Dynamics of Viscoelastic Fluids, Melt Fracture, and the Rheology of Fiber Spinning

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Synopsis

The hydrodynamic theory for the flow of nonlinear viscoelastic fluids is developed. Two new dimensionless groups must be introduced into the complete second-order correction of viscoelastic flow. These groups are called the Weissenberg and viscoelastic ratio numbers. Applications to industrially important problems are discussed. It is argued that the Weissenberg number determines the onset of melt fracture.

1. Introduction

The continuing growth and competition in the plastics, fiber, and elastomer industries have made clear the necessity of a deeper understanding of the processing behavior of polymers and of obtaining quantitative methods for prediction of the rheological properties of these materials as they flow through dies and spinnerets, between calender rolls, and the screw and barrel of extruders. It is well known that polymer solutions and melts possess flow properties not found in common Newtonian liquids such as water, alcohols and petroleum oils. The shear stress–shear rate behavior is observed to be nonlinear,[7,9,49,50] and the fluids are known to possess memory of their deformation history and exhibit recoil upon sudden stoppage of flow.[59,66,94] If stirred in a beaker the same materials will flow radially inwards and appear to climb the stirring rod defying the effect of centrifugal forces,[94] and again, if these fluids are extruded from a tube, they will swell to a diameter far larger than the capillary bore.[4,51,52] Perhaps the most spectacular of the anomalous effects observed in fluid polymer systems is the melt fraction phenomenon in which a flow incompatibility originating in the entrance region of a die[2,11,79,89] or inside of the die[6,91] results in the emerging extrudate being rough and jagged.

Most existing hydrodynamic analyses of the polymer-processing operations[7,48,50] are based upon either solutions of the Navier-Stokes equations or use simple one-dimensional empirical relations between shear stress and shear rate; they are thus incapable of explaining many of the nonlinear effects observed.

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Ideally, what is required to investigate analytically these industrial problems is a hydrodynamic theory of non-Newtonian flow which represents a generalization of the Boltzmann superposition principle[23,86] for infinitesimal strains and rotations to the nonlinear range of behavior and in addition accounts for thixotropy[49] in deforming media. A general constitutive theory accounting for nonlinear viscous and viscoelastic effects, but not thixotropy, has been developed since 1955 by Rivlin and his co-workers.[33,38,39,70,71] Coleman, Noll, and Markovitz[13-16,44] and Giesekus,[27,28,30,31] the latter author having attempted to relate the continuum theory to the molecular structure of deforming polymer fluids.[29,30] Recently White[97] has given a new formulation of this theory of nonlinear viscoelasticity. Thixotropic behavior has received almost no analytical treatment, due in part to a lack of understanding of its significance and mechanisms; existing theoretical studies being limited to those of Mooney and Wolstenholme[60] and Hahn, Ree, and Eyring,[34] whose results, though thought-provoking, are not conclusive.

In this paper, we shall extend the basic concepts of nonlinear viscoelasticity that were developed earlier and look at their implications in two important industrial problems, melt fracture in extrusion and the spinning of fibers. This work continues in the vein of White and Metzner,[100] who applied a simpler theory of viscoelasticity to several industrial problems. A more detailed account of the methods and problems discussed in this paper is given in the author's thesis.[98]

2. Constitutive Theory

It is the purpose of this section to review and extend the basic concepts of the theory of nonlinear viscoelasticity from the point of view introduced in an earlier paper.[97] We postulate that the stress at a point in the deforming medium may be specified by the entire history of the deformation of the immediate material neighborhood of this point.* Assuming the material to be isotropic in the undeformed ground state, incompressible and the deformation to determine the stress in a manner such that strains in the distant past have less effect than strains in the recent past, we may express the stress tensor as an isotropic hereditary functional of the deformation history

$$\tau = -p\mathbf{I} + \mathop{\mathcal{G}}_{\phi=-\infty}^{\phi=t}[\mathbf{e}(t-\phi)] \tag{1}$$

The functional may be expressed in terms of an integral expansion

$$\tau = -p\mathbf{I} + \int_{-\infty}^{t} \Phi(t-\phi)\mathbf{e}\, d\phi + \int_{-\infty}^{t}\int_{-\infty}^{t} \Psi(t-\phi_1, t-\phi_2)\mathbf{e}\,\mathbf{e}\, d\phi_1\, d\phi_2 + \cdots \tag{2}$$

