THE BINGHAM MEDAL, 1959

The Bingham Medal of the Society of Rheology for 1959 will be awarded to Dr. Egon Orowan, George Westinghouse Professor of Mechanical Engineering in the Massachusetts Institute of Technology. The recipient was chosen by a special Bingham Award Committee, consisting of the following members: J. D. Dienes (Chairman), T. Alfrey, Jr., H. Leaderman, A. S. Nowick, and F. D. Dexter.

Dr. Orowan was born in 1902 in Budapest, Hungary, where he also attended school. He studied at the University of Vienna for two years, and then transferred to the Technical University of Berlin-Charlottenburg, where he obtained an Engineering Diploma and a Doctor's degree in Applied Physics.

He then returned to Budapest, and was for a time in charge of the Krypton Gas Works of the United Incandescent Lamp and Electric Company there.

In 1937, he went to England, and from 1937-39 held the position of Research Associate in the Physics Department of the University of Birmingham. During an eleven-year period, 1939-50, he was in charge of the Metal Physics Group and was also Reader in the Physics of Metals in the Cavendish Laboratory at Cambridge University.

In September 1950, he moved permanently to the United States to accept a Professorship at the Massachusetts Institute of Technology, following an appointment at M.I.T. in the spring of the same year as Visiting Professor. He was appointed to the George Westinghouse Professorship in 1951.

Professor Orowan's interests have been directed toward the general mechanical properties of materials, and particularly the underlying physical mechanisms of deformation and fracture phenomena. He has made important contributions to this subject from both the experimental and theoretical aspects, and one of his outstanding contributions was the introduction of the concept of dislocations in metals as a controlling factor in their yield and cleavage crack propagation behavior.

In 1946, he received the gold medal (Thomas Hawksley Award) of the Institution of Mechanical Engineers of London, for his theory of rolling of metals. He has also done important work in interpreting the phenomenon of delayed fracture ("static fatigue") in glass, and in the field of fracture and viscoelasticity of polymers.

He has taken a considerable interest in geological phenomena, as well, and has recently published a paper on the mechanism of tectonic earthquakes. In 1958, he was a Visiting Professor in the Geology Department at the California Institute of Technology.

THIRTIETH ANNIVERSARY MEETING — 1959

Plans are now being completed for the Thirtieth Anniversary Meeting of the Society, to be held at Lehigh University on Wednesday, Thursday and Friday, November 4, 5 and 6. A block of rooms has been reserved for the Society at the Hotel Bethlehem in Bethlehem, Pa., and Society members are strongly urged to make their room reservations immediately, if they have not already done so. Bus service will be available between the Hotel and the Lehigh campus.

A very full program of papers has been scheduled by the Program Committee, under the chairmanship of J. T. Bergen, as will be seen from the detailed program which follows. Two special symposia are included. We are also fortunate to have as a foreign guest Prof. Markus Reiner from Israel, one of the world's distinguished rheologists, who will give an informal talk at Wednesday's luncheon. Special talks will also be given by John D. Ferry and Melvin Mooney, on Wednesday morning and at Thursday's luncheon, respectively.

A viscometer exhibit is planned, and there will be an opportunity to visit some of the Lehigh laboratories, including the Fritz Laboratory of Civil Engineering, which contains one of the show pieces of the University —a Universal Testing Machine weighing 5 million pounds, and standing 7 stories tall.

Social activities have also not been neglected. A cocktail party and smoker have been scheduled, as well as the banquet on Thursday evening, which will feature some interesting Pennsylvania Dutch specialties on the menu. The ladies' program is given in detail below, and Prof. Raymond R. Myers of the Lehigh Chemistry Department, Chairman of the Local Arrangements Committee, would be interested to know in advance the number of ladies who will be attending. Attention is also drawn to the Lehigh-V.M.I. football game on Saturday. The Local Committee will attempt to get tickets in advance, if so requested.

Ladies' Program

Wednesday Morning, November 4
  9:00 Registration begins
11:00 Guided Bus Tour of Lehigh University
Wednesday Afternoon, November 4
12:30 Luncheon: University Center
  1:45 Get-acquainted Party: University Center
  5:30 Cocktails: Hotel Bethlehem
  7:30 Artistic Program

Thursday Morning, November 5
- 10:00 "Autumn Daze"—a holiday bazaar held in the Moravian Christian Education Building (across from Hotel Bethlehem).
- 11:30—2 P.M. Luncheon—cafeteria style (same location)

Thursday Afternoon, November 5
- 1:30—3:00 P.M. Old Moravian Area Guided Tour—A glimpse into the life, customs and architecture of early Bethlehem.
- 7:00 Dinner: Asa Packer Room, University Center

Friday Morning, November 6
- 9:30 Shopping tour in Hess's—an outstanding department store in Allentown.
- 11:00 Luncheon and fashion show in the Patio.

