

RHEOLOGY BULLETIN

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THE BINGHAM MEDAL, 1958

The Bingham Medal of the Society of Rheology for 1958 will be awarded to Ronald S. Rivlin, Professor and Chairman of the Division of Applied Mathematics at Brown University. The award ceremonies will be held after the dinner on November 5 at the annual meeting of the Society. Professor Rivlin will be introduced by Professor E. H. Lee, the former Chairman of the Division of Applied Mathematics at Brown.

Professor Rivlin was educated at St. John's College, Cambridge, where he received a B. A. degree in 1937 in Mathematics and Physics, followed by the M. A. degree in 1939 and the D. Sc. in 1952.

From 1937 to 1942 he was a Research Physicist at the Research Laboratories of the British General Electric Co. in London. From 1942-44 he held the position of Scientific Officer in the Telecommunications Research Establishment in Malvern, England, which was part of the Ministry of Aircraft Production. During the year 1946-47 he was a Visiting Scientist at the National Bureau of Standards in Washington.

During the period 1947-52 Professor Rivlin was a Research Scientist in charge of a group at the Davy-Faraday Laboratory at the Royal Institution in London, and also acted as research supervisor at the British Rubber Producers' Research Association laboratories in Welwyn Garden City. From 1952-53 he was a full-time consultant with the Mechanics Division of the Naval Research Laboratory in Washington.

In 1953 the medalist went to Brown University; he has been a Professor of Applied Mathematics there since that time, and assumed the duties of Chairman of the Division this year. In 1953 he was elected a Fellow of the Washington Academy of Sciences, and during the current year was elected a Fellow of the AAAS.

Professor Rivlin has done work in the field of electric circuit theory, and has also made significant contributions relating to optical refraction and x-rays. But he is probably best known for his work on elasticity theory in the range of higher strains, where the usual linear elasticity laws, which describe behavior in the range of small strains, are no longer adequate. He is currently extending this work to include the phenomena of visco-elasticity in the region of higher (or finite, as contrasted to infinitesimal) strains.

RHEOLOGY ABSTRACTS

A new rheology abstract journal, "Rheology Abstracts: A Survey of World Literature", has recently begun publication. Volume 1, Number 1 was issued for May, 1958. It is being published by Pergamon Press, Ltd. for the British Society of Rheology. An attempt is being made to achieve reasonably complete coverage; a team of abstractors is covering more than 110 journals (including our own Transactions). Abstracts are grouped under seven topic headings (Theoretical; Instruments and Technique; Metals and Other Solids; Polymers, Elastomers and Viscoelastic Materials; Pastes and Suspensions; Liquids; and General), and a subject index will be published yearly. The subscription price is £2 per volume of 4 issues. The U. S. address of Pergamon Press is 122 East 55th Street, New York 22, N.Y.

THE ANNUAL FALL MEETING—1958

The 1958 Annual Meeting of the Society will be held from Wednesday, November 5, through Friday, November 7, at the Franklin Institute, 20th and Parkway, Philadelphia 3, Pennsylvania. Local arrangements are being handled by Mr. Edmund Thelen of the Franklin Institute, who is also serving as Chairman of the Publicity Committee. All technical sessions will be in the Lecture Hall of the Institute. Society members can most conveniently use the entrance on Winter Street, between 20th and 21st Streets.

The official hotel for the meeting will be the new Sheraton, at Pennsylvania Blvd. and 17th Street, which is about five blocks from the Franklin Institute. A block of rooms is reserved there for the Society, and members should write directly to the hotel for reservations, mentioning the Society of Rheology. The Robert Morris Hotel, at 17th and Arch Streets, across the street from the Sheraton, has somewhat less expensive rooms.

Return of the advance registration cards, which were sent out with an announcement of the program on October 1, will be very helpful to the organization committee, and members who have not done so are encouraged to do this as soon as possible, indicating whether or not they will be attending the Wednesday night dinner. A letter to Edmund Thelen at the Franklin Institute is suggested for cases where registration cards may have been mislaid. Registration for the

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meeting or any part of it is \$2.00 for members and \$3.00 for non-members. There is no registration charge for wives, and they are cordially invited, particularly to the social events on Wednesday evening. Charges for the banquet are \$3.50 per person. Checks for both registration and banquet should be made out to The Franklin Institute.

