JOURNAL OF APPLIED POLYMER SCIENCE VOL. 7, PP. 1867-1889 (1963)

Development of Constitutive Equations for Polymeric Melts and Solutions

J. L. WHITE and A. B. METZNER, *University of Delaware, Newark, Delaware*

INTRODUCTION

Engineers designing processing equipment for polymeric solutions and polymer melts have long based their procedures on the stress-deformation rate equations of Newtonian fluids, the only modification being the assumption of a variable viscosity. The elastic properties of real fluids, i.e., the memory of the fluid for its deformation history, have been considered to have no effect on any but oscillatory flows. While such design procedures will predict the correct pressure gradients for steady laminar shearing flows,[29,77] they are incapable of predicting the behavior of fluid polymer systems in more complex flow situations. For example, when a fluid flows into a tube, the entrance length required for the velocity profile to become fully developed is an order of magnitude larger for fluids having appreciable elasticity[29,31] than is predicted by only considering the nonlinear relation between the shear stress and deformation rate.[3,68] The various abnormal exit effects are also well known.[14,29-32,35] In the special case of dilute solutions, fluid elasticity is responsible for reducing the pressure gradients required for ducted flow as much as an order of magnitude at high Reynolds numbers,[10,62] an effect which has found a number of large-scale industrial applications. There are significant effects even in laminar shearing flows of polymer solutions and melts. For instance, when such a fluid flows between two coaxial cylinders, the fluid tends to climb up the inner cylinder[74,75] rather than being thrown out radially by the centrifugal force. Weissenberg has shown similar effects to exist in other geometries and was the first to offer a correct explanation for these phenomena. In a coaxial cylinder or rotating parallel plate geometry a tensile normal stress exists along the streamlines and tends to strangulate the fluid, causing it to move to the center or to climb up the inner cylinder. The significance of this normal stress effect to engineers is well illustrated by the "normal stress" pumps built by Reiner[54] and by Maxwell and Scalora.[26]

A growing effort has been devoted to the measurement of normal stresses in laminar shearing flows and normal stresses as much as thirty times greater in magnitude than the concomitant shearing stresses have been found at high rates of shear.[17,32] This work has recently been reviewed,[77] where it has been shown that most of the available measurements have unfortunately been restricted to deformation rates which are too low to be of much interest industrially. However, progress is being made in this direction and this paper will not be concerned with experimental techniques but with the theoretical prediction of the stresses arising in the flow of viscoelastic materials and the relationships between them. The purpose of this paper is to introduce a constitutive equation (relating deformation rates and their history to the stresses required to sustain such deformation) which may have application in engineering design involving polymeric materials, and to illustrate the use of this equation by solving a number of practical problems.

METHODS OF FORMULATION OF CONSTITUTIVE EQUATIONS FOR VISCOELASTIC MATERIALS

Rheological equations of state for viscoelastic media date back to the latter half of the nineteenth century. The results of early workers such as Boltzmann,[1] Maxwell,[55] and Volterra[72] are not valid for the large deformations of interest in studies of the flow of polymeric melts and solutions. Thus, this work as well as the more recent body of literature in the area of "infinitesimal" or "linear" viscoelasticity, which is of interest in connection with the solution of problems of stress analysis of nearly rigid solids,[1,2,19] is inapplicable to the problems being considered here.

It was not until 1950 that a method of formulation of constitutive equations, valid for large deformations, was clearly outlined. In that year, Oldroyd[40] pointed out that the form of any constitutive equations must be restricted by the requirement that the equations describe properties independent of the frame of reference and that such invariance properties could be obtained by considering a constitutive equation "as defining the properties of an arbitrary element moving as part of the continuum." In order to consider such an element, one introduces a coordinate system ϵ^α, which is fixed in and deforms with the medium. The constitutive equation is then constructed by relating the components of the stress tensor in this convected coordinate system to a suitable kinematic tensor of that coordinate frame. Finally, the constitutive equation is transformed to a fixed space frame in which it may be solved simultaneously with the equations of motion in analysis of real problems. Noll[38,39] has introduced an alternate method of formulation of constitutive equations, and a detailed comparison of these two methods is given elsewhere.[76]

When a curvilinear system of coordinates (such as the convected frame considered here) is used, it becomes necessary to differentiate between tensors transforming by covariant and contravariant laws.[27] Following Oldroyd,[40] stress will be taken to transform by a contravariant law. The fixed space components of the stress tensor τ^{ij} are related to the convected components $\pi^{\alpha\beta}$ by

$$\tau^{ij} = \sum_\alpha \sum_\beta (\partial x^i/\partial \epsilon^\alpha)(\partial x^j/\partial \epsilon^\beta)\pi^{\alpha\beta} = (\partial x^i/\partial \epsilon^\alpha)(\partial x^j/\partial \epsilon^\beta)\pi^{\alpha\beta} \tag{1}$$

The stress τ at a point in the medium at time t is determined by the entire history of the deformation as well as its present state, within an arbitrary small neighborhood of the point. The history of this neighborhood may be specified by consideration of the variation in distance between two differentially separated points fixed in the medium. Taking the scalar product of the distance with itself gives

$$\begin{aligned} ds^2 &= \sum_j dx^j dx^j = \sum_\alpha \sum_\beta \gamma_{\alpha\beta} d\epsilon^\alpha d\epsilon^\beta \\ &= dx^j dx^j = \gamma_{\alpha\beta} d\epsilon^\alpha d\epsilon^\beta \end{aligned} \tag{2}$$

where

$$\gamma_{\alpha\beta} = (\partial x^j / \partial \epsilon^\alpha)(\partial x^j / \partial \epsilon^\beta) \tag{3}$$

is known as the metric or fundamental tensor, which can be seen to be a second order covariant tensor. If a contravariant stress tensor is used, it must necessarily be related to a kinematic tensor obeying the same transformation law. Such a quantity is the conjugate metric tensor $\gamma^{\alpha\beta}$ defined by:

$$\gamma^{\alpha\beta} = (\partial \epsilon^\alpha / \partial x^i)(\partial \epsilon^\beta / \partial x^i) \text{ or } \gamma_{\alpha\delta}\gamma^{\delta\beta} = \delta^\alpha_\beta \tag{4}$$

The constitutive equation of a material isotropic in its initial or ground state is thus given by the functional relationship:

$$\pi^{\alpha\beta} = f^{\alpha\beta}[\gamma^{\delta\gamma}(\phi)]_{-\infty} \tag{5}$$

which has fixed components:

$$\tau^{ij} = (\partial x^i / \partial \epsilon^\alpha)(\partial x^j / \partial \epsilon^\beta) f^{\alpha\beta}[\gamma^{\delta\gamma}(\phi)]_{-\infty}^{t} \tag{6}$$

Equation (6) represents the most general form of constitutive equation for an isotopic continuous medium.

Green and Rivlin[15] point out that the functional appearing in eq. (6) may be expanded in a manner similar to that used in expansion of a function in a Taylor series. From the theory of functionals:[72]

$$\pi^{\alpha\beta} = \sum_{k=1} \int_{-\infty}^{t} \dots \int_{-\infty}^{t} \psi^k [t, \eta_1, \dots \eta_k, \gamma^{\alpha\delta}(\eta_1), \dots \gamma^{x\beta}(\eta_k)] d\eta_1 \dots d\eta_k \tag{7}$$

Both Green and Rivlin[15] and Noll and Coleman[6,39] have developed theories of viscoelastic deformation based on equations similar to eqs. (6) and (7). Other very general formulations, though somewhat different in approach, have been published by Rivlin and Ericksen.[60]

Due to their complexity, these results are not readily usable to solve the problems of interest to the engineer, and simplifications must be made. Lodge[21] and Pao[44] introduced constitutive equations which are equivalent to expressing one term of an expansion similar to eq. (7). However, Lodge's result does not predict the observed dependence of the components of the stress tensor upon the deformation rate, while Pao's theory, which has been presented in incomplete form, still appears to be too complicated to allow analytical solutions of any but the simplest problems. Oldroyd,[40–43] Noll,[38] and DeWitt[8] have used an approach which, in some respects, is similar to that employed when deriving the operator equations of linear viscoelasticity[2,20] as the basis of constitutive equations. The results of DeWitt's and Noll's theories are not in agreement with experimental data.[24] Oldroyd's results are more promising. They are at least in qualitative agreement with experimental data and the number of parameters involved, while large, is not prohibitive. In fact, several papers have appeared in the literature in which attempts to evaluate the parameters in several of Oldroyd's equations have been made.[29,30,42,43] However, no complete determination of the parameters appears to have been accomplished as yet as the amount of effort involved is very large indeed. Remarks similar to those made concerning the work of Oldroyd may be made about the recent papers of Walters.[73]

Thus, with the possible exception of Oldroyd's and Walters' work, there appear to be no constitutive equations general enough to explain the observed behavior of polymeric systems undergoing large deformations but still simple enough to provide a basis for engineering design procedures. It is the purpose of this paper to derive such a constitutive equation, to compare it with available experimental data and to observe some of its implications.