* The necessary discussion of kinematics of deformation is given in the earlier paper.[97] A more extensive treatment is presented in the text by Eringen.[22]

The rheological properties of the medium may be seen to be determined by a series of kernel functions Φ, Ψ, etc. The first kernel function Φ may be related to the relaxation modulus $G(\ )$ of linear viscoelasticity by specializing eq. (2) to infinitesimal strains and integrating by parts. It may be shown in this manner that

$$G(s) = (1/2) \int_s^\infty \Phi\ (m)dm \tag{3}$$

The relaxation modulus and other linear viscoelastic parameters have been the subject of numerous experimental studies notably by Ferry, Tobolsky, and their students which are summarized in the books[23,86] by these researchers. A well known approximate empirical expression used for the relaxation modulus is the so-called Maxwellian distribution

$$G(s) = ce^{-s/\lambda} \tag{4}$$

In this case $\Phi(\ )$ will likewise be exponential.

We see that from $G(\ )$, the Φ kernel may be uniquely determined. Knowledge of higher kernels is not similarly obtainable from linear viscoelastic functions though hopefully the methods of statistical mechanics and thermodynamics[22,98] may lead to useful relationships.

In treating the continuous deformation of a medium, the strain may be expressed (or if not, then approximated) by a Taylor series about the instantaneous strain. As we are using the instantaneous state as the reference state

$$\mathbf{e}(0) = 0$$

and

$$\mathbf{e}(s) = \sum [(-1)^{n+1} s^n / 2n!]\ \mathbf{B}_n \tag{5}$$

where $\mathbf{B}_n$ are kinematic tensors representing physically the rate and accelerations of the distortions of an area element embedded in the deforming medium. These tensors are thus related to the Rivlin-Ericksen tensors[71] which measure the rates and accelerations of deformation of an embedded differential line segment. For incompressible media, the $\mathbf{B}_1$ matrix may be shown to be the deformation rate tensor[97]

$$\mathbf{B}_1 = (\nabla \mathbf{V}) + (\nabla \mathbf{V})^T \tag{6a}$$

and the higher tensors are

$$\mathbf{B}_{n+1} = \frac{D}{Dt}\ [\mathbf{B}_n] - (\nabla \mathbf{V})\mathbf{B}_n - \mathbf{B}_n(\nabla \mathbf{V}) \tag{6b}$$

Equations (6) are equivalent to a series of kinematic tensors used by Giesekus[27,28,30] and White and Metzner.[100]

Substituting this expression for $\mathbf{e}(s)$ in the integral expansion will allow us to write the stress tensor in terms of the $\mathbf{B}_n$ matrices. If we expand these matrices in terms of order n in velocity, we have

$$\tau = -p\mathbf{I} + \sum \mathbf{M}_n \tag{7}$$

where the $\mathbf{M}_n$ are

$$\mathbf{M}_1 = \omega_1 \mathbf{B}_1 \tag{8a}$$

$$\mathbf{M}_2 = \omega_2 \mathbf{B}_1{}^2 + \omega_3 \mathbf{B}_2 \tag{8b}$$

$$\mathbf{M}_3 = \omega_4 (\mathrm{tr}\ \mathbf{B}_1{}^2)\mathbf{B}_1 + \omega_5 \mathbf{B}_3 + \omega_6\ (\mathbf{B}_1 \mathbf{B}_2 + \mathbf{B}_2 \mathbf{B}_1) \tag{8c}$$

$$\mathbf{M}_4 = (\omega_7\ \mathrm{tr}\ \mathbf{B}_1{}^3 + \omega_8\ \mathrm{tr}\ \mathbf{B}_1\mathbf{B}_2)\mathbf{B}_1 + \omega_9(\mathrm{tr}\ \mathbf{B}_1{}^2)\mathbf{B}_1{}^2$$

$$+ \omega_{10}(\mathrm{tr}\ \mathbf{B}_1{}^2)\mathbf{B}_2 + \omega_{11}\mathbf{B}_2{}^2 + \omega_{12}\mathbf{B}_4 + \omega_{13}(\mathbf{B}_1{}^2\mathbf{B}_2 + \mathbf{B}_2\mathbf{B}_1{}^2) \tag{8d}$$

$$+ \omega_{14}(\mathbf{B}_1\mathbf{B}_3 + \mathbf{B}_3\mathbf{B}_1)$$

Equations (7)–(8) may be interpreted in two senses. First they may be considered as a perturbation about a state of rest and second as a perturbation about Newtonian flow.

