μ . Up to four modes were used. All random suspensions were found to be limited at the lower bound of performance by the Weissberg-Prager inequality:¹

The sedimentation volumes of the same combinations in heavy-grade mineral oil are compared. In all cases, the random distributions exhibited the largest sedimented volumes.

¹Weissberg, H. L., Prager, S., "Viscosity of Concentrated Suspensions of Spherical Particles," Paper presented at the 4th International Congress on Rheology, Brown University, August 1963

"Rheological Properties of 1,3,5-Tri- α -Naphthyl Benzene," D. J. PLAZEK and J. H. MAGILL, Mellon Institute, Pittsburgh, Pa.

The viscous and viscoelastic torsional creep properties of 1,3,5-tri- α -naphthyl benzene (TNB) have been studied at temperatures between 24° and 200°C. TNB is a nonpolar small molecule that can be supercooled with relative ease through the freezing point, 197.2°C, to form a glass at 70°C. This investigation extends the earlier capillary measurements of Magill and Ubbelohde. Dilatometric measurements have been

made in the region of the glass temperature, T_g , including those of isothermal volume contraction slightly below T_g . Crystallization rates, measured optically, are also reported.

7:30-9:45 p.m. SESSION E—

General Papers

Room 355

Chairman: Dr. B. Maxwell

"Dynamic Mechanical Properties of Synovial Fluid," R. R. MYERS and S. NEGAMI, Lehigh University, Bethlehem, Pa. and R. K. WHITE, M.D., Orthopedic Research Associates, Allentown, Pa.

Dynamic viscosities and elasticities of synovial fluids aspirated from human knee joints were determined by means of a torsional pendulum rheometer, and were correlated with the type of pathological condition existing in the joint. Although the fluid is essentially a liquid in all of the cases studied, configurational relaxations take place over a long enough time span to develop a resilient response to stresses encountered in the joint. Hydrocortisone injection tends to increase both viscosity and elasticity of synovial fluid in certain types of malady. The degree of complexation of hyaluronic acid, the main constituent, with protein affects the mechanical properties to a significant extent.

"An In Vitro Investigation of Ciliated Activity," C. E. MILLER, F.S.C., Manhattan College, Bronx, New York and H. GOLDFARB, Montefiore Hospital, Bronx, New York

Diseases of the respiratory tract may be related to the altered rheological properties of the respiratory tract mucus and to the altered ciliary shearing capabilities. Flow curves are presented showing that mucus has visco-elastic, thixotropic properties and has discrete yield points. Mechanical models of cilia constructed to perform oscillatory motions comparable to those in vivo are studied as shearing elements in a modification of The Hoppmann-Miller Rotational Fluid Flow Generator. A description of these modifications is presented with special attention being given to the design of special cams needed to carry out the proper oscillation of the simulated cilia. Particle path lines of flow are presented for the mechanical cilia oscillating in and out of phase. Linear velocity of small particles injected into the flow is measured as a function of the frequency of the oscillators and the viscosity of the liquid. The data of the present investigation are correlated with known flow patterns and the action of cilia in vivo.

"Theory Relating Lifetime Statistics to Molecular Processes in the Fatigue Fracture of Fibrous Polymers," DUSAN C. PREVORSEK and JOHN C. WHITWELL, Textile Research Institute and Department of Chemical Engineering, Princeton University.

The theory presented in this paper is based on two assumptions: 1) that most of the scatter of lifetimes

in a fatigue experiment is associated with the random processes leading to rupture, and 2) that the effect of stress history on fracture rate can be approximated by a time-dependent stress-concentration factor.

It is shown that the density functions for lifetimes derived from the expression for the rate of brittle fracture in oriented polymers can be applied to fatigue of fibers in cyclic longitudinal tension. The changes in predicted distributions resulting from a change in cyclic stress or frequency are in agreement with experiment. Distributions approximated through the use of an empirical time-dependence of the stress-concentration factor support the hypothesis that early failures may occur preferentially at pre-existing defects, while failure at longer times probably occurs at defects formed as a result of mechanical action.

"Energy Dissipation of a Cohesive Soil by the Fourier Transformation of Stress Relaxation Response,"
ROBERT L. KONDNER and MICHAEL M. K. HO, Technological Institute, Northwestern University, Evanston, Ill.

The energy dissipation of a cohesive soil is obtained by the Fourier transformation of stress relaxation test data. Energy dissipation is expressed in terms of the loss tangent. The soil response is non-linear. Because of the difficulty in obtaining a mathematical expression to adequately fit the relaxation data over the entire time scale of interest, an approximate method of evaluating the transform is used. The relaxation response functions are approximated by straight line segments to form a piece-wise continuous relation. By using a large number of straight line segments, the error between the actual and approximate transformation can be made negligible. The segment slopes with corresponding values of time are used in a digital computer program to evaluate the transform. The results clearly indicate a decrease of loss tangent with increased applied strain level. For constant strain level, the variation of loss tangent as a function of moisture content is not clearly defined. The loss tangent versus logarithm of time relation gives a characteristic single bell shape distribution for each strain level.

7:30-9:45 p.m. SESSION F—

Thermodynamics and Constitutive Relations. II.
Conference Room

Chairman: Dr. B. Bernstein

"A Thermodynamic Analysis of Deformable Media,"
STEPHEN W. TSAI, Philco Research Laboratories, Newport Beach, California

The nature of the mechanical constitutive equation is still the "missing link" in the formulation of continuum mechanics. Many forms of the equation have been proposed based on: a) intuitive arguments; b) plausible principles; or c) generalization of the linear

theory. Although the nature of the constitutive equation is restricted by a set of principles of mechanics, no specification of the form of the equation is made.