DEVELOPMENT OF EQUATION

Let us first consider the qualitative characteristics of the flow of a concentrated polymer solution or polymeric melt on a molecular scale. A molecular model has been developed by Lodge[21,22] and Yamamoto[78] which is a modification of the kinetic theory of rubber elasticity.[12,70] These authors consider a flowing polymer system to consist of long chain molecules connected in a continuously changing network structure by "interactions" between chains which involve intermolecular forces. If the interchain junctions were permanent and intermolecular forces between the chains could be neglected, then one obtains the perfectly elastic rubber of the kinetic theory. The convected components of the constitutive equation of this material are:[21]

$$\pi^{\alpha\beta} = -\alpha\gamma^{\alpha\beta} - G[\gamma^{\alpha\beta} - \delta^{\alpha\beta}]$$

This equation is found to be in excellent agreement with the stress-deformation behavior of crosslinked rubbers swollen with organic solvents.[70] It is found that the higher the degree of swelling, the smaller the deviations from eq. (8), a fact which is attributed (e.g., ref. 70) to the effect of the solvent in decreasing the molecular forces between chains in regions between the junctions.

Lodge and Yamamoto have suggested that a modification of a theory introduced by Tobolsky and co-workers[66] may be applied to the flow of concentrated polymeric materials. The original work of Tobolsky et al. was concerned with stress relaxation in materials subjected to infinitesimal deformations and was based on the assumption that the stress was proportional to the concentration of interchain junctions still present and which originally existed in the stressed state. These authors show that such an approach leads to Maxwell's equation.[1,2,55] In the flow of high molecular weight polymeric materials, there is a continuous breakdown and reformation of interchain junctions, and a similar assumption may be made concerning the stress. At finite deformation rates, this constitutive equation must be formulated in a convected coordinate system. It should be noted that Lodge[21,22] and Yamamoto[78] have derived constitutive equations on this basis. However, Lodge's result only predicts the observed behavior in the limiting case of low shear rates and Yamamoto's constitutive equation appears to be too complex to be of engineering interest at present.

From the above consideration of the structure of flowing concentrated polymeric materials, it may be suggested that for large deformation rates:

$$D\pi'^{\alpha\beta}/Dt = -G(D\gamma^{\alpha\beta}/Dt) - \pi'^{\alpha\beta}/\lambda \tag{8}$$

where

$$\pi^{\alpha\beta} = -\alpha\gamma^{\alpha\beta} + \pi'^{\alpha\beta}$$

and λ the relaxation time is a function of the invariants of the stress matrix. The dependence of λ upon the stress corresponds to a nonlinear junction breakdown process.

Equation (8) may only be expected to apply to those polymeric systems which, under conditions of large deformations, behave similarly to swollen crosslinked rubber. Thus, this constitutive equation should be most applicable to nonpolar systems. However, under some conditions polar molecules might be expected to approach similar behavior hence these equations may be applied to such systems as approximations under possibly restricted conditions. In any case the above discussion should be considered to indicate only generally (and not quantitatively) the range of applicability of the present development.

Equation (8) is the representation of the constitutive equation in a coordinate system fixed in and deforming with the medium. In order to be useful, the constitutive equation must be transformed to the same coordinates in which rheological phenomena are observed, a fixed space coordinate system. The components of eq. (8) in a curvilinear fixed space frame are (see Appendix A):

$$\delta\tau'^{ij}/\delta t = 2Gd^{ij} - \tau'^{ij}/\lambda \tag{9}$$

where:

$$d^{ij} = {}^1/_2(V^i_{,m}g^{mj} + V^j_{,m}g^{im}) \tag{10a}$$

$$\tau^{ij} = -\alpha g^{ij} + \tau'^{ij} \tag{10b}$$

$$\delta\tau'^{ij}/\delta t = D\tau'^{ij}/Dt - V^i_{,m}\tau'^{mj} - V^j_{,m}\tau'^{im} \tag{10c}$$

For a fixed rectangular coordinate system, eqs. (10) become:

$$d^{ij} = {}^1/_2(\partial V^i/\partial x^j + \partial V^j/\partial x^i)$$

$$\tau^{ij} = -\alpha\delta^{ij} + \tau'^{ij}$$

$$\delta\tau'^{ij}/\delta t = D\tau'^{ij}/Dt - (\partial V^i/\partial x^m)\tau'^{mj} - (\partial V^j/\partial x^m)\tau'^{im}$$

Equation (9) is similar in form to that given by DeWitt.[8] However, De-Witt's time derivative of the stress tensor is somewhat different from that of eq. (10c) and he assumes the relaxation time to be a constant.

Equation (9) may be rewritten in a more convenient form to show its relationship to a purely viscous liquid:

$$\tau'^{ij} = 2\mu d^{ij} - (\mu/G)(\delta\tau'^{ij}/\delta t) \tag{11}$$

where

$$\mu = \lambda G$$

It may be seen that the constitutive equation is identical to that of a purely viscous non-Newtonian fluid except for a term involving the "convected" derivative of the stress tensor. It is this term which accounts for the various normal stress (viscoelastic) effects.

In the remainder of the paper, contravariant superscripts for fixed space components will be changed to subscripts for reasons of clarity.

ANALYSIS OF LAMINAR SHEARING FLOWS

Perhaps the most important of all hydrodynamic problems which arise in industrial applications of polymeric systems is that of laminar shearing flows. Fortunately, this is also the simplest hydrodynamic problem to solve and a large fraction of all meaningful experimental data available to date have been taken on instruments measuring this type of flow. Laminar shearing flows are defined in terms of a fixed orthogonal system of coordinates (e.g., rectangular, cylindrical, or spherical), where the fluid flows steadily in one coordinate direction and its velocity or angular velocity as in Couette flow, varies with distance along a second coordinate. The direction of flow is arbitrarily designated as 1, and the coordinate along which the velocity varies is designated as 2. A more formal kinematic definition of laminar shearing flow is:

$$\mathbf{D}_1 = \| -D\gamma^{\alpha\beta}/Dt \| = 2 \| d_{ij} \| \tag{12a}$$

$$= 2\begin{vmatrix} d_{11}d_{12}d_{13} \\ d_{21}d_{22}d_{23} \\ d_{31}d_{32}d_{33}\end{vmatrix} = \begin{vmatrix} 0\Gamma 0 \\ \Gamma 00 \\ 000 \end{vmatrix} \tag{12b}$$

$$\mathbf{D}_2 = \left\| -D^2\gamma^{\alpha\beta}/Dt^2 \right\| = \begin{vmatrix} 2\Gamma^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \tag{13}$$

$$\mathbf{D}_N = \| -D^N\gamma^{\alpha\beta}/Dt^N \| = 0,\ N > 2 \tag{14a}$$

where the matrices $\mathbf{D}_N$ in fixed space coordinates may be obtained from the formula:

$$(\mathbf{D}_{N+1})_{ij} = (D/Dt)(\mathbf{D}_N)_{ij} - (\mathbf{D}_N)_{im}V_{j,m} - (\mathbf{D}_N)_{mj}V_{i,m} \tag{14b}$$

The quantities $\mathbf{D}_N$ are contravariant analogs of what Noll[39] has called Rivlin-Ericksen tensors and are discussed elsewhere.[76] A similar definition of laminar shearing flow is given by Ericksen.[11] Laminar shearing flows include (a) simple shearing flow between parallel planes, (b) Poiseuille flow in a tube, (c) Couette flow between coaxial cylinders, (d) shearing flow between a cone and plate, and (e) torsional deformation between parallel disks.