There have been some minor changes and adjustments in the program since the mail notice above; the program which follows in this Bulletin should therefore be taken as the definitive version.

PROGRAM FOR FALL MEETING

All sessions in Lecture Room unless otherwise indicated. Time allowed for presentation of papers: 30 min.

Wednesday Morning, Nov. 5

- 9:00 Registration begins in Planetarium Lobby of Franklin Institute.
- 10:45 Opening Remarks by Dr. J.H. Dillon, President of the Society, Lecture Hall.
- 11:00 Discussion of Third Annual Congress of Rheology held at Bad Oeynhausen, Germany, September 23-30, 1958.

Chairman: Robert S. Marvin

Wednesday Afternoon, Nov. 5

- 1:30 Rheology Standards and Principles

VISCOSITY OF N-HEXADECANE

A.B. BESTUL and R.C. HARDY, *National Bureau of Standards, Washington 25, D. C.*

Attempts to prepare high-purity n-hexadecane from commercial cetane by simple laboratory procedures were unsuccessful. Fractional distillation at reduced pressure, of material previously treated with silica gel, produced a few small fractions of about 99.5 mole per cent purity. The kinematic viscosities of the original material and of the fraction of highest purity, 99.63 mole per cent, were found to be the same, 4.4635 cs at 20°. All other fractions had lower viscosities. The viscosity of NBS standard sample of n-hexadecane, 99.94 mole percent, was found to be 4.4642 cs or 3.4540 cp at 20°C. n-hexadecane is not likely to

be suitable for use as a second calibration standard for viscometry until a simple, easily defined routine of purification is developed.

AN ANALYSIS OF AN ABSOLUTE TORSIONAL PENDULUM VISCOMETER

E. A. KEARSLEY, *National Bureau of Standards, Washington 25, D. C.*

Both the period and decrement of a hollow spherical torsional pendulum filled with fluid depend on the viscosity of the fluid, and viscosities have been measured utilizing observations of the decrement [E.N. da C. Andrade and Y.S. Chiong, *Proc. Roy. Soc.* **48**, 247 (1936)]. With the highly developed methods of measuring time intervals now available it appears that a measurement of the period might be the more precise approach. Since no end effects are encountered with a sphere it should be possible to develop an absolute measurement.

Equations for the period and decrement have been developed and coded for an IBM 704. Several curves of period and decrement as a function of viscosity have been calculated, and with them a study has been made of the potential accuracy and practicability of such an instrument.

THE THEORY OF LOCKING MATERIALS

ARIS PHILLIPS, *Department of Civil Engineering, Yale University, New Haven, Conn.*

The concept of the ideal locking material, which has been introduced by Prager, is considered for the case of materials which have two equations of state, one for the change in volume and the other for the change in shape. Possible stress-strain relations are discussed. The concepts of volumetric locking and of distortional locking are introduced, and it is shown by means of an example that there are cases in which these two modes of locking are incompatible over the same region of the body. The fundamental differences between locking materials and ideal plastic materials are pointed out. The problem of locking of a hollow sphere is discussed in detail.

SECONDARY STRESSES IN ANISOTROPIC AMORPHOUS MEDIA

CHARLES MACK, *Research Department, Imperial Oil Limited, Sarnia, Ontario*

Secondary stresses have been the subject of several investigations, since their presence was first demonstrated by Weissenberg in liquids under laminar flow. They have been associated with elasticity by some investigators, and with viscous effects by others. In these theories, secondary stresses are assumed to arise from the deformation or rate of deformation in otherwise isotropic bodies. Since most industrially important materials are not isotropic, a theory of

secondary stresses is given for anisotropic behavior in general. It is shown that non-Newtonian viscosity is the direct outcome of secondary stresses, and their importance for the rheological behavior is discussed. In relating secondary stresses with non-Hookean elasticity, it is found that this type of elasticity is also associated with time effects.

STRESS ANALYSIS FOR LINEAR VISCOELASTIC MATERIALS

E. H. LEE, J. R. M. RADOK and W. B. WOODWARD, *Brown University, Providence, R. I.*

The stress distributions in viscoelastic bodies exhibit features which are in marked contrast with the more commonly understood analysis for elastic bodies. For example, under constant surface loading, the internal distribution of stress can vary widely. Methods of determining such varying stress distributions are discussed, and illustrated through particular examples. The time variation can be dealt with in some problem types by application of the Laplace transform, but it is pointed out that other types of problems fall outside the scope of this method. The influence of the specific prescription of boundary conditions on methods of solution is discussed, and a particular example is presented for which the transform method of attack would not apply.