The present work is concerned with the derivation of the mechanical constitutive equation of deformable media from the principles of reversible and irreversible thermodynamics. The present work extends the concept on decomposition of stress and strain into the reversible and the irreversible components. From the principles of thermodynamics, the relationships between the reversible and irreversible components of both stress and strain can be established, from which a general constitutive equation can be derived. For isotropic media, the general equation is specialized in an explicit form, containing also the exact form of the higher order terms. The resulting equation provides a unified description of much of the well-known behavior of deformable media.

"A Unified Derivation of Constitutive Relations for Irrecoverable Deformation," CHARLES A. BERG, Massachusetts Institute of Technology, Cambridge, Mass.

In the following, constitutive relations are derived for isotropic materials in which local thermodynamic equilibrium obtains and for which the internal energy of each element depends only upon the volume and temperature of the element. The basis of the derivation is the principle that the material possesses a non-negative entropy production function which depends upon the rates of deformation. This principle affords a unified procedure for the derivation of constitutive relations which describe a family of types of irrecoverable deformation including non-linear viscosity, plasticity and viscoplasticity. The procedure possesses expository advantages in that mechanical and thermodynamic considerations predominate over such purely kinematic considerations as isotropy. Moreover, the procedure offers an avenue by which to obtain constitutive relations to describe material behavior more complicated than that considered here.

"Correlations of an Elastic Fluid with Experiments,"
LOUIS J. ZAPAS, National Bureau of Standards, Washington, D. C.

A special case of a simple elastic fluid is presented and compared with experimental data. With the introduction of a specific strain potential function into a recent theory of an elastic fluid, a constitutive equation has been obtained involving three material properties. The data used for comparison with theory were obtained on cross-linked and uncross-linked polymers in large uniaxial and biaxial deformations and the agreement is very encouraging.

For certain cases, e.g. solutions of polymers or melts, the behavior in simple shear can be predicted from the dynamic measurements at small deformation. The comparison with available data is very good.

"Polynomial Constitutive Equations for Viscoelastic Materials with Large Initial Deformation," K. C. VALANIS and R. A. SCHAPERY, School of Aeronautical and Engineering Sciences, Purdue University, Lafayette, Indiana

The constitutive equations of viscoelastic materials, for the special class of deformations consisting of small dynamic displacements superposed on large static deformations, are derived. The derivation is based on a "polynomial formulation" of a general constitutive equation for such materials, as opposed to previous derivations by other authors [1,2,3] which were based on functional forms of the constitutive equations.

It is found that, for this class of deformations, the polynomial and functional forms are equivalent in as far as the incremental state of stress is linearly related to the history of incremental deformation through twelve relaxation functions. These functions will, in general, depend on the initial deformation.

This formulation affords a direct comparison with the alternative formulation which makes use of thermodynamics of irreversible processes that may be regarded as small deviations from an equilibrium state [4]. This comparison results in certain restrictions on the number and character of the relaxation functions.

Polynomial constitutive equations can prove of great utility in cases of materials with a small number of relaxation times, and/or where the material behavior is of interest in a restricted time range. In this event only a small number of terms need be retained in the equation thus reducing it from an integral to a differential form which is easier to treat by standard analytical methods.

In a second part of this paper, Stress-strain-temperature equations governing the linear response of prestrained viscoelastic media to transient temperatures are developed from mathematical and thermodynamic principles.

A constitutive equation, in polynomial form, is first given for initially isotropic viscoelastic materials subjected to small time dependent temperature changes in the presence of large static deformations. A particular polynomial form in the objective time-derivatives of stress, strain and temperature is assumed which, in the isothermal case, can be made equivalent by a limiting process to the functional form of Coleman and Noll [1].

The resulting constitutive equation is such that the stress state at a point is uniquely related to the deformation and temperature through twelve "mechanical" and three "thermal" relaxation functions. Biot's [4] thermodynamic constitutive equation for isothermal behavior of materials is a particular case of the one given here.

1. B. D. Coleman and W. Noll, Reviews of Modern Physics, 33, 239-249 (1961).
2. A. C. Pipkin and R. S. Rivlin, Arch. Rat. Mech.

Anal., 8, 297-308 (1961).

3. G. Lianis, Un. of Washington, Dept. Aero. Eng., Report 63-4 (1963).
4. R. A. Schapery, Journal App. Physics, 35, 1451-1465 (1964).
5. M. A. Biot, J. Appl. Mech., 26, 393-400 (1959).

9:00 a.m.-12:15 p.m. SESSION G—

Network Polymers

Auditorium

Chairman: Dr. D. J. Plazek

"Mechanical Losses and Network Structure in Cross-Linked Rubbers," JOHN D. FERRY, RAY A. DICKIE, RALPH G. MANCKE, and ETSUJI MAEKAWA, Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Viscoelastic properties of cross-linked rubbers reveal slow relaxation mechanisms with relaxation times much too long to attribute to configurational rearrangements within individual network strands on the basis of present molecular theories; the source of these mechanisms is currently being sought in several laboratories. We have measured dynamic properties of natural rubbers and polybutadienes cross-linked with sulfur and dicumyl peroxide. The loss modulus, loss compliance, and loss tangent are higher at low frequencies than would be predicted from the Bueche or Rouse-Mooney theories, reflecting some very slow relaxation processes. The magnitude of the loss tangent increases with decreasing density of cross-linking; increases with increasing proportion of loose strand ends (i.e., decreasing initial molecular weight prior to vulcanization); and is higher for sulfur than for dicumyl peroxide vulcanizates under comparable conditions. The possible roles of free-end strands and strand entanglements in this behavior are discussed.