The second-order approximation is somewhat significant as it contains the first viscoelastic effects beyond Newtonian flows. While it does not show non-Newtonian viscosity, normal stress effects in laminar shear flows are predicted. This second-order fluid is somewhat analogous to Mooney's theory of superelasticity,[57] which Rivlin and his co-workers point out is the complete second-order correction to classical linear elasticity.[69,72,92].

From a careful comparison of the ω_d coefficients with the integral expansion in eq. (2), we obtain the relations of eqs. (9) and (10).

$$\omega_1 = \left(\frac{1}{2}\right)\int_0^\infty s\ \Phi(s)ds \tag{9a}$$

$$\omega_3 = (-1)\left(\frac{1}{4}\right)\int_0^\infty s^2\ \Phi(s)ds \tag{9b}$$

$$\omega_5 = \left(\frac{1}{12}\right)\int_0^\infty s^3\ \Phi(s)ds \tag{9c}$$

$$\omega_{12} = (-1)\left(\frac{1}{48}\right)\int_0^\infty s^4\ \Phi(s)ds \tag{9d}$$

$$\omega_2 = \left(\frac{1}{4}\right)\int_0^\infty\int_0^\infty s_1 s_2\ \Psi\ (s_1,\ s_2)ds_1 ds_2 \tag{10a}$$

$$\omega_6 = (-1)\left(\frac{1}{8}\right)\int_0^\infty\int_0^\infty s_1{}^2 s_2\ \Psi\ (s_1,\ s_2)ds_1 ds_2 \tag{10b}$$

$$\omega_{11} = \left(\frac{1}{16}\right)\int_0^\infty\int_0^\infty s_1{}^2 s_2{}^2\ \Psi\ (s_1,\ s_2)ds_1 ds_2 \tag{10c}$$

$$\omega_{14} = \left(\frac{1}{24}\right)\int_0^\infty\int_0^\infty s_1{}^3 s_2\ \Psi\ (s_1,\ s_2)ds_1 ds_2 \tag{10d}$$

From these results we see that knowledge of two kernels Φ and Ψ allows us to calculate all of the coefficients in $\mathbf{M}_1$ and $\mathbf{M}_2$, two of three in $\mathbf{M}_3$, and three of eight in $\mathbf{M}_4$. Four of these coefficients may be obtained in terms of the relaxation modulus $G(\ )$ and are given in eqs. (11).

$$\omega_1 = \int_0^\infty G(s)ds \tag{11a}$$

$$\omega_3 = \int_0^\infty sG(s)ds \tag{11b}$$

$$\omega_5 = (1/2) \int_0^\infty s^2 G(s)ds \tag{11c}$$

$$\omega_{12} = -(1/6) \int_0^\infty s^3 G(s)ds \tag{11d}$$

Now the relaxation modulus is of course positive, and it follows that the coefficients ω_1 and ω_5 must be positive and ω_3 and ω_{12} are negative.

Coleman, Noll, and Markovitz[16,44] have investigated the relationship of their theory of hereditary media to linear viscoelasticity and arrived at relationships similar to, but more limited than eqs. (9)–(11) for the coefficients of the Rivlin-Ericksen tensors. In fact, the coefficients of the first two Rivlin-Ericksen tensors are identical to ω_1 and ω_3. They further point out that the coefficients of these first two tensors are related by an equation derived by Fujita (and given in the book by Ferry[23]) for the steady-state shear compliance of linear viscoelasticity

$$J_e = \left(\int_0^\infty sG(s)ds \Big/ \left[\int_0^\infty G(s)ds \right]^2 \right) \tag{12}$$