VISCOUS MOTION OF DISLOCATIONS IN CRYSTALS

J. J. GILMAN and W. G. JOHNSTON, *General Electric Research Laboratory, Schenectady, N.Y.*

Direct observations of dislocations in LiF crystals show that there is a quasi-viscous resistance to dislocation motion. This resistance does not involve dislocation interactions, but occurs for dislocations moving in dislocation-free regions of the crystals. The viscosity increases with impurity content, with neutron bombardment, and with decreasing temperature. Measurements have been made over a wide range of dislocation velocities extending from a few atom distances per second up to 10^{12} atom distances per second.

Our microscopic measurements of dislocation behavior have been applied to the calculation of macroscopic stress-strain curves with good results.

5:00 Tour of Franklin Institute Laboratories including the Rheology Section.

Wednesday Evening, Nov. 5

6:00 Cocktails in Franklin Hall Lobby.

6:30 Dinner, in Franklin Hall.

7:45 Recess

8:00 Presentation of Bingham Medal and Medalist's Address, by Dr. Ronald S. Rivlin. Introduction by Dr. E. H. Lee.

Followed by Smoker.

10:30 Adjournment.

Thursday Morning, Nov. 6

9:00 Symposium on Resonance and Relaxation
Introduction - J. D. Ferry

ULTRASONICS AND ITS USE IN RHEOLOGY

T. A. LITOVITZ, *Catholic University of America, Washington, D. C. and Naval Ordnance Laboratory, White Oak, Md.*

Ultrasonic spectroscopy has demonstrated the existence of volume viscosity in most liquids and has shown that there are many different molecular mechanisms responsible. In all cases in liquids, the absorption of sonic waves has been related to relaxation processes and not to resonance effects. In this paper, resonance and relaxation will be discussed in relation to the molecular basis of the ultrasonic loss (or volume viscosity) of liquids.

THERMODYNAMICS OF TRANSPORT PROCESSES IN LIQUIDS

R. E. NETTLETON, *Rice Institute, Houston, Texas*

A number of scalar and tensor parameters are introduced, in addition to the density and temperature, to describe the local non-equilibrium states of a very small subvolume of the liquid. Each parameter, e.g. fractional number of molecules excited in a given vibrational mode, obeys a rate equation, involving a relaxation time which may be calculated from a structural model of the liquid or, in the case of thermal relaxation, with the aid of data on the Raman spectrum. If the rate equations are regarded as force-flux equations in the thermodynamics of irreversible processes, then they are coupled to the stress tensor in such a way that, in accordance with the Onsager-Casimir reciprocity theorem, the pressure involves a linear sum of the affinities governing the rates of the internal irreversible processes. Use of the rate equations to eliminate the relaxation parameters from the stress tensor yields expressions for the complex, frequency-dependent bulk and shear moduli. In the limit of low frequency, the bulk and shear viscosities may be calculated.

MECHANICAL RESONANCE DISPERSION IN CRYSTALLINE SOLIDS

EDWIN R. FITZGERALD, *The Pennsylvania State University, University Park, Pa.*

Measurements of the complex shear compliance at closely spaced intervals in the range of 100 to 5000 cps have resulted in the discovery of sharp resonance dispersions in polycrystalline metals, crystalline polymers, and single crystals of various materials such as sodium chloride, copper sulfate, and quartz. The results indicate that the phenomena of low frequency

resonance dispersion in mechanical compliance are of general occurrence. The data can be analyzed and fitted closely by means of a generalized stress-strain relation involving a linear combination of the strain and its first and second time derivatives. Inclusion of the third derivative leads to an anti-dissipative term which can be used to account qualitatively for a negative absorption or induced emission observed over a narrow frequency region in some materials. The negative absorption seems to be connected with static clamping stresses applied to the sample, decreases slowly with time, and can be reactivated by restressing.