"Dilatometry of Cured Gum Elastomers," W. E. WOLSTENHOLME, U. S. Rubber Company, Wayne, New Jersey

The volume changes that occur during unidirectional stretching of vulcanized gum elastomers were measured with a water-filled stretching dilatometer capable of measuring volume changes of 10^{-5} cc in a thermostatted water bath maintained at 35° or 0°C to $\pm .015^{\circ}\text{C}$. Measurements were made on five gum stocks with elastomers of natural rubber, chloroprene, polyisobutylene, and two nitrile-butadiene polymers.

"Mechanical Behavior of Polymers and Adhesive Joint Strengths. I. Amine-Cured Epoxy Resin," ARMAND F. LEWIS and WALLACE B. RAMSEY, Plastics and Resins Division and Central Research Division, American Cyanamid Company, Stamford, Connecticut

The bulk mechanical properties of a typical thermosetting adhesive resin are examined in view of measured adhesive joint strengths. State of cure and temperature are used to vary the rheological state of

the resin while the changes in state are observed by measuring dynamic mechanical properties, tensile stress-strain behavior of bulk specimens as well as shear and flexural strengths. In an initial analysis no direct correlation between bulk mechanical properties and adhesive joint strengths is observed. However, if the initial portion of the tensile stress-strain curve for the bulk resin in the glassy state is regarded as being identical to the stress-strain behavior which the resin undergoes in an adhesive tensile joint during fracture, the data show that the area under the stress-strain curve between stress equal to zero and stress equal to the adhesion tensile strength (ATS) may be interpreted as the adhesive joint fracture energy, U_a . Illustrating this, a plot of ATS vs. $(EU_a)^{1/2}$, where E is the elastic modulus (slope of stress-strain curve at 0% elongation), yields a straight line as predicted by the Griffith fracture theory. The nature of fracture in the transition zone and rubbery region of the polymer is discussed in view of this result.

"The Relation of the Small-Strain Loss Compliance to the Ultimate Elongation Capability of an Amorphous Elastomer," ROBERT F. LANDEL, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

It will be shown that the ultimate tensile elongation ϵ_b of an amorphous gum elastomer can be related to the energy dissipated, ϵ_d , under small strain dynamic conditions. For a linearly viscoelastic material, $\epsilon_b = \sqrt{\epsilon_d/3} \sqrt{J''}$ where J'' is the shear loss compliance. If ϵ_d is sensibly constant, the time dependence of ϵ_b should be the same as that of J'' . For a real, non-linear material, however, the time dependence of these two quantities will not be identical, but nevertheless they should both maximize at the same time value. This is confirmed by studies on three SBR elastomers and by literature data on carboxy-terminated butadiene and butyl elastomers and an epoxy resin. The dependence of this maximum value of ϵ_b on crosslink density is interpreted with the aid of the theories of Marvin and Bueche for the viscoelastic behavior of crosslinked systems.

"The Statistical Distribution of Ultimate Properties of an SBR Elastomer as a Function of Cross-Link Density," ROBERT F. FEDORS and ROBERT F. LANDEL, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

Five samples of sulfur-cured SBR were prepared with cross-link densities which varied by a factor of 20. Fifty specimens of each sample were tested at 5"/min. at 23°C, and the statistical distributions of the breaking strength and breaking strain were determined as a function of the cross-link density. The distributions were adequately described by extreme value statistics though the number of specimens was too small to provide a clear-cut choice between a Weibull and double exponential distribution. The double exponential form was employed, so that the

cumulative distribution function Φ is given as

$$\Phi(x) = 1 - \exp\left[-\exp\left\{\left(\frac{\delta}{\gamma x_0}\right)(x - x^*)\right\}\right]$$

where x represents either σ or ϵ ; x_0 indicates the maximum value of the distribution and x^* the most probable value; γ and δ are parameters of the distribution of flaws. The value of σ^* passes through a maximum and ϵ^* decreases monotonically with increasing γe , as normally observed when only single specimens of a population are broken. The quantity $\delta\gamma e_0$ also decreases with increasing γe , though less rapidly than ϵ^* , while $\delta/\gamma\sigma_0$ increases monotonically and apparently does not pass through a maximum. These dependencies are discussed in terms of various theories of ultimate properties.

"Some Experimental Observations On The Stored Energy Function For Small Values of Strain Invariants," ANTHONY SAN MIGUEL, JOIE PIERCE JONES, ROBERT F. LANDEL, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

In order to evaluate the stored energy function, W, for elastomeric materials, biaxial experiments must be made. Previous biaxial testers developed at this Laboratory have consisted of an inflated cylinder device (Ref. 1) and a biaxial sheet tester (Ref. 2). A second sheet tester has now been developed which applies unequal, independent loadings to the two principal axes of the sheet.

The maximum strain capability of the tester is 50% for a 6" by 6" by 0.1" sheet. The specimen is gripped by small pins passing through reinforced holes. A self-compensating cross-stretching mechanism aligns the grips in order to maintain a reasonably homogeneous strain field.

Some preliminary results 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 multi-axial or large strain behavior. In particular, these results show that the term $\delta W/\delta I_3$, where I_3 is the third strain invariant, has a significant value in the realm of small strain invariants.

The results from the biaxial sheet tester are also shown to be consistent with those obtained from an inflated cylinder of the same material. Finally, the variation of the partial derivatives of the stored energy, W, with respect to the three strain invariants is discussed.