From eqs. (11) it follows that

$$\omega_3 = -J_e \omega_1^2 \tag{13}$$

An additional series of interesting relationships may be derived by assuming the relaxation function to have an exponential form as in eq. (4). Substitution into eqs. (11) yields

$$\omega_3 = -\omega_1^2/c \tag{14a}$$

$$\omega_5 = -\omega_1\omega_3/c \tag{14b}$$

$$\omega_{12} = -\omega_1\omega_5/c \tag{14c}$$

Experimental data taken in simple kinematic motions may also be used to determine or put restrictions on coefficients. The experiments of Philippoff et al.,[9,62,66] Markovitz and his co-workers[42,43] Kotaka, Kurata and Tamura,[35] and Ginn and Metzner[32] on laminar shearing motions indicate the following inequalities

$$\omega_1 > 0 \tag{15a}$$

$$\omega_2 - 2\omega_3 > 0 \tag{15b}$$

$$\omega_3 < 0 \tag{15c}$$

$$\omega_4 - \omega_6 < 0 \tag{15d}$$

$$\omega_9 + 2(\omega_{11} - \omega_{10} - \omega_{13}) < 0 \tag{15e}$$

3. Hydrodynamic Theory of Viscoelastic Flow

In this section, we consider the dynamics of viscoelastic fluids in a general form looking mainly at the properties of the equations of motion. First we note that there exist two general classes of hydrodynamic flows for which exact solutions are possible, these being known as *laminar shearing* flow and *steady extension*. The basis of the exact solutions is the fact that the strain tensor **e** may sometimes be expressed in terms of a finite number of independent acceleration tensors. These solutions are given for the general nonlinear viscoelastic fluid by Rivlin,[70] Giesekus,[28] Ericksen,[20] and Coleman and Noll[12,13,15,17] and for more restrictive constitutive theories by Mooney,[58]* Oldroyd,[61] Walters,[93] and White and Metzner.[100] This work is discussed in terms of our formulation in an earlier paper.[97] Unfortunately, the methods used for exact solutions are not applicable to most problems.

Approximate procedures for solving viscoelastic flow problems date to the work of Langlois and Rivlin,[36–39] who use perturbation procedures to analyze internal flows in which inertia may be neglected. This method has been applied to external flow about a submerged object by Leslie and Tanner,[40] Caswell and Schwarz,[10] and Giesekus.[31] More recently, Markovitz and Coleman[44] have called attention to the importance of second-order fluids and investigated several problems, including unsteady flows.[45]

If we substitute the constitutive matrix expansion, eq. (7), in Cauchy's law of motion, we obtain

$$\rho \frac{D}{Dt} \mathbf{V} = -\nabla p + \sum \nabla \cdot \mathbf{M}_n + \rho \mathbf{f} \tag{16}$$

For the first-order fluid, this becomes

$$\rho \frac{D}{Dt} \mathbf{V} = -\nabla p + \omega_1 \nabla \cdot \mathbf{B}_1 + \rho \mathbf{f} \tag{17a}$$

and using the incompressibility restriction, we obtain

$$\rho \frac{D}{Dt} \mathbf{V} = -\nabla p + \omega_1 \nabla^2 \mathbf{V} + \rho \mathbf{f} \tag{17b}$$

which are the Navier-Stokes equations.[8,82] It is solutions to this vector equation which were proposed at the 1952 American Chemical Society Extrusion Symposium as the basis of design procedures for screw extruders.

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* Mooney[58] and Philippoff, and Gaskins[25,63,65] make use of an alternate approach to the dynamics of viscoelastic flow, which was suggested by Weissenberg.[94,95] According to Weissenberg's theory, the stress tensor is related to a recoverable strain tensor rather than to the deformation history.

Solutions of the Navier-Stokes equations do not predict non-Newtonian viscosity or normal stresses in laminar shearing flow and the only significant dimensionless group arising in the equations is the Reynolds number.[8,68]

For a second-order fluid, we obtain

$$\rho \frac{D}{Dt} \mathbf{V} = -\nabla p + \omega_1 \nabla^2 \mathbf{V} + \omega_2 \nabla \cdot \mathbf{B}_1{}^2 + \omega_3 \nabla \cdot \mathbf{B}_2 + \rho \mathbf{f} \qquad (18)$$