Introducing eq. (12) into eqs. (11) and (10b) gives:

$$\begin{vmatrix} \tau_{11}\tau_{12}\tau_{13} \\ \tau_{12}\tau_{22}\tau_{23} \\ \tau_{13}\tau_{23}\tau_{33} \end{vmatrix} = - \begin{vmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{vmatrix} + \begin{vmatrix} 2(\mu/G)\tau_{12}\Gamma & \mu\Gamma & 0 \\ \mu\Gamma & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \tag{15a}$$

The stress tensor may be resolved into an isotropic pressure and deviatoric stress tensor.[55]

$$\boldsymbol{\tau} = -p\mathbf{I} + \mathbf{P} \tag{15b}$$

where

$$p = -{}^1/_3 tr\ \boldsymbol{\tau} \tag{15c}$$

Comparing eq. (15a) with eqs. (15b) and (15c), one obtains:

$$p = \alpha - {}^2/_3\ (\mu/G)\tau_{12}\Gamma$$

and:

$$\begin{vmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{vmatrix} = - \begin{vmatrix} p & 0 & 0 \\ 0 & p & 0 \\ p & 0 & p \end{vmatrix}$$

$$+ \begin{vmatrix} ({}^4/_3)\ (\mu/G)\tau_{12}\Gamma & \mu\Gamma & 0 \\ \mu\Gamma & (-{}^2/_3)\ (\mu/G)\tau_{12}\Gamma & 0 \\ 0 & 0 & (-{}^2/_3)\ (\mu/G)\tau_{12}\Gamma \end{vmatrix} \tag{16}$$

Subtracting τ_{22} from all of the components of the diagonal of $\|\tau_{ij}\|$ (since in real problems one usually treats the difference between stresses rather than their absolute values and because this also eliminates arbitrary hydrostatic pressures from consideration) one obtains:

$$\begin{vmatrix} \tau_{11}-\tau_{22} & \tau_{12} & \tau_{13} \\ \tau_{21} & 0 & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33}-\tau_{22} \end{vmatrix} = \begin{vmatrix} p_{11}-p_{22} & \tau_{12} & \tau_{13} \\ \tau_{21} & 0 & \tau_{23} \\ \tau_{31} & \tau_{32} & p_{33}-p_{22} \end{vmatrix}$$

$$= \begin{vmatrix} 2\tau^2_{12}/G & \mu\Gamma & 0 \\ \mu\Gamma & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

Since, in the development, the viscosity was considered to be a variable, it is a function of the invariants of the stress tensor. The function did not need to be specified, and hence any observed behavior may be accommodated within the framework of the present theory. The same is not true of the normal stress terms, since G was assumed to be a constant. Equation (17) shows that a plot of the shear stress vs. the quantity $(P_{11} - P_{22})/\tau_{12}$ should be linear. Further, the normal stresses in the directions perpendicular to the direction of flow (P_{22} and P_{33}) are predicted as being equal in magnitude. These results are similar to the stress–strain behavior in simple shear of an elastic solid following eq. (8) as its constitutive equation and therefore to the behavior of highly swollen crosslinked rubber.[16,58,70,71] In the theory of large elastic deformations, the quantity $(P_{11} - P_{22})/\tau_{12}$ is equal to the amount of shearing strain and the corresponding quantity in a viscoelastic fluid, being likewise linear in the shearing stress, could be termed a "recoverable" shearing strain. This suggestion was first made by Weissenberg[74] and has received some verification from recoil measurements by Pollett[51] and Philippoff.[48] Denoting $(P_{11} - P_{22})/\tau_{12}$ by s, eq. (17) may be rewritten:

$$\begin{vmatrix} P_{11}-P_{22} & \tau_{12} & \tau_{13} \\ \tau_{21} & 0 & \tau_{23} \\ \tau_{31} & \tau_{32} & P_{33}-P_{22} \end{vmatrix} = \begin{vmatrix} (G/2)s^2 & (G/2)s & 0 \\ (G/s2) & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \tag{18}$$

Weissenberg,[74,75] Mooney,[37] and Philippoff[46] have discussed theories of viscoelastic flow based on an analogy to the finite deformation of an elastic solid. These theories, which are only applicable to laminar shearing flows, yield answers identical to eqs. (17) and (18). The constitutive equation derived in this paper (eqs. 9–11) is far more general as its use is not restricted to laminar shearing flows alone but may also be applied to complex hydrodynamic problems. However, its simplification to relationships which are already well known in the special case of laminar shearing flows is very reassuring.

In order to apply the above to any engineering design problem, it is necessary that all of the significant parameters be easily obtainable from experimental data. All of the parameters of eq. (11) may be obtained from two experiments involving laminar shearing flow. First, shear stress–shear rate data may be obtained to evaluate the parameter $\mu(\Gamma)$ or, equivalently, μ as a function of the invariants of the stress or rate of deformation tensor. These data may be obtained from standard capillary tube or rotational viscometer methods.[28,29] Secondly, normal stress data are obtained using techniques of normal stress measurement which have also been reviewed elsewhere.[24,77]

Evaluation of Equation: Comparison with Experimental Data

Since data are not available to evaluate eq. (11) in its complete form, comparisons with experimental results must be limited to the steady state special cases of laminar shearing flows, though it may be noted that Tobolsky and Eyring[67] have correlated stress relaxation and creep data with a one-dimensional form of eq. (9). Because the viscosity can be varied at will to fit experimental measurements, no test of the theory is possible using measurements of the shear stress alone. The test of the theory therefore lies in the predicted relationships between the normal stresses and between these and either the shearing stress or the shear rate.

Roberts[61] and Pilpel[49,50] have carried out extensive measurements to determine relative values of τ_{11}, τ_{22}, and τ_{33} with a modified Weissenberg rheogoniometer. While it is not obvious that all possible sources of experimental aberration were considered,[24,77] within experimental error τ_{22} and τ_{33} were always observed to be identical as predicted by eq. (17). More recently, Philippoff[47] has introduced the use of an instrument for measuring flow birefringence in the 2–3 plane. He records that "for all polymer solutions studied, there was no 'cross of isoclines' even if the birefringence, Δn, in the 1,2 plane, which is usually observed in the flow birefringence instrument, was as great as 1000×10^{-8} units." Recently Coleman and Toupin[7] have objected to this experiment, claiming a lack of rigor in Philippoff's theory[45–47] of birefringence in fluid polymeric systems. However, agreement of the birefringence data[45] with results obtained using other instruments tends to support the validity of Philippoff's premises. The equality of τ_{22} and τ_{33} is also supported by recent studies of Kotaka et al.[18]

A dissenting opinion to these conclusions has recently been voiced by Lodge,[23] who finds $\tau_{22} > \tau_{33}$. It is of interest to note that one of the solutions investigated by Lodge was polyisobutylene in decalin, a solution similar to some which had been used previously by Roberts and by Philippoff to develop their conclusions about the equality of τ_{22} and τ_{33}. As only a summary of Lodge's paper has appeared which does not give a detailed discussion of his experimental procedure or any data, it is difficult to pinpoint the reasons for these opposing observations. Experiments by Markovitz[24] on a coaxial cylinder instrument also have led him to question the equality of τ_{22} and τ_{33}, as have more recent experiments[25] comparing data on cone-plate and parallel plate instruments.

In summary, most existing experimental measurements point to either the predicted equality or to a near equality of τ_{22} and τ_{33}. Thus, while this test of theory is inconclusive because of insufficient data, the majority of the available results are not in disagreement with the predictions.

Accepting, at least for the present, the predicted equality of P_{22} and P_{33} one further measurement of either a normal stress or of a single difference between two normal stresses suffices to define all three. This is a consequence of our definition of isotropic pressure, eq. (15c), which requires that the sum of P_{11}, P_{22}, and P_{33} be zero. A number of authors have evaluated $P_{11} - P_{22}$ but except for the work of Brodnyan, Gaskins, and Philippoff[4] on the polyisobutylene–decalin system, no extensive data have been taken on any high polymer system. While their direct force (rheogoniometric) measurements scatter considerably, their birefringence measurements do not, and in four out of seven solutions, support the constancy of G over at least two decades of shear rate. They note that known impurities in two of the other solutions may cause the variability of G. Similar measurements are available on solutions of polystyrene in decalin and methylcellulose in water,[18] ethyl-cellulose in cyclohexanone and CMC in water,[5] crepe rubber in toluene,[45] and nitrocellulose in butyl acetate[45] but over more modest ranges of shear rate and at low levels of the shear rate. All but the cellulosic solutions support the suggested constancy of G or linearity between $(P_{11} - P_{22})/\tau_{12}$ and τ_{12}.

Recently, data at very high shear rates (5×10^3–10^5 sec.$^{-1}$) have become available[17,31,32] in polymeric solutions. In this case, the predicted constancy of G is not observed in a 5% polyisobutylene solution but data on CMC follow the predicted dependence over a wide range of shear rates. These high shear rate results are somewhat surprising when compared with data in the lower ranges of shear rate which were discussed in the previous paragraph, and further studies will be required.