1. SAN MIGUEL, A. and R. H. SILVER, "A Normal-Incidence Reflective Polaroscope for Viscoelastic Measurements," presented to the Society for Experimental Stress Analysis, Salt Lake City, Utah, May 1964.

2. BECKER, G. W. and R. F. LANDEL, "An Apparatus for Biaxial Stress Relaxation Measurements of Rubber-Like Materials Under Large Deformations," presented to the Division of High Polymer Physics, Philadelphia, Pennsylvania, March 1964.

"The Time-Dependent Visible Dichroism of Dyed Polymer Films," R. YAMADA, Y. SHINDO, K. KAWAI and R. S. STEIN, Polymer Research Institute, University of Massachusetts, Amherst, Mass.

The changes in visible dichroism, birefringence, and modulus are simultaneously observed for dyed polymer films such as polyvinyl alcohol and nylon-6, during relaxation at constant length and during vibrational strain. Results are interpreted according to the method of Chappel in which the dichroism ratio $[(D-1)/(D+2)]$ is assumed proportional to the orientation function of the amorphous regions while the birefringence is proportional to the total orientation of both crystalline and amorphous regions. Measurements on congo-red dyed nylon-6 indicate that the crystalline orientation decreases with time and increases with frequency, whereas the amorphous orientation increases with time and decreases with frequency at short times. The data are best interpreted in terms of a distributed crystal defect model where the initial strain is transmitted through a continuous crystalline matrix and subsequent relaxation results in a relaxation of this crystalline orientation with a redistribution of strain resulting in increased amorphous orientation.

"Rheo-Optical Studies of Polymers," W. R. HAAF and D. G. LEGRAND, General Electric Research Laboratory, Schenectady, New York

Most studies and theories of the mechanisms of stress relaxation in polymers above their glass transition suggest configurational changes of polymer molecules as the primary cause. In recent rheo-optical studies of polyethylene, we observed that density fluctuation changes occur, which appeared to be directly related to the relaxation of stress.¹ We have found from relaxation studies of light scattering and birefringence that similar phenomena occur in polyvinyl chloride and polystyrene. These studies suggest that not only configurational but density changes which occur during relaxation must be explained in any theory for relaxation of deformed polymers.

We will present results of our studies on polyethylene, polyvinyl chloride and polystyrene.

¹LeGrand, D. G. and Haaf, W. R., J. Poly. Sci. C, 5, 153-161 (1964).

"Experimental Study of the Flow of Two-Phase Systems At High Temperature," D. R. AXELRAD, McGill University, Montreal, Quebec.

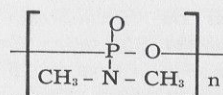
Two-phase systems consisting of a hard particle phase which is dispersed in a soft metal binder have been investigated by the author both analytically and experimentally. Previous publications were concerned with the formulation of the stress-deformation relation of such materials when subjected to constant loads in an isothermal temperature field; this paper deals

with the description of the apparatus employed for the performance of mechanical tests (uni-axial) on specimens of these materials. In particular, a new photoelectric-optical method is described in some detail, which has been used for the direct measurement of deformations in the high temperature field (up to 2000°C).

The strain-time graphs obtained from short-time creep tests of some of these materials are given and future developments to obtain more experimental data on the micro-mechanics involved are indicated. Such data will be required for a more precise formulation of the thermo-rheological behavior of such materials.

"Viscoelastic Relaxation Mechanism of the Polyphosphorylamides," A. EISENBERG and L. TETER, Department of Chemistry, University of California, Los Angeles

The polyphosphorylamides, the repeat unit of which is



are subject to random reorganization and bond interchange at elevated temperatures, but in solution at low temperatures they behave like perfectly normal organic polymers. Thus, in the glass transition region, the flow or relaxation mechanism may be either bond interchange or molecular slippage. As a result of an investigation of the viscoelastic properties of this material of different P:N ratios (therefore of differing chain lengths) by the technique of stress relaxation it is concluded that the relaxation mechanism is molecular slippage.

"Stress Dependence of Poisson's Ratio and of the Softening Temperature of Plastics," LAWRENCE E. NIELSEN, Monsanto Company, St. Louis, Missouri

Poisson's ratio was measured on a variety of plastics as a function of load up to 4000 psi. Poisson's ratio generally remained constant or decreased slightly with load. However, with crazed polyblends, the ratio drastically decreased with both load and time; the value decreased from 0.35 to 0.15 in some cases. The low value can be explained by the formation of cracks perpendicular to the direction of the applied tensile stress.

It has been shown that the lowering of the heat distortion or softening temperature with stress of most plastics can not be explained by the lowering of the glass transition temperature due to an increased volume because Poisson's ratio is less than 0.5. Instead, the lowering of the softening temperature can be explained in terms of the shape of the modulus versus temperature curve. The new theory agrees quite well with the experimental values. Materials with low moduli and a broad softening range have a heat distortion temperature which is strongly dependent upon the load.

"Kinetic Interpretation of Non-Newtonian Flow,"
R. S. BRODKEY, DALE A. DENNY, and H. T. KIM,
Department of Chemical Engineering, Ohio State
University, Columbus, Ohio

A general theoretical approach to the rationalization of Ostwald-type flow behavior has been developed. It is based on the assumption that a reversible chemical or physical change is taking place, the extent of which is indicated by a change in the viscosity. The methods of chemical kinetics are used to render the theory quantitative. The theory is directly applicable to pure materials, e.g. polymer melts, which exhibit Ostwald behavior with or without thixotropic effects. It has been modified for use with two-component systems, e.g. water solutions of polymers. While a satisfactory correlation of data has been obtained for the two component studies, the results for pure materials, though encouraging, must remain tentative until reliable time-dependent data can be obtained.