Friday Afternoon, November 6
- Return to Bethlehem

(Luncheons, tours and incidental expenses will be borne by the women participants.)

PROGRAM OF MEETING

All technical sessions will be held in the University Center. Time for presentation of papers: 30 min.

Wednesday Morning, November 4
- 9:00 Registration Begins: West Foyer, 3rd Floor, University Center
- 10:00 Opening Remarks: Dr. J. H. Dillon, President of the Society. Dr. H. A. Neville, Vice-President of Lehigh University
- 10:15 Technical Session (J. T. Bergen, Chairman)

Rheological Measurements on Elastomers with the Brabender Plastograph

C. C. McCabe, *Elastomer Chemicals Department, E. I. du Pont de Nemours and Company, Inc., Wilmington, Del.*

Rheological properties of elastomers are of primary importance during processing and must be maintained within certain limits for successful operation. The need for new and improved characterization tests is clearly apparent. The shear stress vs. shear rate relationship appears most effective in characterizing elastomers. Because wide variations of these parameters exist in processing equipment, it is necessary to determine this relationship over a wide range if processability is to be predicted.

The Brabender Plastograph affords a means of measuring rheological characteristics as a function of shear rate and temperature in either uncompounded or compounded stocks. Typical results for selected elastomers obtained under various operating conditions are discussed and compared to data obtained from other testing instruments and processing equipment. Inadequacy of single point characterization typical of widely used tests is emphasized. Results are interpreted with respect to molecular theories of flow for viscoelastic polymers.

The Influence of Viscometer Design on Non-Newtonian Measurements

R. McKennell, *Ferranti Ltd., Moston, Manchester 10, England.*

Uncertainty arising from viscometric data obtained from non-Newtonian fluids is minimised by observing two principal conditions: the shear rate should be uniform throughout the measured sample; and a consistent experimental procedure, including the amount and duration of shear, should be adopted. The effect of shear rate variation within the sample fluid is discussed for some viscometers in common industrial use. An outline is given of the methods available for eliminating variations in shear rate, and hence the tedium of applying corrections to flow curves for different types of non-Newtonian behaviour. A viscometer is described which combines uniform shearing conditions with a flexible automatic flow curve recorder giving a wide range of rheological test programs. The recorder enables the duration of shear to be minimised in the higher ranges so that shear-induced heating in the thin layer of fluid is greatly reduced. Comparative data are presented for several rotation viscometers to show this effect.

Flow Down an Inclined Plane

Ray D. Hoffman and Raymond R. Myers, *Lehigh University, Bethlehem, Pa.*

The flow of Newtonian and shear-thinning liquids down an inclined plane was studied with the objective of estimating the degree of non-Newtonian behavior from a simple test. An empirical relation called the flow decay curve was obtained, by means of which a wide variety of materials was characterized by the decrease in velocity of the advancing front with distance of flow. In general the decrease was an exponential function of distance, and the magnitude of the exponent provided an index of shear thinning, independent of viscosity. The flow decay curve was compatible with a theoretical equation based on hydrodynamic flow principles.

- 11:45 *"Impressions of Rheological Research in Europe"*
  J. D. Ferry, Department of Chemistry, University of Wisconsin, Madison, Wis.

Wednesday Afternoon, November 4
- 12:30 Luncheon—University Center
  Informal after-luncheon address: Prof. Markus Reiner, Israel Institute of Technology, Haifa, *"Reminiscences on the Society's First Thirty Years"*
- 1:45 Technical Session (Edward Collins, Chairman)

The Rheology of Asphalt†:
II. Flow Characteristics of Asphalt

FREDERICK H. GASKINS,* JOHN G. BRODNYAN,** WLADIMIR PHILIPPOFF,*** and EDMUND THELEN, *The Franklin Institute Laboratories for Research and Development, Philadelphia, Pa.*

The rheological behavior of ten asphalts has been investigated. The asphalts were selected by members of The National Asphalt Research Center to be representative of industrial stocks. These were investigated under conditions of steady-state shear and laminar flow. Two instruments were utilized: a coni-cylindrical (rotational) viscometer and a high-pressure capillary tube viscometer. The results of the investigation show that asphalts are visco-elastic bodies, which exhibit both Newtonian and non-Newtonian flow behavior with no evidence of yield value, structural breakdown or work-hardening. Thus asphalts, deliberately selected to represent the extremes of conditions of formation, are similar to concentrated polymer solutions and molten polymers in their response to stress. The extreme variations noted in the rheological behavior of asphalts can generally be accounted for by the parameters—time, temperature and stress.