An explanation of the resonances is suggested by calculations of Fermi, Pasta, and Ulam for non-linear systems in which no tendency toward equipartition of energy among modes was found. Accordingly it is proposed that: (1) in crystalline solids, because of the non-linear nature of the binding forces, equipartition of energy among the various modes of vibration does not take place; instead energy actually is passed back and forth among relatively few of the available modes, (2) the frequency of the energy exchange, in contrast to the lattice frequencies themselves, may be very low, e.g., in the audio-frequency range, (3) the observed resonance dispersions occur at frequencies corresponding to these various acoustic exchange frequencies. This lack of energy equipartition will not necessarily be noticed in specific heat measurements of solids, but may have some consequences in other areas.

RADIOFREQUENCY SPECTROSCOPY APPLICATIONS

WILLIAM L. ROLLWITZ, *Southwest Research Institute, 8500 Culebra Road, San Antonio 6, Texas*

Radiofrequency Spectroscopy covers the heretofore unused portion of the electromagnetic spectrum used for absorption spectroscopy. The measurements involved are based upon the absorption of radiofrequency energy by nuclei and/or free electrons when they are simultaneously subjected to both a steady magnetic field and a radiofrequency field. The amount of energy absorbed will give a quantitative analysis. The width and shape of the absorption line will give a measure of the chemical and physical environment of the nuclei or electrons. The saturation energy will give added information on internal environment. These measurements can be made under many dynamic conditions so that the chemical and/or physical changes can be measured as a result of varying external environment.

It is therefore possible to apply these Radiofrequency Spectroscopy techniques to quality control and measurement, as well as to research, in such fields as high polymers, plastics, metals, petroleum products, rubber, paint, starch, etc.

11:15 General Discussion

Thursday Afternoon, Nov. 6

1:30 Viscoelasticity Theory and Practice

SOME GENERALIZATIONS OF LINEAR VISCOELASTIC STRESS-DEFORMATION RELATIONSHIPS

HERSHEL MARKOVITZ, *Mellon Institute, Pittsburgh, Pa.*

Oldroyd has developed a method for generalizing rheological equations of state of limited applicability so that they have correct invariance properties and are of a universally valid form. In this paper a general Maxwell body is taken as a basis for various generalizations of the Oldroyd type. These results are then examined for their implications with respect to the rate of shear dependence of the shearing and normal stresses in steady state flow.

DYNAMIC MECHANICAL PROPERTIES OF CONCENTRATED SOLUTIONS OF POLY-N-BUTYL METHACRYLATE*

P.R. SAUNDERS, DONALD M. STERN, SHELDON F. KURATH, CHAROEN SAKOONKIM, and JOHN D. FERRY, *Department of Chemistry, University of Wisconsin, Madison, Wisconsin*

Measurements of the real and imaginary parts of the complex compliance (J^*) have been made on solutions of poly-n-butyl methacrylate (molecular weight 3.05×10^6) in diethyl phthalate at concentrations of 30, 40, 50, and 60% by weight, using the Fitzgerald transducer apparatus over wide ranges of frequency and temperature. Except for certain anomalies mentioned below, the method of reduced variables provided single composite curves with temperature shift factors which followed the WLF equation; the parameter a_f varied from 2.2 to 2.8×10^{-4} , and for the 50% and 60% solutions, whose glass transition temperatures were determined refractometrically as -67° and -46°C ., the parameter f_g was 0.024. At the lowest temperatures and highest frequencies, the reduced data for the 60% solution showed an anomaly which was tentatively identified as a β -mechanism but could not be separately resolved. At temperatures and frequencies corresponding to the neighborhood of the maximum in J'' , the reduced data for all four solutions showed an anomaly like that in the undiluted polymer, where the maximum shifts upward and to lower reduced frequencies with increasing temperature. This behavior can be interpreted in terms of a temperature dependence of the number of entanglement coupling points, with an apparent heat of dissociation of 2.1 kcal. in all solutions. Retardation and relaxation spectra have been calculated for each solution, and from these the concentration dependences of the monomeric friction coefficient and other parameters have been obtained.

*This work was supported in part by the Ordnance Corps, Department of the Army.