1:45-4:00 p.m. SESSION I—

Viscosity-Structure Relations Auditorium
Chairman: Dr. E. A. Collins

"The Dependence of the Zero Shear Melt Viscosity and the Related Friction Coefficient and Critical Chain Length On Measurable Characteristics of Chain Polymers," T. G. FOX, Mellon Institute, Pittsburgh, Pa.

Empirical relationships which appear to apply generally relating the Newtonian viscosity coefficient of concentrated amorphous polymer systems to the average dimensions of the polymer coil and to the volume available to the chains are indicated by systematic studies on well characterized flexible chain polymers. Available π -Z-T data for a wide variety of well defined linear and branched polymers and polymer-diluent mixtures are well represented by the single equation

$$\eta = 4.8 \times 10^8 \left(\frac{X}{4.7 \cdot 10^{-15}} \right)^\alpha \cdot \zeta$$

$$\alpha = 3.4 \text{ for } X \geq 4.7 \times 10^{-15}$$

$$\alpha = 1.0 \text{ for } X \leq 4.7 \times 10^{-15}$$

Here $X = \left(\frac{\bar{s}_0^2}{v_a} \right) \Phi_1$, where $\frac{\bar{s}_0^2}{v_a}$ is the unper-

turbed mean-square radius of gyration of the macromolecules, v_a the volume per chain atom, and Φ_1 the volume fraction of polymer; values of the friction factor per chain atom, ζ , computed from viscosity data by this equation agree with independently determined values in the literature. This result confirms Bueche's theory for the viscosity of short chains and supports his theory for the viscosity of long chain macromolecules. Attempts to provide a single general relationship to express ζ -T data for different systems, over wide ranges of temperature and structure, including the type and concentration of diluent present, have not been successful.

"A Comparison of Some Flow Properties of Linear and Tetrachain Branched 'Monodisperse' Polystyrene,"
D. P. WYMAN and W. J. FRAZER, Marbon Chemical Division, Borg-Warner Corporation, Washington, West Virginia and L. J. ELYASH, Mellon Institute, Pittsburgh 13, Pa.

A series of linear and tetrachain branched star-type polystyrenes with narrow chain length distributions and molecular weights ranging between $1-5 \times 10^5$ were prepared by anionic polymerization techniques. Melt viscosities of these polymers were measured at varying shear rates in a capillary rheometer. At comparatively low shear rates ($0-50 \text{ sec}^{-1}$) a tetrachain star-type polymer exhibited a significantly lower viscosity than a linear polymer of the same total molecular weight. As the rate of shear was increased, however, the linear and branched polymers of the total molecular weight showed very nearly the same melt viscosities. Not only did viscosity appear to be independent of branching at high shear rates, but it also tended to become independent of molecular weight in the range $1-5 \times 10^5$. Melt viscosity data for both the linear and branched narrow distribution polymers when plotted in the form of reduced viscosities vs a function of shear rate (as suggested by Bueche) fell upon one "master curve".

"Solution and Bulk Properties of Branched Polymers,"
G. C. BERRY.

Some experimental and theoretical studies on the solution and bulk properties of model branched polymers will be reviewed. In particular, the solution and bulk viscosities of comb-shaped polyvinyl acetates and of star-shaped polystyrenes of known structures will be discussed. Other solution properties will also be considered briefly. Theoretical calculations pertinent to the understanding of these properties will be alluded to as required.

Bueche's calculation for the melt viscosity η of branched chains with interchain entanglement yields the result $\eta_{br}/\eta_l = g^{3.5}$, where $g < 1$ is the ratio of the radii of branched and linear chains. Experiments on model star-shaped branched polystyrene confirm this result whereas studies on model comb-shaped and randomly branched polymers do not. The latter, in fact, yield $\eta_{br}/\eta_l > 1$ for some structures. Possible reasons for this difference will be considered.

Certain calculations predict that the ratio $f_\theta(g) = ([\eta]_{br}/[\eta]_l)_\theta$ is approximately $g^{1/2}$ for some star-shaped structures, in approximate agreement with experiment. Results on certain model comb-shaped polymers, however, do not agree with this result. In particular, for these structures $f(g) = [\eta]_{br}/[\eta]_l$ in good solvents is approximately $g^{1/2}$, but $f_\theta(g)$ is nearly $g^{3.2}$. Possible reasons for the difference between $f_\theta(g)$ for star and comb-shaped polymers will be discussed in terms of the differences in the segment density distribution for these structures.

"The Effect of Branching on the Melt Rheology of Polyethylene," L. BOGHETICH and R. F. KRATZ, Research Department, Koppers Co., Inc., Monroeville, Pennsylvania

Linear and branched ethylene polymers were examined in a capillary rheometer with capillaries of L/D ratios in excess of 60 and at temperatures of 175° to 250°C. The polymers selected have the following characteristics: identical number-average molecular weights; weight-average molecular weights of 120,000 to greater than 1,000,000; and branching of nil to twenty branches per molecule. The usual corrections for shear stress and shear rate are considered for their significance and effect on the calculated viscosities. The corrected viscosities are expressed as functions of temperature and shear stress. The empirical correlations of molecular weight, branch size, and branch frequency (or inter-branch chain length) with the parameters of the viscosity functions are discussed in the light of entanglement theory and relaxation phenomena. It is concluded that the effects of long- and short-chain branches on melt flow are observably different and distinguishable.