The Rheology of Asphalt:
III. Dynamic Mechanical Properties of Asphalt

JOHN G. BRODNYAN, FREDERICK H. GASKINS, WLADIMIR PHILIPPOFF, and EDMUND THELEN, *The Franklin Institute Laboratories for Research and Development, Philadelphia, Pa.*

The dynamic mechanical properties of ten asphalts, representing three major categories, have been determined. During the investigation, four instruments were utilized: the FIL dynamic tester, a torsion crystal, a compression tester and a rebound (impact) tester. Dynamic measurements were made in shear at 10^{-6} to 10^1 cps and at 20 kc using forced sinusoidal vibrations; in addition, compression and impact tests were performed. The results show that asphalts resemble concentrated polymer solutions and molten polymers in that they are visco-elastic bodies. This established the validity of the time-temperature superposition principle by (a) demonstrating that the dynamic properties for each type of asphalt can be reduced to one of a family of three curves, and (b) making measurements at ultrasonic frequency which correlated with those obtained in the sonic range. Later results by Van der Poel further confirm these facts. Other bitumens, such as coal tar, cracked asphalt and filled asphalt, follow the same general characteristics. The frequency or time-scale and the ranges of temperature involved in the experiments are necessarily extremely wide; for example, curves representing the shear moduli of asphalts at 25°C were produced which covered twenty-five logarithmic decades or more.

Stress Optical Properties of Silicones

W. PHILIPPOFF,* *Franklin Institute, Philadelphia, Pa.*

The stress optical properties of silicone solutions have been reported in previous papers. However, the extensive description of the experiments including a check of the angle χ measured in flow birefringence and with the one determined by the Weissenberg rheogoniometer have not yet been given. This is now done. Furthermore, the stress optical properties of silicone rubber, a transparent polymer cross-linked by atomic radiation, was investigated. The stress optical coefficients C of the silicone solutions in toluene and of the cross-linked rubbers are very similar. However, there are significant departures that allow us, according to the existing theory, to calculate the segment length of the silicone rubber which amounts to about 20 units. This lies between the 2.5 units reported for Hevea rubber and 45 for polyethylene at high temperatures.

* Present address: Esso Research and Engineering Co., Linden, N. J.

Flow Properties of Lithium Stearate-Oil Dispersions

WALTER H. BAUER, DUANE O. SHUSTER, and STEPHEN E. WIBERLEY, *Walker Laboratory, Rensselaer Polytechnic Institute, Troy, N. Y.*

Lithium stearate-oil dispersions, prepared by cooling from 205°C to 25°C, showed initial critical yield stresses, initial creep under stress, and sustained flow stresses which were a function of rate of shear and time of flow at a given shear rate. Measurements in capillary viscometers and in a cone-plate viscometer showed that the flow curves based on capillary results, corrected for entrance effects, gave flow curves, shear rate versus shear stress, approximating those obtained from cone-plate results after the dispersions had been subjected to high rates of shear. Critical yield stress changes and changes in flow characteristics resulting from shear were not restored in rest during the time of the tests. Original properties were restored when dispersions were reheated to 205°C and cooled to 25°C. Residual critical yield stresses after shearing were resored rapidly. At any shear rate, d log D/d log τ was greater for the dispersions prepared by cooling without stirring than for the stirred dispersions, where D is shear rate and τ is shear stress.

Additional lithium stearate-oil dispersions were prepared with the addition of a third component. Added components were phenyl alpha naphthyl amine, 2,6 ditertiary butyl paracresol, cyclohexanol, glycerol, metacresol, diphenyl amine, 2 ethyl-hexanoic acid, and stearic acid. Principal effects of the third components were changes in the magnitudes and relative magnitudes of the initial critical yield stress and in the critical creep stress. Dispersions with glycerine exhibited a rapidly restored critical yield stress after sustained flow.

Results are discussed in relation to theories of the structure of soap-oil dispersions.

Rheology and Dental Materials

RICHARD H. ROYDHOUSE, *Northwestern University Dental School, Chicago, Ill.*

The variety of materials and techniques used by dentists and the conditions and requirements for successful use make an analysis of properties in a rheological sense seem essential. A review of dental and other literature reveals the paucity of investigations of this nature. Examples of materials and techniques are described. A general basis for the rheological description of dental materials is given in phenomenological terms and as the paper is entirely exploratory in nature, criticism and suggestions are invited.

An investigation into the rheology of impression materials (sodium-calcium alginate systems) and some mathematical derivations show the need for revision of descriptive equations such as those due to Stefan, Peek, and Scott for parallel plate plastometers. Some conclusions for dental applications can be made from the results of this investigation.