DYNAMIC MECHANICAL AND CREEP PROPERTIES OF A CONCENTRATED CELLULOSE NITRATE SOLUTION

DONALD J. PLAZEK*, *Department of Chemistry, University of Wisconsin, Madison, Wisconsin*

Low frequency torsion pendulum and creep measurements have been made on a solution of cellulose nitrate in diethyl phthalate (23.0% by weight of polymer) to supplement previously reported work with a Fitzgerald-Ferry double transducer. The torsion pendulum measurements were made at temperatures from -25° to $+35^{\circ}\text{C}$ within a frequency range extending from 0.07 to 9.0 cycles per second. Creep runs, also made in torsional shear, were made at temperatures from -33° to $+65^{\circ}\text{C}$. At the temperatures where crystallinity was present (5°C and below), the deformation, γ , at long times can be described by the expression $\gamma = \gamma_0 + \beta t^{1/3}$, where t is the time and γ_0 and β are constants.

In spite of the presence of crystallinity, all of the results were independent of thermal history and the dynamic results at -10°C and above could be and were reduced to a reference temperature ($T_0 = 25^{\circ}\text{C}$). The necessary shift factors, a_T , are given by

$\log a_T = -8.48 (T - T_0) / (166 + T - T_0)$. At lower temperatures the dispersion is appreciably broadened by the crystallinity.

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VISCOELASTIC BEHAVIOR OF CRYSTALLINE POLYETHYLENE AND POLYPROPYLENE

J. A. FAUCHER, *Research Department, Union Carbide Chemicals Co., S. Charleston, W. Va.*

An attempt is made to apply the theory of linear viscoelasticity to the crystalline polymers polyethylene and polypropylene. It appears that this can be done if suitable restrictions are made in temperature range and amount of strain. Data were obtained by the method of stress relaxation. Curves at different temperatures can be superimposed to give a single master curve, and the shift factors so obtained fall on a straight line in an Arrhenius plot. The distributions of relaxation times are calculated for both polymers and found to be very similar. The two are compared with amorphous polypropylene whose behavior is much like polyisobutylene.

AN APPARATUS FOR MEASURING THE DYNAMIC MECHANICAL PROPERTIES OF HIGH POLYMERS AT LOW FREQUENCIES

R. H. SHOULBERG, F. H. ZIMMERLI, and O. C. KOHLER, *Rohm and Haas Co., Philadelphia, Pa.*

An apparatus is described for low-frequency measurements (0.0004 to 1 cps) of the dynamic properties

of polymers. The apparatus is basically a modified version of the Morrisson-Zapas-De Witt machine at The Mellon Institute [Rev. Sci. Inst., **4**, 357 (1955)]. The modifications consist principally in (1) using reflected light beams from a mercury arc source to trace both input and response curves on a photosensitive film, thus providing a common time base for recording without resorting to the use of any intermediate electrical system, and (2) using a constant impedance network to independently vary the recorded amplitude of the input and output traces, thus allowing accurate measurements of amplitude ratios over the entire frequency range without altering the geometry of the specimen. The calibration of the instrument and data treatment are discussed, and examples of the measurements taken on solid samples are given.

OPEN MEETING OF COMMITTEE ON COMMUNICATION PROBLEMS IN RHEOLOGY

R. R. MYERS (*Chairman*), D. R. BROOKFIELD, F. R. EIRICH, L. STOLOFF and R. N. TRAXLER

The Committee on Communication Problems in Rheology, sponsored by six American Chemical Society Divisions, the ASTM and the Society of Rheology will meet in open session for the purpose of establishing and defining those broad aspects of flow concerning which no serious disagreement exists among practicing rheologists.

Recommendations will be made that flow phenomena be described using a broad classification of behavior based on the dependence of applied stress S on shear rate D . A material whose S/D ratio decreases as D increases will be called viscolactic, and one whose S/D ratio increases as D increases will be called visconattic.

Reasons for adoption of new terminology will be given, and participation by Society membership before, during and after the session is invited.

4:30 Business Meeting

Friday Morning, November 7

9:00 General Papers

ON THE THERMOSTATICS OF CONTINUOUS MEDIA

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

This paper discusses materials in states of rest; that is, in states which are achieved in the limit of very slow measurements. When in such a state, every material possesses a strain energy function, and behaves as either a perfect fluid or a perfectly elastic solid. A strain energy function cannot be completely arbitrary. Its possible forms are limited by symmetry considerations (i.e. objectivity and isotropy) and by the second law of thermodynamics. The restrictions caused by symmetry have been understood for some time; in this paper we investigate the thermodynamic requirements. In the course of a derivation of the

laws of hydrostatics and elastostatics from thermodynamics, certain inequalities are obtained. These inequalities, which express the thermodynamic restrictions on a strain energy function, have important implications when applied to the theory of finite elastic strain.