1:45-4:00 p.m. SESSION J—

Hydrodynamics of Viscoelastic Flow

Conference Room

Chairman: Dr. J. L. White

"Approximate Constitutive Equations for Viscoelastic Flows," A. C. PIPKIN, Brown University

Constitutive equations for various types of viscoelastic flow are discussed. The approximate character of these equations is emphasized. It is pointed out that the choice of the constitutive equation to be used in a given flow problem depends strongly on the type of problem considered, and not merely on the physical properties of the fluid. It is shown that the instability paradox found by Coleman, Duffin, and Mizel can be interpreted as an error of approximation.

"Effect of Dilute Polymer Solute on the Boundary Layer," F. W. BOGGS

The reduction of fluid resistance in pipes through the use of polymeric additives has been known for some time, and has been the subject of numerous studies.^{1,2} Recently, interest has grown in the possible use of this effect to reduce fluid drag. This paper aims to explain some of these effects.

It is shown that the second order fluid leads to an equivalent of the Orr-Sommerfeld equation which differs predominantly in the viscid solution. This modified viscid solution leads to different conditions of stability for the boundary layer.

It is also shown that the turbulent field is modified. In particular, in the equation of energy transfer between wave number, terms are present in the second

derivatives of the Reynolds stress. This leads to important differences in the ultimate distribution of energy between wave numbers in the turbulent field.

Both of these effects would lead one to expect important differences in the structure of the boundary layer of dilute polymer solutions, particularly where the velocity gradients are large.

1. Dodge, D. W. and Metzner, A. B., *Am. Inst. Chem. Eng.*, 5, No. 2, p. 189

2. Fabula, A. G., Presented at the Fourth International Congress on Rheology, Brown University 1963.

"Unsteady Flow Of An Oldroyd Fluid In A Circular Tube," IRWIN ETTER and W. R. SCHOWALTER, Department of Chemical Engineering, Princeton University, Princeton, New Jersey

Solutions to the equation of motion have been obtained for a viscoelastic fluid which obeys the Oldroyd "three-constant" constitutive equation

$$\tau_{ij} + \lambda_1 \frac{\delta \tau_{ij}}{\delta t} = 2\eta_0 \left[\dot{\epsilon}_{ij} + \lambda_2 \frac{\delta \dot{\epsilon}_{ij}}{\delta t} \right]$$

where τ_{ij} = ij-component of the stress tensor

$\dot{\epsilon}_{ij}$ = $\frac{1}{2}(v_{i,j} + v_{j,i})$ = the ij-component of the rate of deformation tensor

$\frac{\delta}{\delta t}$ = the convected time derivative

$\eta_0, \lambda_1, \lambda_2$ = constants

The solutions apply to a fluid at rest which at zero time is subjected to

- (i) a step change in pressure gradient
- or (ii) a sinusoidally varying pressure gradient.

From these results one can predict the response of the fluid to an arbitrary time-dependent pressure gradient. Curves are presented which show how the flow of a viscoelastic fluid, when subjected to a step change in pressure, can overshoot the final steady-state flow. Amplitude and phase relationships between different variables are presented for a sinusoidally varying pressure gradient.

Comparisons are made with available experimental data.

"Finite Deformations Under Pressurization In An Infinitely-Long, Thick-Walled, Elastic Cylinder Ideally Bonded To A Thin Elastic Case," J. H. BALTRUKONIS and R. N. VAISHNAV, The Catholic University of America,, Washington, D. C.

Using the tensor-analytic approach of Green and Zerna, an expression relating the internal pressure in an infinitely-long, hollow, elastic cylinder with a thin elastic casing to the geometry of the cylinder in the strained and unstrained states has been derived. Assumption of incompressibility is made. The strains in the elastic case are assumed to be infinitesimal, whereas, as long as they are consistent with the above requirement, no restriction is placed on the magnitude

of the strains in the cylinder. The result is specialized for the case of a Mooney material for which expressions of stresses and strains in the cylinder are also presented. In the latter case, an additional restriction is placed on the magnitude of the strains in the cylinder; namely, that of being within the limits of validity of the Mooney expression for the strain energy function. The results of the analysis are applied in the solution of a practical problem and, in this case, the discrepancies between finite and infinitesimal strain theories are discussed.

WEDNESDAY, OCTOBER 28

9:00 a.m.-12:15 p.m. SESSION K—

Physics and Mechanics of Random Media. I.

Auditorium

Chairman: Dr. Z. Hashin

"Statistics of Random Media," H. L. FRISCH, Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

We briefly sketch the relation between random media and certain stochastic processes. In particular, we develop the fundamental identities satisfied by "two-phase" random media correlation and probability density functions and give applications of their use in physics. We then consider the question of whether a given consistent sub-family of probability densities may be extended to obtain a stochastic process characterizing the random medium. In this connection we define and discuss "symmetric" random media. Finally, we review certain aspects of the "statistical geometry" of random subdivisions of space into crystals, random packings of spheres, percolation processes in random crystals and random plane networks.

"Statistical Theory of Flow Through Porous Media," ADRIAN E. SCHEIDEGGER, University of Illinois, Urbana, Ill.

This paper discusses the various attempts along the lines of statistical mechanics that have been made to explain certain phenomena occurring in flow of fluids through porous media. The latter concern particularly processes of mixing of miscible phases during their passage through a porous medium.