On Anomalies in the Measurement of the Complex Modulus

S. R. BODNER, *Division of Engineering, Brown University, Providence 12, R. I.*

Resonance tests on aluminum and lead specimens reveal multiple resonance peaks, i.e., resonances in addition to the usual natural frequencies of the system, when the specimens are subjected to uniform static stress or contain residual stresses. The multiple resonance peaks can be interpreted in the same manner as the resonance dispersions observed by E. R. Fitzgerald. Experiments have been carried out which show that the phenomenon is directly related to the presence of either residual or applied static stresses. Related experiments on the variation of the multiple resonance peaks during creep, and on the effect of vibrations of different frequencies on creep rates are also reported.

5:30   Cocktails—Hotel Bethlehem
7:30   Smoker—Hotel Bethlehem
Thursday Morning, November 5
9:00   Technical Session (F. H. Gaskins, Chairman)

Dynamic Compressibility of Natural Rubber-Sulfur as a Function of Pressure, Temperature, and Frequency

J. E. MCKINNEY, *National Bureau of Standards, Washington 25, D.C.*

Dynamic compressibility measurements were made on 12% vulcanized natural rubber-sulfur, varying the static pressure (0–1000 kg/cm^2), temperature (-30 to 70°C), and frequency (50–1000 cps), using a technique employing piezoelectric volume expander transducers. A structural relaxation was observed whose relaxation times varied with temperature in agreement with the WLF Equation. The glass transition measured at 1000 cycles per second (temperature at which a maximum in the loss component occurs) was found to vary linearly with pressure over the above range by .024°C/kg/cm^2. With the correct choice of shifting factors involving pressure and temperature, all of the reduced data can be plotted on a single master curve.

Concentration Dependence of the Stress Optical Coefficient in Dilute Solutions

W. PHILIPPOFF,* *Franklin Institute, Philadelphia, Pa.*

In previous papers it could be shown that the stress optical coefficient C is reasonably independent of concentration at high concentrations of polymers. However, existing data on measurements in dilute solutions of both birefringence and viscosity at the same rate of shear were not available. Measurements on a 3% solution of polyisobutylene in "white oil" have been reported. These measurements have now been extended to more dilute solutions. Since the "white oil" itself shows flow birefringence, it is therefore very suitable for investigating the superposition of the properties (viscosity and flow birefringence) of the solute polyisobutylene on the properties of the solvent. The evaluation of the results showed that below a certain stress all concentrations give a constant stress optical coefficient, as long as the χ angle does not depart too much from 45°. This is in agreement with the findings of Peterlin and Signer (P-S). However, when the angle χ assumes lower values than 45° a systematic departure from this behavior appears. Using the P-S treatment it is shown that the higher concentrations show systematic departures from a constant C. If, on the other hand, one follows Sadron's suggestion and adds tensorially the properties of the solvent and solute at constant shear stress, one obtains a constant value for C for the higher concentration and a noticeable levelling off for the lower ones.

* Present address: Esso Research and Engineering Co., Linden, N. J.

Thermodynamics of Stretching of Nylon Fibers

MALCOLM L. WILLIAMS, *Research Center, the Chemstrand Corporation, Decatur, Ala.*

The application of the thermodynamics of stretching to rubber indicated that the force of extension was related to an entropy change. According to the statistical theory of rubberlike elasticity, this entropy change was explained in terms of the configuration of a random coil, used as a model for the polymer. In order to hypothesize a satisfactory model for a semi-crystalline polymer such as nylon, it is likewise necessary to know how the force of extension is divided into energy and entropy changes. Therefore, stress-temperature data are presented for undrawn, non-spherulitic nylon 66 extended up to 50% at 160°C. That part of the extension reversible enough for the application of equilibrium thermodynamics is shown to depend primarily on an entropy change, provided corrections are applied for the effects due to dilation accompanying the extension. Nevertheless, the mechanism involved does not seem to be rubberlike, since use of a random coil model, where the crystallites are assumed to be merely cross-links, leads to a calculated molecular weight between cross-links much too low. The nature of the assumptions involved in the thermodynamic treatment will be discussed.

Rupture of Rubber

L. Mullins, *British Rubber Producers' Research Association, Welwyn Garden City, England*

The paper describes development of work started some ten years ago on the application of an energy criterion to describe the rupture of rubber. It is shown that, by the use of an energy balance theory analogous to that proposed by Griffith to explain the fracture of glass, it is possible to correlate the rupture behaviour of rubber samples of widely differing shapes and sizes. This experimental study provides a stringent test of the validity of the energy criterion for the rupture of rubber and demonstrates the basic significance of the value of the rupture energy obtained. Values of this rupture energy of the order of 10^6 ergs cm^{-2}, were obtained. This is considerably in excess of the energy required to create new surfaces and indicates that, in the rupture of rubber, the irreversible dissipation of energy in highly deformed regions around the rupture path dominate the rupture process. The important role of these dissipative forces is also demonstrated by a study of the dependence of rupture energy on rate, temperature and the nature of the rubber polymer. It is found that using Ferry's method of reduced variables, previously applied to viscous and viscoelastic properties, the rupture energy of all the rubbers examined can similarly be described in a simple unifying way by two basic curves relating its dependence on rate, and the interdependence of rate and temperature.