THE TEMPERATURE DEPENDENCE OF FLOW BIREFRINGENCE PARAMETERS

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

The origin of flow birefringence of liquids has been until now attributed to an orientation effect caused primarily by the rate of shear. However, we have reason to believe that this is not so; rather, the birefringence is primarily caused by the stresses in the liquid — especially the shear stress. To decide this question we have used the technique already applied by Cerf, namely, the investigation of birefringence at different temperatures. Temperature influences primarily the viscosity. Investigations in a wide range of rates of shear and temperatures allow the correlation of the results either at constant rate of shear or constant shearing stress. The instrument used is the same as in our previous publications. The first material, a low molecular weight polyisobutylene (OB oil) was investigated at temperatures from 12 to 73°, where the viscosity changes by a factor of about 200. The orientation angle in the whole range was exactly 45°. The degree of birefringence at constant rate of shear varied as the viscosity. Plotting it against the shear stress we got one single curve giving a stress-optical coefficient $C = -975$ Brewsters. The second material was a "white oil" investigated in the same range of temperatures. The result was the same; however, the stress optical coefficient was +500 Brewsters. The third material to be investigated was a 2% polyisobutylene solution in the same white oil. It gave an orientation angle different from 45° dependent on the rate of shear. However, the orientation angle and the degree of birefringence could be combined into one single curve valid for the different temperatures when one used the maximum shearing stress as the independent variable; the results were $C = -516$ Brewsters. These representative three runs show to our satisfaction that the flow birefringence is primarily caused by the stresses in the flowing solutions. The rate of shear necessary for the occurrence of the effects is determined by the viscosity.

THE BEHAVIOR OF JETS OF VISCO-ELASTIC FLUIDS

F. H. GASKINS and W. PHILIPPOFF, *Franklin Institute Laboratories, Philadelphia, Pa.*

The stability of liquid jets is well known to be described by the theory of Rayleigh which uses the density and surface tension of the liquid as important parameters. Further investigations have taken into

account the viscosity, the combination of these three parameters being known as the Weber number. However, polymer solutions are now known to have an elasticity in flow; the mechanism of breakup of solutions of polymers has heretofore not been investigated. We have used a constant volume-driven extrusion device by means of which the velocity of the emerging jet could be calculated exactly, which gave us an additional parameter as compared with the standard pressure-driven device. A number of pure liquids and polymer solutions were investigated. The general result was that the "vena contracta" causes an increase of the velocity of the free flying jet by about 20% for pure liquids, as compared to the predetermined "continuity velocity." This can be explained by the old theory of Hagenbach. Viscoelastic polymer solutions, however, showed a decrease of velocity as compared either to the normal liquids or to the "continuity velocity." Very probably that difference is caused by the elastic energy accumulated in the jet which absorbs some of the kinetic energy of the emerging liquid. The quantitative evaluation showed that we can determine the elastic stress of the liquid and therefore also the normal stress by measuring the difference between the jet velocity and the velocity of the solvent.

EFFECTS OF DRAWING ON THE MECHANICAL BEHAVIOR OF NYLON 6 FILAMENTS

J. H. DUSENBURY, C. WU, C. J. DANSIZER, and A. HAUSER, *Textile Research Institute, Princeton, N. J.*

The extensional properties, bending moduli, and torsional moduli have been determined for a series of nylon 6 filaments ranging in draw ratio from 1.00 to 5.48. The extensional properties were measured with an Instron tester; the bending and torsional moduli were measured with an electrostatic vibroscope. Both the extensional and bending moduli increase smoothly with increasing draw ratio, whereas the torsional modulus is essentially independent of the draw ratio. These findings are in good agreement with those reported previously for two other melt-spun filaments: nylon 66 and Dacron. The actual values observed for the nylon 6 moduli, however, are about 2/3 the corresponding values observed in the case of nylon 66. During load-extension experiments the filaments of lower draw ratio were observed to go through relatively long periods of extension without appreciable changes in load; they were, in effect, being cold-drawn under the test conditions. The values observed for the ratio of the bending modulus to three times the torsional modulus suggest that there is no preferential orientation in the undrawn filaments and that these filaments exhibit increasing molecular orientation with respect to the filament axis as the extent of drawing increases. These views are in general agreement with the results of x-ray diffraction studies carried out on the same materials.