The considerable complexity of even this, the first approximation beyond Newtonian flow, is evident. However an interesting simplification of eq. (18) may be made for the case of plane flows. Introducing the Stokes stream function $\psi(x,y)$[8,84]

$$\begin{aligned} u &= \partial\psi/\partial y \\ v &= -\partial\psi/\partial x \\ w &= 0 \end{aligned} \qquad (19)$$

into eq. (18) and eliminating the pressure p between the x and y components, one obtains (assuming curl $\mathbf{f}$ to be zero)

$$\rho \frac{D}{Dt} [\nabla^2 \psi] - \omega_1 \nabla^4 \psi = \omega_3 \left[\left(\frac{\partial^2}{\partial x \partial y} \right)(B_{xx}{}^{(2)} - B_{yy}{}^{(2)}) + \left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} \right)B_{xy}{}^{(2)} \right]$$
$$(20)$$

or equivalently

$$\left[\rho \frac{D}{Dt} - \omega_1 \nabla^2 \right] \nabla^2 \psi = \omega_3 \left[\frac{D}{Dt} \left(8 \frac{\partial^4 \psi}{\partial x^2 \partial y^2} - \nabla^4 \psi \right) \right.$$
$$+ 2 \left(\frac{\partial^2 \psi}{\partial x \partial y} \right)\left(\frac{\partial^4 \psi}{\partial x^4} - \frac{\partial^4 \psi}{\partial y^4} \right) + 2 \left(\frac{\partial^2 \psi}{\partial x^2} \right)\left(3 \frac{\partial^4 \psi}{\partial x^3 \partial y} - \frac{\partial^4 \psi}{\partial x \partial y^3} \right)$$
$$\left. - 2 \left(\frac{\partial^2 \psi}{\partial y^2} \right)\left(3 \frac{\partial^4 \psi}{\partial y^3 \partial x} - \frac{\partial^4 \psi}{\partial y \partial x^3} \right) \right] \qquad (21)$$

It is seen that the contribution of $\mathbf{B}_1{}^2$ has disappeared from the equations of motion and we must only consider effects due to the second acceleration tensor. For nonplanar two-dimensional flows the contribution of $\mathbf{B}_1{}^2$ remains present.

We now discuss the application of the principle of dynamic similarity[8] to the equations of motion for a second-order viscoelastic fluid. This principle, which was first used by Osborne Reynolds[68] to determine a criterion for turbulence in Newtonian fluids, consists in placing the equations of motion in dimensionless form by introducing a length L and velocity U characteristic of the system and noting how the resulting dimensionless groups specify the properties of the solutions of these equations. The solution of the dimensionless equation of motion for a reduced velocity profile V/U will be identical, for specified boundary conditions, whenever all the dimensionless groups have the same value no matter what the overall dimensions of the system be. Further, the stability of the system and the introduction of

different flow regimes will be determined by these groups and they together with the geometry of the system will specify frictional drag. Denoting dimensionless terms in the equations of motion by asterisks, the steady-state form of eq. (18) may be written

$$(\mathbf{V}^* \cdot \nabla^* \mathbf{V}^*) = -\nabla^* \left(\frac{\rho}{\rho U^2}\right) + \left(\frac{\omega_1}{LU\rho}\right) \nabla^{*2} \mathbf{V}^*$$

$$+ \left(\frac{\omega_1}{LU\rho}\right)\left(\frac{\omega_3 U}{\omega_1 L}\right)\left[\nabla^* \cdot \mathbf{B}_2^* + \left(\frac{\omega_2}{\omega_3}\right) \nabla^* \cdot \mathbf{B}_1^{*2}\right] \quad (22)$$

There are seen to be three significant dimensionless groups, one of which we are already familiar with—the Reynolds number $LU\rho/\omega_1$, the ratio of inertial to viscous forces. The group $\omega_3 V/\omega_1 L$ signifies the ratio of viscoelastic forces (as represented by the second acceleration tensor) to the viscous forces and finally ω_2/ω_3 denotes the ratio of the forces due to the $\mathbf{B}_1^2$ matrix to those of the second acceleration tensor. For planar flows, the last dimensionless group will have no significance. The group $\omega_3 U/\omega_1 L$ will be named for K. Weissenberg and the group ω_2/ω_3, the viscoelastic ratio number. (The reasons for these designations will become clear with further discussion.) We introduce the notation

$$[LU\rho/\omega_1] = N_{Re} \qquad \text{(Reynolds number)} \qquad (23a)$$

$$[(-1)\omega_3 U/\omega_1 L] = [J_e\omega_1 U/L] = N_{we} \qquad \text{(Weissenberg number)} \qquad (23b)$$

$$[\omega_2/\omega_3] = N_{VR} \qquad \text{(Viscoelastic ratio number)} \qquad (23c)$$