Dynamics of Frictional Compressible Fluids — Application to Plastico-Dynamics

C. Torre, *Research and Development Laboratory, M. W. Kellogg Co., Jersey City, N. J.*

The dynamics of frictional compressible fluids is formulated mathematically by eleven equations. There are three equations of motion of a continuum: the continuity equation, the "specifying" equation and six stress-rate of strain relations. The eleven unknowns are: six stresses, three velocities, pressure and density.

The system contains eleven quasi-linear partial differential equations. To obtain the real characteristics (hyperbolic case) which are different from zero, we have to complete Stokes' stress-rate of strain relations by stress and pressure derivatives with respect to time and space (methods of rheology).

Assuming a density which is a given scalar function of space and time or a constant density, we shall relate our system of equations to the plastico-dynamics of a solid body. The governing differential equations are of the Hamilton-Jacobi type, while the characteristic directions are expressed in Hamilton's or canonic differential equations. Results describing the motion of plastic mass have been obtained.

A Thermodynamic Approach to Rheology

Harry H. Hull, *R. R. Donnelley and Sons Co., Chicago, Ill.*

The elastic component of the work of deformation is equal to that portion of the work which has not been converted into heat. This is an available or thermodynamic free energy. Two variables control this free energy of elastic deformation—the rate of shear and the amount of deformation in shear; hence, the free energy of a substance is not defined solely by two of the three variables—pressure, temperature and volume. Two additional variables are required to define the thermodynamic state of a substance which has been deformed. This requires that the phase rule be changed to $F = C - P + 4$, and permits the development of a series of partial differential equations involving these five variables.

A perfect viscous fluid is defined as one which has no elastic component of deformation no matter what the rate of shear or amount of deformation in shear. This fluid obeys the phase rule $F = C - P + 2$ under either static or deforming conditions.

A perfect viscoelastic fluid is defined as one in which the free energy increases with the rate of shear but for which there exists a condition at each rate of shear such that the free energy does not vary with the amount of deformation in shear. The phase rule for this fluid is $F = C - P + 3$. Partial differential equations involving P, V, T and rate of shear are developed for this fluid. It is shown that the elastic component of the work of deformation must result in a Weissenberg effect. The converse is also true.

Any change in molecular orientation caused by deformation indicates a change in entropy and this implies a change in free energy and elastic deformation. These ideas are extended to other conditions of equilibrium and to a limited extent to the general case.

Thursday Afternoon, November 5

12:30	Luncheon—University Center
	Informal remarks by Dr. Melvin Mooney
1:45	Technical Session (H. Markovitz, Chairman)
	Symposium on Mechanics of Continua

Modern Theories of Materials

C. Truesdell, *University of Indiana, Bloomington, Ind.*

Theoretical work on rheological materials shows three distinct phases:

1. Early work, to 1945. Simple models, mainly one-dimensional and linear, are constructed by analogy to discrete systems. Various coefficients are named.

2. Intermediate period, 1945–1955. Ideal materials exhibiting non-linear response are defined explicitly as exact mathematical realizations of a simple idea. Their properties are studied by means of general theorems and special exact solutions.

3. Current phase, from 1955. The most general constitutive equations consistent with the observed phenomena are determined.

Work of the second and third kinds is summarized, with particular reference to the different roles of methods of invariance.

Open problems are stated.

Stress Analysis for Viscoelastic Bodies Subject to Temperature Variation

L. W. Morland and E. H. Lee, *Division of Applied Mathematics, Brown University, Providence, R. I.*

The temperature-frequency shift concept is used to formulate the stress-strain-time-temperature relation

for a linear viscoelastic body with varying temperature. This is combined with the strain compatibility relations, the equilibrium equations, and the boundary conditions to formulate the mathematical system for determining stress distributions. Use of a pseudo-time based on the temperature-time shift concept is tried in order to simplify the constitutive equations, but it leads to serious complications in the equilibrium equation and in the expressions for strain components. Examples are shown of stress analysis with a non-homogeneous temperature field, and the marked influence of the temperature variation on the stress distribution is demonstrated.

Hypo-elasticity and Elasticity

BARRY BERNSTEIN, *U.S. Naval Research Laboratory, Washington, D.C.*

The equations of hypo-elasticity are not in general sufficient to define a material. It is necessary in addition to indicate one stress-strain configuration. Conditions may be written which test whether any or all materials satisfying a given set of hypo-elastic equations are elastic in the sense of Cauchy or in the sense of Green. If the hypo-elastic material is a work hardening material, it must be elastic in the sense of Green.