Few data exist for molten polymers. While birefringence data[9] on a polyethylene melt at low shear rates show a constant value of G no other measurements appear to be available which are subject to rigorous interpretation.

In conclusion, nonpolar solutions appear to follow the predictions of eqs. (16–18) closely, over the wide ranges of shear rate investigated, provided the solutions are dilute or of modest concentration (viscosities below about 1 poise). For higher concentrations and at higher shear rates, the picture requires further clarification.* For polar systems (in particular solutions of cellulosic polymers), the constitutive equation fails at low shear rates. The recoverable shear $(P_{11} - P_{22})/\tau_{12}$ increases at a smaller rate than τ_{12}, i.e., in order to correlate these data, G must be an increasing function of shear rate. However, data at higher shear rates (ca. 10^4 sec.$^{-1}$) indicate that eq. (17) may be a good representation of these systems. While the available data for polymeric melts are inadequate to be conclusive they presently support the predicted constancy of G.

There is a great need for reliable experimental data on a larger number of polymeric systems. From an engineering viewpoint, especially important are data at high shear rates and on molten polymers. Until such results are available, few conclusive statements are possible about the applicability of the constitutive equation derived in this work, but the presently available results are quite encouraging.

APPLICATION OF CONSTITUTIVE EQUATION. ANALYSIS OF FLOW PROBLEMS

1. Laminar Flow in a Tube (Isothermal conditions)

Denoting the axial coordinate by x or 1, the radial coordinate by r or 2 and the tangential direction by θ or 3, the equations of motion[55] become:

$$0 = -\partial p/\partial x + (1/r)\, \partial/\partial r\, (r\, \tau_{12}) \tag{19a}$$

$$0 = -\partial p/\partial r + \partial P_{22}/\partial r + (P_{22} - P_{33})/r \tag{19b}$$

* After the present manuscript was completed, another study by Kotaka et al. (*Rheologica Acta*, **2**, 179 (1962)) was published. High molecular weight polystyrene solutions in toluene generally support the proposed constancy of G at modest concentrations, in agreement with the above discussion. Their low molecular weight polystyrene solutions do not exhibit a constant value of G.

Integrating both equations with respect to the radius r yields:

$$\tau_{12} = (r/2)(\partial p/\partial x) \tag{20a}$$

$$p(r, x) = p(0, x) + P_{22} + \int_0^r [P_{22} - P_{33}]\, d\ln r \tag{20b}$$

From eq. (20a) the velocity distribution and flow rate may be obtained if a relationship between the shear stress and shear rate is assumed. Furthermore, the general scale-up methods derived for purely viscous non-Newtonian materials[33,36] may be used for viscoelastic fluids. Equation (20b) may be used to calculate the variation of normal stresses with radial position:

$$\tau_{11} = -p + P_{11} = -p(0) + P_{11} - P_{22} - \int_0^r [P_{22} - P_{33}]\, d\ln r \tag{21a}$$

$$\tau_{22} = -p + P_{22} = -p(0) - \int_0^r [P_{22} - P_{33}]\, d\ln r \tag{21b}$$

From eqs. (17), (20a) and (21):

$$\tau_{11} = -p(0) + 2\tau^2_{12}/G = -p(0) + (2\tau_w^2/G)(r/R)^2 \tag{22a}$$

or (33):

$$\tau_{11} = -p(0) + 2(K'^2/G)(8V/D)^{2n'}(r/R)^2 \tag{22b}$$

$$\tau_{22} = -p(0) \tag{22c}$$

The force per unit area measured on a pressure gage at the wall or with the static pressure taps of a pitot tube will be equal to $(-\tau_{22})$, the radially directed stress exerted by the fluid. Equation (22c) shows that this will just be equal to the isotropic pressure at the centerline of the tube $p(0)$, for all fluids for which $P_{22} - P_{33} = 0$. However, an impact opening of a pitot tube would measure, after subtraction of the kinetic energy term, the longitudinal stress $(-\tau_{11})$. At the centerline, where P_{11}, P_{22}, and P_{33} are all zero because the fluid deformation is zero, this would just be equal to $p(0)$. However, at all other radial positions, this instrument would not measure the centerline pressure, and the deviation of the measurement from $p(0)$ will increase as the square of the distance from the centerline and, at given radial position, with the square of the pressure gradient or τ_w.

2. Dynamics of a Viscoelastic Jet

When a fluid stream leaves the end of a horizontal tube, the velocity profile and the normal stresses decay until, sufficiently for downstream, the jet approaches a constant diameter in the absence of gravitational effects. This problem has received some attention in the recent literature.[14,17,29–32,35] The extrudate diameter may be obtained by means of a macroscopic momentum balance between the end of the tube and a section across the jet taken after it has reached a constant diameter, as follows:

$$\int_0^R 2\pi r\, \tau_{11}\, dr = \int_0^R 2\pi r\, \rho u^2\, dr - \rho(\pi d_j^2/4)v_j^2 \tag{23}$$

Eliminating the jet velocity from eq. (23) by means of the continuity equation and solving for (D/d_j) gives

$$(D/d_j)^2 = 2 \int_0^1 (u/V)^2 (r/R)\, d\,(r/R) - (2/\rho V^2) \int_0^1 (r/R)\, \tau_{11}\, d\,(r/R) \tag{24}$$

If the fluid considered were Newtonian, then it would be expected that the final term on the right hand side of eq. (24) would be zero and the first integral would be equal to $^4/_3$ numerically. Experiments on aqueous glycerine and corn syrup solutions[31,32,34] have shown that the left hand side of eq. (24) is somewhat smaller than $^4/_3$ (i.e., an abnormally large jet is found) at Reynolds numbers below 150. At higher Reynolds numbers the $^4/_3$ value is obtained. Experiments with purely viscous nonNewtonian fluids give similar results.[32] First considering the situation at Reynolds numbers greater than 150, eq. (22a) may be substituted into eq. (24) to give

$$(D/d_j)^2 = 2 \int_0^1 (r/R)\, (u/V)^2\, d\,(r/R) - (8/N_{Re'})\, [(K'/G)(8V/D)^{n'}] \tag{25}$$

The last term in eq. (25) is the ratio of the elastic to the inertial forces, the quantity in brackets being the ratio of the elastic to twice the viscous forces and is equivalent to half of Weissenberg's recoverable shear parameter evaluated at the wall of the tube. Thus, the larger the value of the recoverable shear at the tube wall, the greater the resulting expansion.

The shear stress–shear rate relationship, hence the velocity term appearing in eq. (25) may be closely approximated by a simple empirical equation. One such simple (two-parameter) relation which is usually found to work well in problems dealing with flow through tubes is the power law*.[28,29] In this case the integral in eq. (25) is equal to $(3n + 1)/(2n + 1)$.

At lower Reynolds numbers (i.e., with molten polymers) the first term on the right of eq. (25) may be obtained using the available results of measurements on purely viscous fluids.[17,32] While this serves to define the term correctly in principle, it is not yet obvious whether the correction is of significance, as no extensive data on viscoelastic fluids are yet available in this region.

3. Normal Stresses in Screw Extruders

Another industrially important example of flow of a molten polymer is between the barrel and rotating screw of an extruder. In recent years attempts have been made to analyze the hydrodynamics of screw extrusion

* The reasons for its comparative success have frequently been stated but still do not appear to be generally appreciated, possibly in view of the fact that it must always break down at low shear rates. In the special case of flow through tubes, when one integrates to obtain the total flow it is the product of velocity and radial position which appears in the integrand. Since this product approaches zero near the centerline (where the shear rates approach zero) the breakdown of the power law or use of an incorrect velocity in this region is inconsequential. This is the only reason for the utility of the power law but it fortunately embraces the majority of problems of practical interest. Obviously its attempted use in other geometries (e.g., flow through annuli or between flat plates) where this fortuitous pairing of the velocity with a term approaching zero at low shear rates does not exist, would be abortive. Some of the resulting ludicrous predictions have been reviewed elsewhere.[28]

and to derive quantitative design procedures (for a recent review, see Squires[64]). Most of these analyses have been based upon solutions of the Navier-Stokes equations for Newtonian fluids. Indeed the complexity of the geometry does not allow for very exact analyses much more difficult than this.

One very simple geometry which has been suggested as an approximation of the actual operation consists of two plates separated by a distance h, the upper plate moving parallel to the lower plate with a velocity U. The melt is assumed to flow between the plates against a pressure gradient $\partial p/\partial z$ at an angle ϕ to the direction of the upper plate.