The friction factor for the drag due to a second order viscoelastic fluid may be expressed

$$f = f(N_{Re}, N_{We}, N_{VR}, \text{geometry}) \qquad (24)$$

Equation (24) is entirely suitable for use to develop dimensionless correlations for the slow flow of viscoelastic fluids.*

We now turn to a detailed discussion of the physical significance of the terms N_{We} and N_{VR}. If one considers the steady laminar shearing flow of a viscoelastic fluid, the ratio of normal stresses in the direction of shearing to the direction of flow may be expressed for slow motions[97,98] as

$$(\tau_{22} - \tau_{33})/(\tau_{11} - \tau_{33}) = \omega_2/(\omega_2 - 2\omega_3)$$

$$= N_{VR}/(N_{VR} - 2) \qquad (25)$$

* Dimensionless friction factor correlations are not new to non-Newtonian fluid dynamics. Work up to 1956 in this area is comprehensively reviewed by Metzner[49] and a version updated to 1959 has recently been published.[50] Dodge and Metzner[19] developed a friction factor–Reynolds number plot for purely viscous non-Newtonian fluids in turbulent flow in pipes, while Slattery and Bird[80] have published a correlation for drag on spheres by purely viscous non-Newtonian fluids. The only existing work of this type which considers the viscoelastic properties of non-Newtonian fluids is the unpublished study of Sailor, Park, and Metzner on turbulent flow in tubes.[75]

In 1948, Weissenberg[95] conjectured the equality of normal stresses in the directions perpendicular to flow, i.e.,

$$\tau_{22} = \tau_{33} \tag{26}$$

and experimental results of Roberts,[74] Kotaka et al.,[35] and Philippoff[64] have supported him. Now Markovitz,[42,43] on the basis of several different experiments, has argued that Weissenberg's conjecture is in error. Summarizing existing data, Ericksen[21] concludes the normal stress ratio of eq. (25) to be about one-tenth, and Ginn and Metzner[32] on the basis of extensive new data find it to vary from zero to -0.25. The viscoelastic ratio number then appears to exist in the range $-0.2 < N_{VR} < +0.4$. The Ericksen value of N_{VR} would be 0.2.

In his analysis of viscoelastic flow, Weissenberg emphasized the significance of the *recoverable* shearing strain. At the First International Rheological Congress held in 1948, Weissenberg argued as follows:[95]

" As a dimensionless quantity of tensorial character, we may quote here the recoverable strain. Just as the Reynolds Number coordinates the rheological states with respect to simulitude in the relative proportions of the forces of inertia and of internal friction, so the recoverable strain does with respect to simulitude in anisotropy in the sheared states..."

In a slow laminar shearing flow, the recoverable elastic strain, s, is classically

$$s = J_e \tau_{12} = J_e[\omega_1 \Gamma] \tag{27}$$

$$s \approx J_e \omega_1 U/L = N_{We} \tag{28}$$

The Weissenberg number is seen to represent physically the amount of recoverable strain in the fluid. It should also be noted that

$$s = J_e \omega_1 \Gamma [\omega_1 \Gamma / \omega_1 \Gamma]$$
$$= -\omega_3 \Gamma^2 / \omega_1 \Gamma \tag{29}$$
$$= (\tau_{11} - \tau_{22})/2\tau_{12}$$

Philippoff and his co-workers[66] have experimentally determined the recoverable shearing strain in a coaxial cylinder instrument and used the results to compute normal stresses. This method would appear to have semiquantitative value.

Turning to the third-order fluid, we obtain the equation of motion

$$\rho \frac{D}{Dt} \mathbf{V} = -\nabla p + (\omega_1 + \omega_4 \mathrm{tr}\, \mathbf{B}_1{}^2)\, \mathbf{B}_1 + \omega_2 \nabla \cdot \mathbf{B}_1{}^2 + \omega_3 \nabla \cdot \mathbf{B}_2$$
$$+ \omega_5 \nabla \cdot \mathbf{B}_3 + \omega_6 \nabla \cdot [\mathbf{B}_1\mathbf{B}_2 + \mathbf{B}_2\mathbf{B}_1] + \rho \mathbf{f} \tag{30}$$

It is obvious that the complexity here is becoming so great that simplifying approximations may have to be introduced. Some such approximations have been studied[98] and will be published in the near future.