The statistical theories that can be proposed are based on the following theoretical models: Random walk of individual fluid particles, quasi-turbulent flow analogy, analogy with thermodynamics, and, finally, general statistical mechanics. In all cases, one ends up with equations that are very similar to a diffusivity or a Buckley-Leverett equation.

"The Viscosity of Suspensions," STEPHEN PRAGER, University of Minnesota, Minneapolis, Minnesota, H. L. WEISSBERG, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee

If Brownian motion of the suspended particles is ignored, the behavior of a suspension can be approached, at least for low rates of shear, from the standpoint of the creeping flow Navier-Stokes equation. Here the principle of minimum energy dissipation may be applied to furnish lower bounds on the viscosity bounds which remain valid even at higher concentrations.

To take Brownian motion into account, some simplification must be made elsewhere, if the problem is to remain tractable. For example, one may treat the suspended particles as points which interact with one another through central forces. The Navier-Stokes equation must then be replaced by a many-particle diffusion equation, and the mathematical form of the problem changes completely. Nevertheless, variational methods once more turn out to be useful, and one can obtain upper and, in certain cases, also lower bounds on the viscosity.

1:45-5:00 p.m. SESSION L—

Physics and Mechanics of Random Media. II.

Auditorium

Chairman: Dr. S. Prager

"Statistical Continuum Theories," by MARK BERAN, Towne School, University of Pennsylvania

There are presently a large number of problems in continuum physics that may be treated from a statistical point of view. In this paper we shall discuss what is meant by the statistical solution to a continuum problem. We shall initially use the nature of the stress and strain fields in a heterogeneous material as an example. We shall then emphasize the essential similarity of all statistical continuum theories. The more developed statistical continuum theories like the statistical theory of turbulence and the theory of partial coherence will be compared to the statistical theory of heterogeneous materials. For the heterogeneous material problem we shall derive the hierarchy of statistical moment equations from the equations of elasticity for medium with variable elastic properties. We conclude with a discussion of iteration procedures used in solving the statistical moment equations.

"Dielectric Constants, Permeabilities, and Conductivities of Random Media," WILLIAM FULLER BROWN, JR., University of Minnesota

A material property is often described by a proportionality factor between a solenoidal vector (electric or magnetic induction, electric current density) and an irrotational vector (field intensity); in an isotropic dielectric, for example, $D = \epsilon E$. Often one wishes to calculate the effective ϵ for a random mixture of two homogeneous materials, with constants ϵ_1 and ϵ_2 , filling volume fractions p_1 and p_2 . There are exact formulas for the cases of boundaries all parallel or

all perpendicular to the field, and an approximate formula for spheres 1 in a matrix 2 with $p_1 \ll 1$. For a statistically isotropic random mixture with arbitrary p_1 , many approximations of unknown reliability have been proposed. Recently two rigorous results have been derived. (1) A series expansion in $\epsilon_1 - \epsilon_2$ requires, besides p_1 , additional statistical information, dependent on the probabilities $p^{(n)}$ of finding n points r_1, r_2, \dots, r_n all simultaneously in material 1. (2) Given only ϵ_1, ϵ_2 , and $p^{(1)}$ ($=p_1 = 1 - p_2$), We can state that $\epsilon' < \epsilon \leq \epsilon''$, where ϵ' and ϵ'' are calculable and attainable. The present paper reviews these rigorous theories and presents closer bounds, based on additional information dependent on $p^{(2)}$ and $p^{(3)}$.

"Elasticity of Random Media," ZVI HASHIN, Towne School, University of Pennsylvania

Random elastic media are defined as materials in which the stress-strain law at any point is given by the Hooke's law of classical linear elasticity while the elastic moduli of the body are random space functions. Attention is restricted to the case where the elastic moduli are statistically homogeneous functions. In the most important case of a mixture of several discrete uniform phases these functions are piecewise constant. The present work is primarily concerned with the prediction of the macroscopic elastic properties of such media on the basis of phase geometry and phase elastic moduli. The purpose here is to review existing work and also to discuss new results which are as yet unpublished. A general discussion of the definition of effective elastic moduli is given. Attention is also given to the meaning of a macroscopic theory of elasticity of random media and the presence of couple stress effects is pointed out. Several classes of random media are defined on the basis of phase geometry, the most important being suspensions, multiphase materials and polycrystals. The concept of statistical isotropy or other statistical symmetry is defined. The theory of prediction of effective elastic moduli of dilute spherical particle suspensions is discussed, including a new result for couple stress constants. Principles of variational bounding methods are outlined since these have proved to be powerful tools in the theory of effective elastic behavior. Application and results are discussed for finite statistically isotropic spherical particle suspensions and transversely isotropic fiber reinforced materials. Results of bounding methods for multiphase materials of arbitrary phase geometry are discussed and compared with experimental results. Attention is then directed to the theory of prediction of effective elastic moduli of polycrystalline aggregates in terms of single crystal moduli. Known results for cubic constituting crystals are discussed and compared with experiment. New results for polycrystalline mixtures are given.

1:45-5:00 p.m. SESSION M—

Experimental Nonlinear Viscoelastic Flow
Conference Room

Chairman: Dr. M. H. Birnboim

"Recoil of Viscoelastic Fluids," N. N. KAPOOR, E. A. BRUMM, J. W. KALB, and A. G. FREDRICKSON, University of Minnesota, Minneapolis, Minnesota

Recoil of a number of viscoelastic fluids in a pipe has been studied. Flow was initiated by application of a pressure difference across the pipe; when flow was fully developed, the pressure difference was removed. Both flow and recoil were recorded on movies by using a simple tracer technique. Oscillatory recoil was found in a solution of aluminum dilaurate in toluene; this is in qualitative agreement with theory. However, the theory needs to be revised with more realistic boundary and initial conditions.