A METHOD OF GENERALIZING THE EFFECT OF TEMPERATURE AND RATE ON THE STRESS-STRAIN CURVES OF NYLON

JOHN B. MILES, *Chemstrand Corporation, Decatur, Ala.*

It has been found possible to considerably simplify the description of the stress-strain curve of nylon as a function of temperature and of the rate of elongation. The stress-strain curves obtained at a constant rate of elongation in the range of temperature from 21°C to 150°C can be accurately represented by one master curve with the units along the stress axis multiplied by a constant which depends on the temperature. Thus the stress P is given by

$$P = f(e) \times g(T)$$

where e and T are the strain and temperature, respectively, and $f(e)$ is a function of e only, and $g(T)$ of T only. The temperature function, $g(T)$, has been determined over this temperature range.

A similar type of relationship has been found for different rates of elongation at constant temperature in the range from 0.2 to 200% elongation per minute.

The characteristics of the master curve, $f(e)$, are discussed, with possible interpretation in terms of the mechanism of deformation.

GLASS BEAD-POLYVINYL CHLORIDE COMPOSITES UNDER LARGE DEFORMATIONS

THOR L. SMITH, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif.*

The mechanical properties of five composites containing up to 60% by volume of glass beads (40–80 microns) embedded in a polyvinyl chloride-dioctyl sebacate resin were studied under large deformations. Elongated ring-like specimens were extended in a dilatometer at 0°, 25° and 50°C and the volume increase was measured as a function of extension. At small extensions, the volume remained constant, but above a critical extension or yield point, the volume increased due to the formation of vacuoles around the beads. Above the yield point, Poisson's ratio (defined in terms of Hencky strain) was calculated from the rate of volume change with extension and was found to be independent of extension and temperature but to decrease linearly with the volume fraction of glass. The yield point varied with the temperature and varied with the volume fraction of beads as predicted by a theoretical equation. Some stress-strain data for the composites are also presented and are discussed in relation to the dilatometric data and the vacuole formation which results from failure of the adhesive bonds between the resin and glass beads.

Friday Afternoon, November 7

1:30 Adhesion; Dispersions

THEORY AND ANALYSIS OF PEEL ADHESION

DAVID H. KAEUBLE, *Central Research Dept., Minnesota Mining and Manufacturing Co., St. Paul, Minn.*

An idealized type of tensile peel is defined which substantially represents real systems in the range of low peel forces. The theory applies to the steady-state unbonding of (a) a flexible and a rigid member and (b) two flexible members. Failure interface propagation is discussed in terms of two stress mechanisms. The first is boundary cleavage which involves compression-tension bond stress, and the second boundary shear involving bond stress in simple shear. The theory is general with respect to the stripping angle, and a definition of work of peel is developed which is independent of this variable. Experimental confirmation of theory is provided by photographic studies of the peel process. A new experimental device is described which permits precise measurement of peel force over a wide range of controlled angles of peel, rate and temperature. Bonds involving both soft visco-elastic interlayers and no interlayer are evaluated and discussed in terms of the theory.

POLYETHYLENE ADHESIVE JOINTS

J. J. BIKERMAN, *Massachusetts Institute of Technology, Cambridge 39, Mass.*

Polyethylenes as adhesives are suitable materials to test the validity of the two rival theories (of adhesive joints) emphasizing either molecular adhesion or weak boundary layers. Our experiments seem to decide in favor of the latter hypothesis. Polyethylenes, from which substances apt to produce weak boundary layers were removed, adhered to metals and glasses, and the breaking stress of the joints was closely related to the breaking stress of the polyethylene in bulk. This was true both for butt joints prepared in tension and for peeling. Because the stress-strain curves of some polyethylenes can be represented by an equation of the form: stress = (strain)ⁿ, the peeling force was calculated for such systems; however, the theory assumes no plasticity while almost all polyethylenes flow in the adhesion tests.