Before concluding this section, we shall briefly discuss the boundary conditions to be used on the equations of motion for viscoelastic fluids. The jump condition on Cauchy's first law of motion for stationary surfaces is equality of the stress vectors on both sides of the diaphragm.[22] Thus, for example, if the fluid has a free surface on which there is only negligible drag of the air, then it will mean that the stresses in the fluid will be small and the velocity gradients essentially zero. A more important boundary condition is that at a solid boundary. This boundary condition for Newtonian fluids was the subject of an extensive historical controversy involving notably Navier, Poisson, and Stokes, who differed as to whether the fluid adjacent to a solid surface adhered to that surface or slipped along it. The answer eventually accepted was that given by Stokes[83] in 1848 (in which he reversed an earlier position[82]) that there was no slippage at solid boundaries. The controversy rose again in the study of non-Newtonian polymer solutions and slurries in the 1920's. Mooney derived an expression for calculating wall slip velocity in a capillary tube and has presented data showing its existence in suspensions and uncured elastomers.[56] Decker and Roth[18] have argued that raw elastomers exhibit slippage in a Mooney shearing disk viscometer.[59] Maxwell and Galt[46] claim to show slippage in molten polyethylene flowing through a capillary, but objections to their experiments may be raised. Toms[87] uses arguments of the Mooney type[56] to show slippage in capillary flow of a monochlorobenzene solution of poly(methyl methacrylate). However numerous sets of experimental data exist which show that slippage does not exist with polymer melts and solutions and the majority of researchers are in agreement with this. When slippage does occur we would expect, as has been pointed out by Mooney,[56,59] that the solid boundary slip velocity is a unique function of the point shearing stress.

4. The Weissenberg Number and the Bagley-Tordella Melt Fracture Criterion

Melt fracture or elastic turbulence first received detailed attention in the 1940's, notably by Spencer and Dillon,[81] who, perceiving rough and jagged polymer extrudates emerging from dies, attributed to an exit effect caused by the interaction of "elastic" bulging and solidification due to cooling. Later Tordella[89] pointed out a die entrance effect occurring together with the extrudate roughness and argued that it was the cause of the exit phenomenon. Tordella's hypothesis was born out by later researches of Clegg,[11] Metzner, Carley, and Park[51] and Bagley and his co-workers.[2,3,79] The fracture phenomenon is known not to be unique to molten plastics and to occur in raw elastomers[47,59] and silicones.[5]* Recently Benbow[6] and Tordella[91] have called attention to a "stick-slip" mechanism which may cause the onset of fracture inside of the die for certain materials. It must be emphasized that the kinematics of melt fracture are still uncertain.

* Metzner and Whitlock[54] have found an anomolous flow effect similar to fracture occurring in concentrated suspensions.

The point we wish to consider here is the theoretical basis for the determination of the criterion for the onset of melt fracture. The method which we use is that proposed many years ago by Osborne Reynolds[68] to determine a criterion for the onset of turbulence in laminar flow of Newtonian fluids in tubes. By studying the dimensionless groups arising from the equations of motion for a second-order fluid, their physical significance and magnitude, then noting that melt fracture takes place in planar as well as nonplanar flows; it would seem that the phenomena should occur at a critical value of the Weissenberg number. For a die having a typical characteristic length as a cross-sectional dimension D (e.g., capillary diameter or slit thickness) the criterion is $\omega_1 J_e U/D$, with allowance for some effect of N_{VR} and geometry, as well as the Reynolds number. Tordella[89,90] has, however, pointed out the smallness of the Reynolds number at the onset of melt fracture. We emphasize that we are considering this phenomenon to be generally caused by a hydrodynamic incompatibility due to, or greatly enhanced by viscoelastic forces and are in no way assuming the onset to occur in the mouth or within the die.

Turning to the literature on melt fracture we find two significant early studies of the onset criterion by Spencer and Dillon[81] and Tordella.[90] This latter author conjectured that the phenomenon was initiated at a critical value of the recoverable elastic strain. More recently, Bagley,[1] determining the recoverable strain from the Philippoff-Gaskins end effect experiment,[65] finds s_R to be 6.0–7.5 at the onset of elastic turbulence in linear polyethylene. Bagley cites data on other polymer melts which agree with this. Tordella[91] has reinforced this conclusion by using instantaneous modulus experiments and obtaining results agreeing with Bagley. We immediately note from eq. (28) that the Bagley-Tordella melt fracture criterion is identical to our prediction of a critical Weissenberg number.