The equations of motion become, for steady flow in this geometry:

$$0 = -\partial p/\partial z + \partial \tau_{12}/\partial y \tag{26a}$$

$$0 = -\partial p/\partial y + \partial P_{22}/\partial y \tag{26b}$$

with boundary conditions:

$$v_z(h) = U \cos \phi \tag{27a}$$

$$v_z(0) = 0 \tag{27b}$$

In order to calculate the velocity distribution and flow rate in the channel it is necessary to relate the shear stress to the velocity gradient. In this geometry use of the power law would *not* lead to a good approximation and other empirical formulae, capable of predicting the behavior of fluids at low shear rates as well as at higher levels, must be employed. For purposes of clarity in illustration, however, the simplest possible choice, that of a constant viscosity, will be made. This choice also represents the behavior of real systems at low shear rates. Since the detailed calculations of the velocity profiles are summarized elsewhere[64] only the results, needed subsequently for calculation of the normal stresses, need be given. They are:

$$v = (yU\cos\phi)/h + (1/2\mu)(\partial p/\partial z)(y^2 - yh) \tag{28}$$

$$Q = \int_0^h vw\,dy = hwU\cos\phi/2 - (wh^3/12\mu)/\partial p/\partial z \tag{29}$$

Or, in terms of the average velocity $\bar{v}$:

$$v = U\cos\phi[3(y/h)^2 - 2(y/h] - 6\bar{v}[(y/h)^2 - (y/h)] \tag{30}$$

and

$$Q = \bar{v}wh \tag{31}$$

From eqs. (15) and (30), the normal stresses are given by:

$$\tau_{22} = \tau_{33} = -p^* \tag{32}$$

$$\tau_{11} = -p^* + 2(\mu^2/G)[(U\cos\phi/h)(6y/h - 2) - 6(\bar{v}/h)(2y/h((2y/h) - 1)]^2 \tag{33}$$

where p^* denotes the isotropic pressure at y*, the position in the channel at which the melt has a zero velocity gradient.

The isotropic pressure $p(p = -{}^1/_3(\tau_{11} + \tau_{22} + \tau_{33}))$ is thus seen to be a function of the position parameter y/h. Therefore the density of the fluid must, in principle, also vary with *radial* position in an extruder. This could obviously be of great significance near transition points or in precise calculations which allow for internal heat generation by viscous forces and the heat consumption due to volumetric expansion of the polymer.[69] Since too few data are available to enable reliable estimates of the modulus G at the shear rates of interest, it is not yet possible to state conclusively whether these effects are likely to be of major significance in molten polymers or not. Obviously there is a need for experimental data from which the elastic stresses may be calculated.

4. Helical Flow

Another hydrodynamic problem related to screw extrusion is flow between two rotating coaxial cylinders in the presence of an axial pressure gradient. This kinematic situation, known as helical flow, thus consists of Couette flow superimposed upon flow through an annulus. Helical flow of viscoelastic fluids was first investigated by Rivlin[59] and, more recently, interesting discussions were given by Coleman and Noll.[6] Denoting the axial direction by 1, the radial direction by 2 and the angular direction by 3, the kinematics of helical flow may be specified by the D tensors

$$\mathbf{D}_1 = \begin{vmatrix} 0 & -dv_1/dr & 0 \\ -dv_1/dr & 0 & -r(d\omega/dr) \\ 0 & -r(d\omega/dr) & 0 \end{vmatrix} \tag{34}$$

$$\mathbf{D}_2 = -\begin{vmatrix} 2(dv_1/dr)^2 & 0 & 2r(dv_1/dr)/(d\omega/dr) \\ 0 & 0 & 0 \\ 2r\ (dv_1/dr)\ (d\omega/dr) & 0 & 2\ (r\ d\omega/dr)^2 \end{vmatrix} \tag{35}$$

$$\mathbf{D}_N = 0 \qquad N > 2 \tag{36}$$

The stress tensor may be easily calculated from eqs. (10–11) to be

$$\begin{vmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{vmatrix} = -\begin{vmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{vmatrix} + \begin{vmatrix} 2\tau_{12}^2/G & \tau_{12} & 2\tau_{12}\tau_{23}/\mu G \\ \tau_{12} & 0 & \tau_{23} \\ 2\tau_{12}\tau_{32}/\mu G & \tau_{23} & 2\tau_{23}^2/G \end{vmatrix} \tag{37}$$

It is interesting to note that there is a shear stress τ_{13} caused by the elastic properties of the fluid which is not present in helical flow of a Newtonian fluid.

The three components of the equations of motion become:

$$\rho r\omega^2 = -\partial\alpha/\partial r + \partial\tau'_{22}/\partial r + (\tau'_{22} - \tau'_{33})/r \tag{38a}$$

$$0 = -(1/r^2)(\partial/\partial r)(r^2\tau_{23}) \tag{38b}$$

$$0 = -\partial\alpha/\partial z + (1/r)(\partial/\partial r)(r\tau_{12}) \tag{38c}$$

To solve this problem, the following boundary conditions are applied

$$v_1\ (R) = v_1\ (\kappa\ R) = 0$$
$$v_3\ (R) = 0;\ \ v_3\ (\kappa R) = \kappa R\Omega$$

If a relationship between the shear stress and shear rate is known, the force equilibrium equations may be solved directly for the velocity profiles. It should be noted, however, that since the viscosity, which is a function of the invariants of the stress tensor, no longer varies radially with only τ_{12} or τ_{23}. Therefore, the solutions already available for annular flow, which are based on simple empirical models for laminar shearing flows (such as the power law) will no longer suffice for calculating of velocity profiles and flow rates.*

The difference between the normal stresses perpendicular to the walls of the inner and outer cylinders may be calculated. Neglecting centrifugal forces, one obtains

$$(\tau_{22})_R - (\tau_{22})\kappa R = \int_{\kappa R}^{R} ((\tau'_{33} - \tau'_{22})/r)dr \tag{39}$$

$$= \int_{\kappa R}^{R} 2\tau^2_{23}dr/Gr \tag{40}$$

From eq. (38b), it follows that

$$(\tau_{22})_R - (\tau_{22})\kappa R = \int_{\kappa R}^{R} [2(\tau_{23})R^2R^4/Gr^5]dr \tag{41}$$

$$[(\tau_{23})_R^2/2G]\left[\frac{1}{\kappa^4} - 1\right]$$

A similar result may be derived for the other independent normal stress term τ_{11}. Again, an appreciable radial variation in the isotropic pressure is possible in molten polymers or other highly elastic fluids.

5. Analysis of the Normal Stress Pump

A fifth problem of interest to engineers is that of the forces developed in the steady shearing flow of a viscoelastic fluid between two parallel rotating disks as in a centripetal pump†.[26,74] The usual notation convention is introduced: The direction of flow (i.e., the angular direction) is denoted 1, the radial direction 3, and the direction perpendicular to the disks by 2. The three components of the equations of motion[55] become:

$$-\rho v_1^2/r = -\partial p/\partial r + \partial P_{33}/\partial r + (P_{33}-P_{11})/r \tag{42a}$$

$$0 = \partial p/\partial z + \partial P_{22}/\partial z \tag{42b}$$

$$0 = \partial \tau_{12}/\partial z \tag{42c}$$

The force perpendicular to the plates is:

$$F = - \int_0^a 2\pi r \tau_{22} dr \tag{43}$$

* The work on simple annular flow problems is comprehensively reviewed by Fredrickson and Bird[13] and Metzner.[28]

† The equations presented in this section describe the stresses developed in a centripetal or "normal stress" pump only under the limiting condition of no throughput. As the pressures developed under this condition represent the maximum available, they are of considerable interest, however. A similar phenomenon is found when rubber rods are twisted, experiments having shown that an axial tension develops which tends to elongate the rod.[56] This latter observation is known as the Poynting effect.

where from eq. (42a) it follows that (neglecting centrifugal forces):

$$\begin{aligned}\tau_{22}(r) &= -p(r) + P_{22}(r)\\ &= P_{22} - P_{33} + \int_a^r (P_{11}-P_{33})d\ln r \end{aligned} \tag{44}$$

Combining eqs. (43) and (44), one obtains:

$$F = -\int_o^a 2\pi r(P_{22}-P_{33} + \int_a^r [P_{11}-P_{33}]d\ln r)\, dr \tag{45}$$

Introducing eq. (17) yields:

$$F = -\int_o^a 2\pi r \int_a^r (2\tau_{12}^2/G)d\ln r\, dr \tag{46}$$

In order to integrate eq. (46) it is necessary to relate the shearing stress τ_{12} to the radius of the disc. To do this one must assume a relation between the shear stress and the shear rate. In this geometry the "power law" may be written:*

$$\tau_{12} = K\Gamma^n = K(r\omega/l)^n \tag{47}$$

Substitution of eq. (47) into eq. (46) yields:

$$F/\pi a^2 = [K^2/(n+1)G](a\omega/l)^{2n} = [P_{11}-P_{22}]_a/(2n+2) \tag{48}$$

Equation (48) gives the force F which must be applied to the plates of radius a in order to keep them separated by the desired distance l.