Theory of Anisotropic Fluids

J. L. ERICKSEN, *Johns Hopkins University, Baltimore, Maryland*

Almost no research has been done on properly invariant theories of anisotropic fluids. Preliminary researches on anisotropic viscoinelastic fluids have suggested that simpler theories of this type are better able to describe some observations on high polymer solutions than comparably simple theories of isotropic fluids. Such theories seem not to be included as special cases of very general theories of fluids which now exist. After briefly clarifying these points, we discuss the formulation and some predictions of a rather simple theory of transversely isotropic viscoelastic fluids.

On the Concepts of Equilibrium in Continua, Part I

BERNARD D. COLEMAN, *Mellon Institute*, and WALTER NOLL, *Carnegie Institute of Technology, Pittsburgh, Pa.*

This paper deals with bodies *B* which are regarded as smooth manifolds of material points. We attempt to develop a rigorous theory of thermostatics for such bodies in arbitrary states of finite strain. The concepts of mechanical and thermal equilibrium are given precise definitions. Two physical postulates are assumed which imply restrictions on the constitutive equations of thermostatics.

On the Concepts of Equilibrium in Continua, Part II

BERNARD D. COLEMAN, *Mellon Institute*, and WALTER NOLL, *Carnegie Institute of Technology.*

The results presented in Part I are here specialized

to simple fluids and general isotropic materials to illustrate the physical significance of these results. Stability questions and the relationship of the present work to Gibb's thermostatics of fluids are also discussed.

5:00   Business Meeting
7:00   Dinner — Asa Packer Room, University Center
8:00   Presentation of Bingham Medal, by Dr. C. Richard Soderberg, former Dean of Engineering and Institute Professor, M.I.T.

     Medalist's Address, by Dr. Egon Orowan

Friday Morning, November 6
9:00   Technical Session (E. H. Lee, Chairman)

Rheological Properties of Molecules in Fibers

FRANCIS H. REE, SEIHUN CHANG, TAIKYUE REE and HENRY EYRING, *Department of Chemistry, University of Utah, Salt Lake City, Utah*

Using an extensometer, the stress-relaxation curves and the elongation-contraction curves for nylon 66, nylon 6 and dacron were obtained. We found the following experimental facts: (1) The simple Eyring-Halsey three-element model (Text. Res. J. *15*, 451 (1945)) holds only over the range of relatively small stresses and strains. (2) The elongation-contraction curves for all samples are similar in form. (3) An elongation curve has an inflection point at a definite point of stress and strain. (4) All elongation curves of a sample, which were obtained by pulling at a constant rate after letting the fiber relax for a given time, Δt, between successive elongation-contraction experiments, pass through the inflection point. Above the inflection point, the smaller the value of Δt, the steeper the slope of the elongation curve, while the reverse is true below the inflection point. (5) The inflection point is a function of the structure of the sample, the rate of elongation, and the ambient temperature.

From the above experimental facts, it is concluded that below the inflection point thixotropic breakdown of structure occurs while above the inflection point hydrogen bond formation is accompanied by the usual flow mechanism.

The relaxation curves obtained under various conditions give interesting information concerning the structure of fibers and rheological properties of high polymeric molecules. The experimental results and detailed discussion will be given in the paper.

The Significance of Rheology in the Making and Using of Paper

ALFRED H. NISSAN, H. G. HIGGINS and A. LAGANI, JR., *Dept. of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, N. Y.*

A brief review of paper making indicates that rheology is an important factor at many points. The most significant are (1) rheology of fiber suspensions; (2) rheology of wet webs of fibers with 1:4 to 1:2 solid to water ratios and (3) rheology of air-dry paper in use. The first two subjects are briefly reviewed.

Attempts at fitting mechanical models of springs and dashpots to represent paper behaviour are sum-

marised and reasons for their rejection advanced. Instead, interpretations based on molecular and thermodynamic parameters are advanced as a basis for a theory of the rheological behaviour of hydrogen-bonded solids. Predictions of the theory appear to be confirmed not only by paper but also by ice, cellulose sheets, nylon and other hydrogen-bonded materials. Attempts are made to explain by means of this theory the influences of water, chemical substitution, time and other factors on the rheological constants of paper. The essential contribution of the theory is that it relates these behaviours to an important parameter, n, the number of hydrogen-bonds per unit volume of material. Thus, changes in rheological behaviour reflect changes in n; these changes can be treated by methods of chemical kinetics.