FOUR SEPARATE "REGIMES OF FLOW" OR SYSTEMS OF BLOOD RHEOLOGY*

WILLIAM H. DUNHAM, FANN HARDING DUNHAM, and MELVIN H. KNISELY, *Department of Anatomy, Medical College of South Carolina, Charleston, S. C.*

Blood flow patterns resulting from different properties of cells, combinations of cells, and plasma,

during health and disease have not been thoroughly analyzed. At least four regimes of flow are known:

1. Newtonian flow, which consists of a parabolic velocity distribution of a homogeneous fluid around the axis of flow. This occurs when plasma alone flows through a cylindrical vessel.

2. Poiseuillian flow, the commonly described flow pattern, which consists of alternate concentric cylinders of cells suspended in plasma, and plasma, radially symmetrical around the axis of the vessel.

The above two regimes of flow occur during health when blood cells are not agglutinated; during disease blood cells often agglutinate into masses having different sizes and different degrees of internal rigidity. The following two types of flow sometimes occur during disease:

3. Plug flow; this is a plastic flow during which the "yield value" of the masses has been exceeded at their boundaries.

4. Gravitationally layered flow, as seen with the observer looking horizontally, which consists of several layers of settled, stationary, and/or sliding cellular constituents, often agglutinated, of different sizes, shapes, densities and elastic properties. And above these there is often a layer of moving plasma containing suspended small particles such as small masses, free erythrocytes and leukocytes. This flow is not radially symmetrical around the axis of the vessel.

Between branchings, segments of arteries and of veins are truncated cones, not cylinders. (Jeffords and Knisely, 1956)

Saunders and Knisely (1954) found that the maximal internal diameters to which the terminal mesenteric arterioles can distend as they are impacted with masses of sludge are: for hamsters and mice, 9 micra; for rats and rabbits, 8 micra; for cats, 11 micra; and for dogs, 10 micra. These are the narrowest vessels of the vascular system.

The above four separate regimes of flow will be considered in terms of the forces of the plasma, influenced by the vessel walls, acting on the surfaces of the suspended particles.

The lecture will be illustrated by lantern slides and motion pictures taken through a horizontally aimed microscope. As far as we know, rheologists have not ordinarily used horizontally aimed microscopes to study the flow of suspensions.

The walls of small living blood vessels are nearly transparent, which permits direct observation of the behavior of particles in "flowing" suspensions.

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THE VISCOSITY OF ELLIPSOIDS IN CONCENTRATED SOLUTIONS

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Kuhn and Kuhn's¹ theory for the viscosity of ellipsoids in dilute solutions has been extended to concentrated solutions using Mooney's functional method. From the available experimental data the constants involved were calculated and found to be within 2% of the theoretical values. The dependence of the relative viscosity on volume fraction is seen to agree with the experimental results presented by Yang².

¹W. Kuhn and H. Kuhn, *Helv. Chim. Acta.* **28**, 97 (1945); W. Kuhn, H. Kuhn and P. Buchner, *Ergeb. exakt. Naturwiss.* **25**, 1 (1951).

²J. T. Yang, *J. Amer. Chem. Soc.* **80**, 1783 (1958).

THE "EFFECTIVE" SOLID VOLUME - VISCOSITY RELATIONSHIP OF RIGID SPHERES VERSUS THE DIMENSIONS OF THE MEASURING INSTRUMENT

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A viscosity-solids relationship that is based upon the effect of the solid phase in altering the "effective" dimensions of the measuring instrument is proposed.

The "effective" solid volume fraction has been found to vary with the ratio between the shearing area of the instrument and the diameter of the solid particles relative to the volume of sample under shear. The absorption or interaction forces at the solid-liquid interface affect the "effective" solid-volume fraction V_E in direct relation to the specific surface of the solid phase and the amount of shear.

Two simple equations are used to relate the solid-volume fraction (V) to the "effective" solid-volume fraction over a range of shear that shows both pseudo-plastic and dilatant flow.

A MECHANISM FOR NON-NEWTONIAN FLOW IN SUSPENSIONS OF RIGID SPHERES

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A mechanism for non-Newtonian flow behavior based on shear-induced separation of doublets is proposed and developed semi-quantitatively. The resultant viscosity vs. shear stress relationship is identical in form with that of Williamson, and contains a single dimensional parameter. The equation is applied satisfactorily to data of Maron et al. on synthetic rubber latex and polymer solutions. Dependence of high and low shear viscosity limits on concentration is described by a somewhat novel semi-theoretical equation.