If this device is to be used as a "screwless extruder" or centripetal pump by connecting a small die of diameter D and equivalent length L to the center of one of the disks, an interesting problem which arises is that of determining the total volumetric pumping rate Q through the die. For this purpose one is not interested in the average force applied (eq. 48) but rather the pressure at the entry to the tube. Since the tube or die diameter is usually very small compared to that of the disks one may obtain this pressure $(-\tau_{22})$ by setting the upper limit of integration on eq. (44) to zero. Again, introducing eq. (17) and the power law and integrating, one obtains:

$$(-\tau_{22})_{r=o} = (K^2/Gn)(a\omega/l)^{2n} \tag{49}$$

Since this pressure is equal to the pressure drop through the die, using the well-known equation for flow of power law fluids through cylindrical tubes[28, 29, 64]

$$D\Delta P/4L = K[(3n+1/4n)(32Q/\pi D^3)]^n \tag{50}$$

gives:

$$Q = (\pi D^3/8)[n/(3n+1)](a\omega/l)^2(K/4Gn)^{1/n}(D/L)^{1/n} \tag{51}$$

It may be noted that the predicted extrusion rate is proportional to the second power of the angular velocity of the rotor and inversely proportional to l^2.

* One may wish to note that in this geometry, unlike the case of flow through round tubes, the power law is not a good approximation as the region in which it breaks down contributes significantly to the overall problem. Thus, eq. (48) and the subsequent use made of it are given here for illustrative purposes rather than for rigorous design usage.

Recently, Srivastava[65] has considered the additional effects of secondary flows between two rotating disks when the fluid obeys the constitutive equation of Reiner and Rivlin.[53,57,71] Unfortunately, as was first pointed out by Roberts[61] and is now generally acknowledged, the Reiner-Rivlin equations do not appear to depict properties found in real fluids. Srivastava's work is still of interest in that it represents a first approximation and as such indicates a method of approach which may be used with better constitutive equations.

CONCLUDING REMARKS

A constitutive equation for a viscoelastic fluid, of sufficient simplicity to be used for engineering design, has been proposed and compared with experimental data. The comparison appears to be favorable for nonpolar hydrocarbon systems over a significant range of shear rates. In systems containing groups of high polarity, it is found that at low shear rates (below about 100 sec.$^{-1}$) the predicted equality of P_{22} and P_{33} is apparently fulfilled, but the normal stress difference (P_{11}–P_{22}) increases at a smaller rate than predicted by eq. (16). However, at higher shear rates, limited data indicate that the behavior of such systems may be represented by the proposed constitutive equation.

Under conditions of laminar shearing flow, the present constitutive equation is identical to Weissenberg's theory of viscoelasticity. The results obtained in this analysis should be regarded as a verification and extension of Weissenberg's theory. Rather than working by analogy to the behavior of an elastic solid, the analogy has been derived and the final form of the constitutive equation allows for extension to more complex problems.

While normal stresses in most cases do not interfere with flow patterns in steady flows they may alter the distribution of forces and pressures significantly. In unsteady flows, such as in "exit effect" and "inlet effect" problems, in boundary layers, creeping flows, and in turbulent and oscillatory flows, the effects of the viscoelastic properties are also significant. Recently Sharma,[63] Leslie,[20] and Rajeswari and Rathna[52] have attacked unsteady flow problems, but results in this field are still at a very early stage of development.

Nomenclature

a	= radius of disk
D	= diameter of tube
$\mathbf{D}(\ )/\mathbf{D}t$	= $\partial (\ )/\partial t + V \cdot \nabla (\ )$
$\mathbf{D}_N$	= $\lVert - D^N\gamma^{\alpha\beta}/Dt^N \rVert$
d_j	= jet diameter
d^{ij}	= $^1/_2\,(V_{,m}^{\,i} g^{mj} + V_{m,}^{\,j} g_m^i)$, the rate of strain tensor
F	= vertical upward force in flow between rotating disks
G	= modulus of elasticity
g_{ij}	= metric tensor of fixed curvilinear coordinate system

g^{ij}	=	conjugate metric tensor of fixed curvilinear coordinate system
1_k	=	unit vector in a Cartesian fixed space coordinate system
K	=	power law constant
K'	=	$\tau_w/(8V/D)^{n'}$.
l	=	distance between (spacing of) parallel plates
n	=	exponent in power law
n'	=	$d\,[\ln(\tau_w)]/d\,[\ln(8V/D)]$.
N'_{Re}	=	$D^{n'}V^{2-n'}\rho/8^{n'-1}K'$
$\mathbf{P}$	=	$\lVert P_{ij}\rVert$ = deviatoric stress tensor
p	=	isotropic pressure $= -{}^1/_3\, tr\, \tau$
Q	=	volumetric flowrate
R	=	radius of tube (or of outer tube of an annulus)
r	=	radius
s	=	lineal distance (in Eq. 2 only)
s	=	$(P_{11}-P_{22})/\tau_{12}$, the "recoverable shear"
t	=	time
u	=	local velocity in tube
U	=	plate velocity
V	=	$\int_0^R 2\pi r u dr/\pi R^2$, the mean or "bulk" velocity
V^j	=	j component of velocity vector
v_1	=	tangential velocity in torsional shearing flow between parallel plates
$V_{i,m}$ or $V^i_{,m}$	=	covariant derivative of velocity in i direction with respect to m coordinate
x or x^j	=	Cartesian fixed space coordinates
y	=	curvilinear fixed space coordinates
z	=	distance measured normal to surface of plates
α	=	hydrostatic pressure
Γ	=	shear rate
$\gamma_{\alpha\beta}$	=	metric tensor in convected coordinate system
$\gamma^{\alpha\beta}$	=	conjugate metric tensor in convected coordinate system
$\nabla(\ )$	=	$1_1\,\partial(\ )/\partial x_1 + 1_2\,\partial(\ )/\partial x_2 + 1_3\,\partial(\ )/\partial x_3$
δ^{ij}, δ^i_j, δ_{ij}	=	Kronecker delta (equal to unity when $i = j$ and equal to zero when $i \neq j$)
η_k	=	dummy variable used to denote time
θ	=	tangential direction
κ	=	ratio of inner to outer radii of an annulus
λ	=	relaxation time
μ	=	viscosity
ϵ^a	=	convected coordinates
π	=	3.14 . . . .
$\pi^{\alpha\beta}$	=	convected components of stress tensor
$\pi'^{\alpha\beta}$	=	$\pi^{\alpha\beta} + \alpha\gamma^{\alpha\beta}$
ρ	=	density
$\boldsymbol{\tau}$	=	stress tensor
τ^{ij}, τ_{ij}	=	fixed space components of stress tensor
τ'_{ij}	=	$\tau_{ij} + \alpha g_{ij}$

τ_w = shearing stress at wall of tube
ϕ = dummy variable used to denote time
ψ = relaxation function
ω = angular velocity

APPENDIX A

Transformation of Constitutive Equation From a Convected To a Fixed Frame

In this appendix, the transformation of eq. (8) to give eqs. (9) and (11) will be given in detail. Substitution of $\mu = \lambda G$, into eq. (8) gives:

$$\pi'^{\alpha\beta} = -\mu(D\gamma^{\alpha\beta}/Dt) - (\mu/G)(D\pi'^{\alpha\beta}/Dt) \quad \text{(A-1)}$$

Relating eq. (A-1) to a fixed Cartesian frame:

$$(\partial\epsilon^\alpha/\partial x^i)(\partial\epsilon^\beta/\partial x^j)\tau'^{ij} = -\mu D/Dt[(\partial\epsilon^\alpha/\partial x^i)(\partial\epsilon^\beta/\partial x^j)\delta^{ij}] - (\mu/G)D/Dt[(\partial\epsilon^\alpha/\partial x^i)(\partial\epsilon^\beta/\partial x^j)\tau'^{ij}] \quad \text{(A-2)}$$

and:

$$(\partial\epsilon^\alpha/\partial x^i)(\partial\epsilon^\beta/\partial x^j)\tau'^{ij} = -\mu[(\partial\epsilon^\alpha/\partial x^i)\overset{o}{\overline{\partial\epsilon^\beta}}/\partial x^j(\delta^{ij} +)\overset{o}{\overline{\partial\epsilon^\alpha}}/\partial x^i(\partial\epsilon^\beta/\partial x^j)\delta^{ij}]$$

$$-\mu/G[(\partial\epsilon^\alpha/\partial x^i)(\partial\epsilon^\beta/\partial x^j)D\tau'^{ij}/Dt + \overset{o}{\overline{(\partial\epsilon^\alpha/\partial x^i)}}(\partial\epsilon^\beta/\partial x^j)\tau'^{ij} + (\partial\epsilon^\alpha/\partial x^i)\overset{o}{\overline{(\partial\epsilon^\beta/\partial x^j)}}\tau'^{ij}] \quad \text{(A-3)}$$