A Re-Interpretation of the Rouse-Bueche Theory of Viscoelastic Behavior*

R. S. MARVIN, *National Bureau of Standards, Washington 25, D.C.*

The Rouse and Bueche theories of the viscoelastic response of a rubberlike polymer were derived considering the response of a single polymer molecule to force, displacement, or velocity fields resulting from macroscopic forces or deformations applied to a bulk sample. From this point of view, Ferry and Bueche have derived expressions for the response of a bulk sample containing a distribution of molecular weights, finding the equilibrium compliance proportional to $M_z M_{z+1}/M_w$.

An alternative point of view for the derivation is presented here, in which the *form* of the function can be shown to be equivalent to the empirical Voigt or Maxwell representations. From this point of view the expressions of these theories (or the equivalent model) correspond to the response of the bulk sample rather than that of a single chain.

The constants are calculated from the equilibrium kinetic theory, the resistance per unit length of the particular polymer, the critical molecular weight where the dependence of viscosity on molecular weight undergoes an abrupt change in form, and the molecular weight of the sample. They are calculated entirely from measurements of molecular weights and steady-flow viscosities, and represent very well the response over the whole time scale of interest. Also the effect of entanglements is introduced in a more direct fashion than in previous work.

Results for steady-state dynamic response are presented, and the problem of the calculation of transient response (creep and stress relaxation) discussed.

Rheology in Search of Structures, Part II

ANDRIES VOET and WM. N. WHITTEN, JR., *J. M. Huber Corporation, Borger, Texas*

An investigation was made of the structures in dispersions of carbon blacks in white mineral oil. A selection of twelve blacks was made, representative of the commercially available types.

In addition to the conventional rheological approach, measurements were made of the electrical conductivities and dielectric constants in quiescent dispersions as well as in dispersions deflocculated by shear or by chemical means.

A detailed picture of the structural involvement could be derived from conductivity data, such as the minimum in the conductivity-shear rate relation, the induction period and the rate of rebuilding of destroyed structures as well as the magnitudes of minimum and maximum conductivities. These conclusions are supported by dielectric data and can be explained from the standpoint of potential energy curves representing particle interaction.

Rheological data, however, do not allow straightforward conclusions about the structure. Yield values, derived either from a rheological diagram, obtained with the aid of a high-shear rotational viscometer, or by means of a parallel plate viscometer fail to show a correlation with actual structures. Oil adsorption data, when obtained under carefully controlled conditions, show a limited correlation with structure. A somewhat better correlation was found to exist for the specific plastic viscosity.

The Behaviour of Particles in Laminar Shear

S. G. MASON, *Physical Chemistry Division, Pulp & Paper Research Institute of Canada, Montreal and Department of Chemistry, McGill University, Montreal, Canada*

Particles suspended in a liquid subjected to a velocity gradient undergo rotational and translational movements and, when they are deformable, changes in shape. The general behaviour of solid spheres, fluid drops, rigid and flexible rods and fibres will be described with the aid of cine photomicrographs.

The relevance of these phenomena to theories of viscosity of dilute suspensions will be discussed.

Heat Transfer to Non-Newtonian Fluids Under Laminar Flow Conditions

A. B. METZNER and D. F. GLUCK*, *University of Delaware, Newark, Del.*

Rates of heat transfer to non-Newtonian fluid systems passing through smooth round tubes under laminar flow conditions have been studied both experimentally and theoretically, for the case in which viscous heat generation may be neglected. The data of three independent investigators have been correlated with an average deviation of 12%. The final equation contains the conventional Grashof number type of correction to account (empirically) for natural convection effects. It was interesting to note that up to 30% of the total heat was transferred by natural convection even in systems which were highly non-Newtonian, hence viscous, in nature.

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Mechanism of Peeling

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Taking into consideration both the pulling and bending actions of the external force, the differential equations for bending of a partly attached tape in a peeling test have been derived. The equations relating the peeling load to the adhesive force were derived under the assumption that the peeling may proceed step by step from the attached end when the adhesive force is overcome by either the tensile stress along the interface (shearing peeling) or that which is perpendicular to the interface (tensile peeling). To verify the validity of the equations obtained, the dependence of the peeling load, P, on the angle, α, between the direction of the action of the load and the adhering surface has been investigated using plasticized polymer films. Furthermore, the temperature dependence of the peeling resistance of adhesive tapes stuck onto a glass surface has been studied. In the case of a stiff adhesive having a glass transition temperature higher than room temperature, the plots of the peeling load against temperature show a curve with a maximum, notwithstanding that adhesion should decrease with temperature. On the contrary, in the case of a pressure sensitive tape, the peeling resistance lessens with temperature. From these results, the mechanism of peeling is discussed in connection with the physical and rheological properties of the adhesive tapes.