"Rheological Analysis of Elastomers with the Mooney Shearing Disk Viscometer," JAMES L. WHITE, NOBORU TOKITA.

Mooney's shearing disk viscometer [Ind. Eng. Chem., Anal. Ed., 6, 147 (1934), Rubber Age, 61, 567 (1947), Proc. Int. Rubber Conf., pg. 368, Washington (1959)] is one of the most important analytical research and process control instruments for elastomers. In this paper a new method is developed for computing the shear stress and shear rate of materials from data obtained on this instrument. In addition, the non-linear viscoelastic behavior of elastomers in the viscometer is analyzed with special emphasis upon normal stress effects. Experimental data for natural rubber, SBR and polyisobutylene are discussed.

"Evaluation of Constitutive Equations: Results Obtained at High Deformation Rates," A. E. UEHLER and A. B. METZNER, University of Delaware, Newark, Delaware

This paper reports data obtained on solutions of polyisobutylene in decalin at shear rates between about 10^4 and 1.3×10^6 sec.⁻¹, approximately a decade higher in shear rate than previously reported. Under these conditions the stress difference ($P_{11} - P_{22}$) was found to be nearly a linear function of shear rate $\dot{\Gamma}$ and was approximately fifteen times greater in magnitude than the shear stress for a 1% solution.

Combining the present experimental results with other data previously available at high shear rates, the equation:

$$P_{11} - P_{22} = K_0 \dot{\Gamma} C^{1.25}$$

was found to describe the normal stresses for polymer concentrations C between 1.0 and 5.0% and shear rates between 10^4 and 10^6 sec.⁻¹, where k_0 is a proportionality constant. Confidence intervals are given.

The above results were compared with the trends predicted by four constitutive equations. The equations of Coleman and Noll and of Ericksen were

found to be consistent with the present results; those of Oldroyd and of White and Metzner were not unless the specific parameters appearing in these latter equations are permitted to vary with deformation rate.

"The Rotating-Sphere Elastoviscometer," K. WALTERS, Socony-Mobil Oil Co., Dallas, Texas

Consideration is given to the flow of a "simple" fluid due to a sphere immersed in it rotating slowly about a vertical diameter. Expressions are obtained for the stream function (which describes the streamline projections on any plane containing the axis of rotation) and also the couple acting on the sphere. These expressions are given in terms of constants usually deduced from viscometric measurements.

"Measurement of P_{22} - P_{33} in Axial Annular Flow," C. R. SHERTZER, Department of Chemical Engineering, University of Delaware, Newark, Del.

In this development, it is shown how data on the difference in radial thrusts at the inner and outer walls of an annulus, containing a viscoelastic fluid in laminar axial flow, may be interpreted to yield the normal stress difference P_{22} - P_{33} without recourse to any assumptions. Rivlin's original suggestion (1) that such data could yield this normal stress difference was implemented by Hayes and Tanner (2), who obtained values for P_{22} - P_{33} by assuming that the quantity varied as the shear rate raised to some empirically determined power.

Here it is demonstrated that by careful application of a standard mathematical technique, the appropriate stress equation of motion may be integrated then differentiated to give a rigorous expression for P_{22} - P_{33} directly. The result requires that an iterative method be used to converge on the final (P_{22} - P_{33})-vs-shear rate correlation. The necessary annular flow parameters are obtained from the work of Frederickson and Bird (3).

(1) R. S. Rivlin, J. Rational Mech. Anal. 5, 179 (1956)

(2) J. W. Hayes and R. I. Tanner, pap. No. 53, 4th Int. Cong. Rheol.

(3) A. G. Frederickson and R. B. Bird, IEC 50, 347 (1958)

"Study of Flow Induced in Visco-Elastic Liquid by a Rotating Cone," W. H. HOPPMANN, II, and C. N. BARONET, Rensselaer Polytechnic Institute

Preliminary to a comprehensive study of the proper equations of motion of a rotating visco-elastic liquid, an extensive series of photographs of lines of flow has been obtained. The liquid studied was polyisobutylene dissolved in cetane. The flow visualization was obtained by means of a dye which was injected

into the liquid in a systematic manner. In addition to the pictures of the flow patterns, measurements of torque and thrust were made on the cone at various angular velocities. The photographic study was limited to the case of a cone of vertex angle 110°. The torque and thrust measurements were determined for cones with vertex angles of 176°, 160°, and 110°.

The speed range of the experiments was zero to one revolution per second. The concentrations of the solutions of polyisobutylene in cetane ranged from 5% to 10% by weight. The polyisobutylene was vistanex in the molecular weight range 64,000 to 81,000. All experiments were conducted in the temperature range 22°C to 27°C. The torque and thrust were measured on the rotating cone with the aid of especially designed transducers which are fully described.

Typical pictures of flow are presented along with curves showing interesting results for thrust and torque as functions of angular velocity. The higher concentrations show well defined maxima.

REGISTRATION, WINTER MEETING
MIRAMAR HOTEL-MOTEL

Santa Barbara, California

Send request before January 1, 1965, to:

Mr. Charles C. Surland
Department 4520
Aerojet General Corporation
P. O. Box 1947
Sacramento 9, California

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Affiliation

Address

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Please enclose preregistration fee only. Society of Rheology member \$3....., Nonmembers \$6....., One year introductory Society membership plus registration \$12.....