The quantity $\overset{o}{\overline{\partial\epsilon^\alpha}}/\partial x^i$ is:[40,76]

$$\overset{o}{\overline{\partial\epsilon^\alpha}}/\partial x^i = -(\partial V^m/\partial x^i)(\partial\epsilon^\alpha/\partial x^m) \quad \text{(A-4)}$$

From eqs. (A-3) and (A-4)

$$(\partial\epsilon^\alpha/\partial x^i)(\partial\epsilon^\beta/\partial x^j)\tau'^{ij} = (\partial\epsilon^\alpha/\partial x^i)(\partial\epsilon^\beta/\partial x^j)[\mu(\partial V^i/\partial x^m)\delta^{mj} + \mu(\partial V^j/\partial x^m)\delta^{im} - \mu/G(D\tau'^{ij}/Dt - \tau'^{mj}\partial V^i/\partial x^m - \tau^{im})\partial V^j/\partial x^m]$$

or:

$$\tau'^{ij} = 2\mu d^{ij} - (\mu/G)(\delta\tau'^{ij}/\delta t) \quad \text{(A-6)}$$

where:

$$d^{ij} = {}^1/_2[(\partial V^i/\partial x^m)\delta^{mj} + (\partial V^j/\partial x^m)\delta^{im}] \quad \text{(A-7)}$$

$$\delta\tau'^{ij}/\delta t = (D\tau'^{ij}/Dt) - (\partial V^i/\partial x^m)\tau'^{mj} - (\partial V^j/\partial x^m)\tau'^{im} \quad \text{(A-8)}$$

If one is concerned with curvilinear coordinates, eq. (A-6) remains un-changed; but eqs. (A-7) and (A-8) become,[27] for a coordinate system having a metric tensor g_{ij}:

$$d^{ij} = {}^1/_2(V_{,m}^{\ i} g^{mj} + V_{,m}^{\ i} g^{im}) \tag{A-9}$$

$$\delta\tau'^{ij}/\delta t = (D\tau'^{ij}/Dt) - V_{,m}^{\ i}\tau'^{mj} - V_{,m}^{\ i}\tau'^{im} \tag{A-10}$$

where $V_{,m}^{\ i}$ is a covariant derivative and g^{ij} is the conjugate metric tensor.

References

1. Alfrey, T., *Mechanical Behavior of High Polymers*, Interscience, N. Y., 1948.

2. Alfrey, T., and E. F. Gurnee, in *Rheology*, Vol. I, Academic Press, N. Y., 1956.

3. Bogue, D. C., *Ind. Eng. Chem.*, **51**, 874 (1959).

4. Brodnyan, J. G., F. H. Gaskins, and W. Philippoff, *Trans. Soc. Rheol.*, **1**, 109 (1957).

5. Brodnyan, J. G., F. H. Gaskins, W. Philippoff, and E. G. Lendrat, *Trans. Soc. Rheol.*, **2**, 285 (1958).

6. Coleman, B. D., and W. Noll, *J. Appl. Phys.*, **30**, 1508 (1959); and *Arch. Rat. Mech. Anal.*, **3**, 289 (1959).

7. Coleman, B. D., and R. A. Toupin, Paper presented at 1961 Soc. of Rheology Meeting, Madison, Wis.

8. DeWitt, T. W., *J. Appl. Phys.*, **26**, 889 (1955).

9. Dexter, F. D., J. C. Miller, and W. Philippoff, *Trans. Soc. Rheol.*, **5**, 193 (1960).

10. Dodge, D. W., and A. B. Metzner, *A.I.Ch. E. J.*, **5**, 189 (1959).

11. Ericksen, J. L., in *Viscoelasticity, Phenomenological Aspects*, J. T. Bergen, ed., Academic Press, N. Y., 1960.

12. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, 1953.

13. Fredrickson, A. G., and R. B. Bird, *Ind. Eng. Chem.*, **50**, 347 (1958).

14. Gaskins, F. H., and W. Philippoff, *Trans. Soc. Rheol.*, **3**, 181 (1959).

15. Green, A. E., and R. S. Rivlin, *Arch. Rat. Mech. Anal.*, **1**, 1 (1957).

16. Green, A. E., and W. Zerna, *Theoretical Elasticity*, Oxford University Press, London, 1954.

17. Houghton, W. T., M.Ch.E. Thesis, University of Delaware, Newark, Delaware (1961); see also R. E. Hurd, B.Ch.E. Thesis, University of Delaware (1962).

18. Kotaka, T., M. Kurata, and M. Tamura, *J. Appl. Phys.*, **30**, 1705 (1959).

19. Lee, E. H. in *Viscoelasticity, Phenomenological Aspects*, Academic Press, New York, 1960; and *Rheol. Acta*, **1**, 426 (1961).

20. Leslie, F. M., *Quart. J. Mech. Appl. Math.*, **14**, 36 (1961).

21. Lodge, A. S., *Proceedings Second International Rheological Congress*, Butterworth, London, 1954, p. 229.

22. Lodge, A. S., *Trans. Faraday Soc.*, **52**, 120 (1956); and in *The Rheology of Elastomers*, Pergamon, London, 1958.

23. Lodge, A. S., *Rheol. Abs.*, **4**, (3) 29 (1961).

24. Markovitz, H., *Trans. Soc. Rheol.*, **1**, 37 (1957); and with R. B. Williamson, *ibid.*, **1**, 25 (1957); see also in *Viscoelasticity, Phenomenological Aspects*, Academic Press, New York, 1960.

25. Markovitz, H., and D. R. Brown, *Proc. Int. Symp. on Second-Order Effects in Elasticity, Plasticity and Fluid Dynamics, Haifa.* Pergamon Press, N. Y., and Jerusalem Academic Press, 1962.

26. Maxwell, B., and A. J. Scalora, *Mod. Plastics*, **37**, (2) 107 (1959).

27. McConnell, A. J., *Applications of Tensor Analysis*, Dover, New York, 1931.

28. Metzner, A. B., in *Processing of Thermoplastic Materials*, E. C. Bernhardt, Ed., Reinhold, N. Y., 1959.

29. Metzner, A. B., in *Handbook of Fluid Dynamics*, V. L. Streeter, Ed., McGraw-Hill, New York, 1961.

30. Metzner, A. B., E. L. Carley, and I. K. Park, *Mod. Plastics*, **37**, No. 11, 133 (1960).

31. Metzner, A. B., W. T. Houghton, R. A. Sailor, and J. L. White, *Trans. Soc. Rheol.*, **5**, 133 (1961).

32. Metzner, A. B., W. T. Houghton, R. E. Hurd, and C. C. Wolfe. *Proc. Int. Symp. on Second-Order Effects in Elasticity, Plasticity and Fluid Dynamics, Haifa.* Pergamon Press, N. Y., and Jerusalem Academic Press, 1962.

33. Metzner, A. B., and J. C. Reed, *A.I.Ch.E. J.*, **1**, 434 (1955); see also *Ind. Eng. Chem.*, **49**, 1429 (1957).

34. Middleman, S., and J. Gavis, *Phys. Fluids*, **4**, 355 (1961).

35. Middleman, S., and J. Gavis, *Phys. Fluids*, **4**, 963 (1961).

36. Mooney, M., *J. Rheol.*, **3**, 210 (1931).

37. Mooney, M., *J. Colloid Sci.*, **6**, 96 (1951).

38. Noll, W., *J. Rat. Mech. Anal.*, **4**, 3 (1955).

39. Noll, W., *Arch. Rat. Mech. Anal.*, **2**, 197 (1958).

40. Oldroyd, J. G., *Proc. Roy. Soc.* (*London*), **A200**, 523 (1950).

41. Oldroyd, J. G., *Quart. J. Mech. Appl. Math.*, **4**, 271 (1951).

42. Oldroyd, J. G., *Proc. Roy. Soc.* (*London*), **A245**, 278 (1958).

43. Oldroyd, J. G., D. J. Strawbridge, and B. A. Toms, *Proc. Phys. Soc.* (*London*), **64B**, 44 (1951). See also B. A. Toms, *Rheol. Acta*, **1**, 137 (1958); also with D. J. Strawbridge, *Proceedings*, Second International Rheological Congress, Butterworth, London, 1953, p. 99; and *Trans. Faraday Soc.*, **49**, 1225 (1953).