Theory and Analysis of Peel Adhesion: Bond Stresses and Distributions

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Previous theory is extended to provide expressions, general with respect to stripping angle, for the boundary stresses and bond stress distributions. The treatment is developed in terms of two stress mechanisms. Boundary cleavage involves tension-compression stress and predominates at high angles of peel. At some low range of peel angles, predicted from theory, boundary shear provides the controlling mechanism. Measurement of peel force as a function of angle of peel and rate identify the transition in failure mechanism from cleavage to boundary shear and provide comparison data for theoretical force-angle functions. The results of direct measurement of the internal cleavage stresses, by means of a new experimental device termed the "split-beam transducer", further characterize this bond failure mechanism.

Experiments on Peeling

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The force W_0 required to peel an aluminum or nickel ribbon glued to a rigid glass plate with a polyethylene or a poly(vinyl acetate) was determined and compared with the theory (partly new). The experimental force was smaller than the calculated (often in a ratio between 2 and 5), and the difference was due to two distinct stress concentrations. For highly extensible adhesives, their elongation in the pull direction was associated with Poisson's contraction in a direction normal to the pull; the stress distribution caused by this lateral contraction made W_0 a linear function of ribbon width w instead of being proportional to w. For near-Hookean adhesives of a low total elongation, W_0 was found proportional to w; the stress concentration dangerous for these materials occurred at the boundary between the adhesive and the ribbon at the sharp bend of the latter. The postulated damage to brittle adhesives caused by the ribbon deformation could be reproduced without bending, namely by stretching the ribbon beyond its yield stress.

The Peeling Force of Adhesive Joints

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During the peeling of adhesive joints the strained region is bounded by either one curve and one straight line or two curves. The latter case has been discussed in a previous paper. In the former case, applying to the bent adherend the theory of beams on elastic foundations, after modification to allow for large bending angle, it can be readily shown that the vertical displacement y of the adherend is $y = aL^2 - a^3L^4/3$, where $a = (3E_1/4Ey_0\delta 3)^{1/4}$, E_1, E, y_0 and δ being the Young's Moduli and the thicknesses of the adhesive film and the adherend, respectively, and L the length of adherend. The peeling force, generally known as adhesion strength, is numerically equal to the sum of resistance to peeling offered by individual strings, of which the maximum value allowed is limited by the adhesion between the adhesive and the adherend. When a 3-element model, consisting of an elastic spring E_1 in series with a parallel combination of a second Hookean spring E_2 and a dashpot η, is used to represent the mechanical behavior of the adhesive, the peeling force is calculated as

$$F = \frac{WaE_1}{y_0}\left[f_0L^3 + \frac{2E_1f_1}{(E_1 + E_2)b^3}\left\{1 - bL + \frac{b^2L^2}{2} - \frac{b^3L^3}{6} - \exp(-bL)\right\}\right]$$

where $b = (E_1 + E_2)/\eta v$, v being the peeling speed, W the width of the joint, and f_0 and f_1 functions of L showing the geometry of the strained region. The first term of the expression gives the peeling force at very high peeling speed where the adhesive acts like a Hookean solid. The rest of the expression is the correction terms for the peeling speed used. The application of this force equation to actual cases is discussed.

The Tensile Strength and Tacky Behavior of Polymeric Liquids

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The tensile strength of liquids appears to have considerable importance in describing tacky behavior in unfilled systems. An apparatus is described whose operation involves the rapid separation of flat plates between which the liquid is contained, the bottom plate being a block of known mass whose vertical motion is followed by a high speed motion picture camera (4000 frames per second), permitting measurement of the instantaneous forces operating across the liquid coupled with a simultaneous recording of the events occurring during the plate separation. Five high molecular weight liquids, with viscosities in the Newtonian flow range of from 60 poises to 1.2×10^6 poises, were studied. Photographic sequences showing seven different types of tacky behavior are shown; viscous and elastic deformations, cohesive and adhesive breaks, and single and multiple filament formation (the latter with cavitation) are distinguishable in the various modes of failure. Stress analyses of the several types of film failure reveal liquid tensile strengths in the range from about ten to several hundred bars.

Effect of Viscosity on the Penetration of Adhesives into Paper

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(To be read in summary by R. R. Myers)
End of Symposium

Fluid Mixing in Agitated Vessels

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Fluid motion in an agitated tank has been studied by following the motion of tracer particles, in both Newtonian and non-Newtonian fluid systems. Measured velocity distributions were differentiated to obtain local shear rates and local rates of power dissipation.

The above analysis indicated that the contents of an agitated vessel may be considered as consisting of two portions: a small region near the impeller which is nearly "perfectly-mixed", and a surrounding region in which the rates of turbulent mixing are nearly zero. The equation describing mixing rates which was based on this model has been experimentally verified in Newtonian fluids. While no experimental verification has as yet been obtained in non-Newtonian systems, the tracer-particle work indicates that in this case the model would be obeyed even more closely than in Newtonian fluids.

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