44. Pao, Yoh-Han, *J. Appl. Phys.*, **28**, 591 (1957).

45. Philippoff, W., *J. Appl. Phys.*, **27**, 984 (1956); and *Rheol. Acta*, **1**, 371 (1961).

46. Philippoff, W., *Trans. Soc. Rheol.*, **1**, 95 (1957); and *ibid.*, **5**, 163 (1961).

47. Philippoff, W., *Trans. Soc. Rheol.*, **5**, 149 (1961).

48. Philippoff, W., F. H. Gaskins, and J. G. Brodnyan, *J. Appl. Phys.*, **28**, 1118 (1957).

49. Pilpel, N., *Trans. Faraday Soc.*, **50**, 1321 (1954).

50. Pilpel, N., *Trans. Faraday Soc.*, **51**, 1307 (1955).

51. Pollett, W. F. O., *Proceedings*, Second International Rheological Congress, Butterworth, London, 1954, p. 85.

52. Rajeswari, G. K., and S. L. Rathna, *Z. Angew. Math. Phys.*, **13**, 43 (1962).

53. Reiner, M., *Am. J. Math.*, **67**, 350 (1945).

54. Reiner, M., *Bull. Res. Council Israel*, **2**, 65 (1952); also *Proc. Roy. Soc.* (*London*), **A240**, 173 (1957); and *ibid.*, **A247**, 152 (1958).

55. Reiner, M., *Lectures on Theoretical Rheology*, North Holland, Amsterdam, 1960.

56. Rivlin, R. S., *J. Appl. Phys.*, **18**, 444 (1947).

57. Rivlin, R. S., *Proc. Roy. Soc.* (*London*), **A193**, 260 (1948).

58. Rivlin, R. S., in *Rheology*, Vol. I, F. R. Eirich, Ed., Academic Press, New York, 1956.

59. Rivlin, R. S., *J. Rat. Mech. Anal.*, **5**, 179 (1956).

60. Rivlin, R. S., and J. L. Ericksen, *J. Rat. Mech. Anal.*, **4**, 323, 681 (1955). See also J. L. Ericksen, *Trans. Soc. Rheol.*, **4**, 29 (1960).

61. Roberts, J. E., *Min. Sup. Rep.*, #ADE 13/52 (1952); also *Proceedings*, Second International Rheological Congress, Academic Press, New York, 1954, p. 91; and *Nature*, **179**, 487 (1957).

62. Sailor, R. A., Ph.D. Thesis, University of Delaware, Newark, Delaware, in preparation.

63. Sharma, S. K., *J. Phys. Soc. Japan*, **14**, 1421 (1959); and *Appl. Sci. Res.*, **9**, 43 (1959).

64. Squires, P. H., in *Processing of Thermoplastic Materials*, E. C. Bernhardt, Ed., Reinhold, N. Y., 1959.

65. Srivastava, A. C., *Quart. J. Mech. Appl. Math.*, **14**, 353 (1961).

66. Tobolsky, A. V., *Properties and Structure of Polymers*, Wiley, New York, 1960, pp. 206–217; also M. S. Green and A. V. Tobolsky, *J. Chem. Phys.*, **14**, 80 (1946).

67. Tobolsky, A. V., and H. Eyring, *J. Chem. Phys.*, **11**, 125 (1943).
68. Tomita, Y., *Bull. JSME*, **4**, 77 (1961).
69. Toor, H. L., *Ind. Eng. Chem.*, **48**, 922 (1956); *Trans. Soc. Rheol.*, **1**, 177 (1957).
70. Treloar, L. R. G., *Physics of Rubber Elasticity*, 2nd ed., Oxford University Press 1958.
71. Truesdell, C., *J. Rat. Mech. Anal.*, **1**, 125 (1952).
72. Volterra, V., *Theory of Functionals*, Dover, New York, 1930.
73. Walters, K. G., *Quart. J. Mech. Appl. Math.*, **15**, 64 (1962); and *Arch. Rat. Mech Anal.*, **9**, 411 (1962).
74. Weissenberg, K., *Nature*, **159**, 310 (1947).
75. Weissenberg, K., *Proceedings*, First International Rheological Congress, I, 29, North Holand, Amsterdam, 1949.
76. White, J. L., M.Ch.E. Thesis, University of Delaware, Newark, Delaware (1962)
77. White, J. L., and A. B. Metzner, in *Progress in International Research on Thermodynamic and Transport Properties*, A.S.M.E. and Academic Press, N. Y., 1962, p. 748.
78. Yamamoto, M., *J. Phys. Soc. Japan*, **11**, 413 (1956).

Synopsis

The importance and characteristics of viscoelastic fluid behavior are briefly reviewed, as are theoretical predictions of the relationships between the stresses developed in such a fluid and its deformation rate and history. It is seen that most of the equations available for the prediction of these stresses (variously termed "constitutive equations" or "rheological equations of state") either do not predict the properties of real materials correctly or, alternately, are of such overriding complexity that they cannot be applied to the solution of any but the simplest real problems. A new constitutive equation in which all the significant parameters may be evaluated from only two sets of experiments is developed. Comparison with available experimental results, while not entirely conclusive, indicates that the equation may predict correctly the behavior of nonpolar solutions and polymeric melts and that it may work well on polar systems in the range of high deformation rates, i.e., the region of primary industrial interest. Several problems of interest to the plastics industry are worked to illustrate the use of this constitutive equation.

Résumé

L'importance et les caractéristiques du comportement d'un fluide viscoélastique sont brièvement passés en revue, ainsi que les prévisions théoriques des relations entre les tensions développées dans un tel fluide et sa vitesse de déformation et son historique. Il apparaît que la plupart des équations de prévision de ces tensions (différemment désignées par "équations de constitution" ou "équation rhéologiques d'état") ne prévoient pas correctement les propriétés du matériau réel ou alternativement sont d'une telle complexité qu'ils ne peuvent s'appliquer la solution d'aucun problème très simple. On décrit une nouvelle équation de constitution dans laquelle tous les paramftres significatifs peuvent être évalués à partir de 2 séries d'expériences. Quoique la comparaison des résultats expérimentaux ne soit pas entièrément concluante, celle-ci contre néanmoins que l'équation peut prévoir correctement le compartment de solutions nonpolaires et de pllyméres fondus et que l'on peut travailler sur des systèmes polaires dans le cas de deformations élevêes c.à.d. la région d'intéret industriel. Plusieurs problèmes intéressant l'industrie des plastiques sont étudiés afin d'illustrer l'usage de telles équations de constitution.

Zusammenfassung

Ein kurzer Überblick über die Bedeutung und die Charakteristika des viskoelastischen Verhaltens fluider Medien wird gegeben, ebenso über die theoretischen Erwartungen für die Beziehung zwischen den in einem solchen fluiden Medium auftretenden Spannungen und seiner Verformungsgeschwindigkeit und Geschichte. Es zeigt sich, dass die meisten zur Vorherbestimmung dieser Spannungen vorhandenen Gleichungen (verschiedentlich als "konstitutive Gleichungen" order "rheologische Zustandsgleichungen" bezeichnet) entweder keine korrekten Angaben für die Eigenschaften realer Stoffe liefern oder derartig komplexen Charakter haben, dass sie nur zur Lösung der allereinfachsten realen Probleme verwendet werden können. Eine neue konstitutive Gleichung wird entwickelt, bei der alle signifikanten Parameter aus nur zwei Versuchsreihen ermittelt werden können. Ein Vergleich mit vorhandenen Versuchsergebnissen ist zwar nicht völlig schlüssig, lässt aber erkennen, dass diese Gleichung das Verhalten unpolarer Lösungen und Polymerschmelzen richtig darstellen kann und dass sie bei polaren Systemen im Bereich hoher Deformationsgeschwindigkeiten, d.h. im technisch in erster Linie interessanten Gebiet, gut verwendbar sein wird. Die Verwendung solcher konstitutiver Gleichungen wird an einigen für die Kunststoff-industrie interessanten Problemen gezeigt.

Received August 10, 1962
Revised November 15, 1962