Having shown that existing experimental data is in agreement with our theory, we may move one step further by writing

$$(N_{We})_{crit} = (J_e/8)\omega_1 \, 8U/D = J_e(\tau_{12})_R/8 \tag{31}$$

and using an expression given by Ferry[23] for the steady-state shear compliance of linear polymers

$$J_e = (2/5) \, M/RT \tag{32}$$

we obtain the expression

$$M(\tau_{12})_R = 20 \, \rho RT \, (N_{We})_{crit} \tag{33}$$

The constancy of the product of molecular weight and wall shear stress at the onset of melt fracture was first pointed out by Spencer and Dillon[81] for polystyrene melts, and, more recently, Bagley[1] has shown it to be true for linear polyethylene and quotes experiments by Howells which indicate this relationship to hold for poly(methyl methacrylate). (Bagley justifies

this result by conjecturing that the shear stress is related to the recoverable strain by the modulus of the kinetic theory of rubber elasticity.[92])

We should note that melt fracture is only known to occur in the region of non–Newtonian viscosity. However, the second–order fluid approximation is not unreasonable here.

A difficulty arises in our theory when we consider polymer solutions as values of the Weissenberg number are reached in capillary flow far in excess of those in which fracture is found in melts.[52,53,78] However polymer solutions have, in general, far lower viscosities and steady-state shear compliances than melts, and the critical Weissenberg number is not reached until the second-order fluid is no longer even approximately valid. One is also in a region of significantly large Reynolds numbers.

5. Rheology of Fiber Spinning

In this section, we shall discuss in some detail the significance of nonlinear viscoelasticity in the spinning of fibers from high polymers. Little has appeared in the literature about the technical details of this important process, the most substantial publications being articles by Preston on wet spinning,[67] Lodge on melt spinning,[41] and Frey and Sippel on dry spinning.[24] Here we shall mainly be concerned with the last two procedures. The rheology of fiber spinning has received even less attention, and we can refer only to the review by Roberts[73] and papers by Ziabicki and Kedzierska.[101–103]

Briefly, in melt spinning of fibers, the polymer is melted and extruded vertically through the many holes in the face of a plate known as a spinneret. The spinneret disk is about 0.25 in. thick and the holes about 0.010 in. in diameter. A cross blast of gas is usually used to cool and solidify the vertically descending fiber filaments, most yarns being solid about 2 ft. below the spinneret. The individual filaments are brought together and pass over feed rolls on to a surface bobbin, such actions creating an additional tensile stress in the descending fibers.

When degradation is significant in the molten state, fibers are usually dry-spun. The polymer is dissolved in a suitable solvent and extruded at reasonably high temperature through a spinneret. A gas is blown co- or countercurrently to the descending fiber filaments to absorb the evaporating solvent.

The first point to be discussed is the criterion of good solvents for a polymer in dry spinning. The method currently most used in the fiber industry is "spinnbarkeit" (the ability to form liquid threads spontaneously). Some time ago the author was preparing polymer solutions in part to test for "spinnbarkeit" and noted the coincidence of this property with the fluids' strong tendency to climb the stirring rod in the beaker where it was being mixed (Weissenberg effect). Similar observations have been recorded by Toms.[88] Fiber spinnability and spinnbarkeit would appear to require either that the stretching (i.e., Trouton) viscosity increases with defor-

mation rate and/or filament stability is greatly enhanced over Newtonian fluids.

First consider the motion of a viscoelastic polymer solution being stirred in a beaker, which we may approximate by laminar shearing flow between concentric coaxial cylinders, the outer cylinder being stationary and the inner rotating with angular velocity Ω. This problem has been treated exactly for general viscoelastic fluids by Giesekus[28] and Coleman and Noll[13] and we may use their results to analyze surface elevation in stirring polymer solutions. If we specialize to second-order fluids, the integrals obtained by these authors may be integrated. Denoting the radius of the outer cylinder by R and the inner cylinder by κR and solving for the axially upward stress at radius r, we obtain

$$P_z = -\tau_{zz}$$

$$= \left[\frac{2J_e\, \omega_1{}^2\Omega^2R^4\,(1 - 2N_{VR})}{[(1/\kappa^2) - 1]^2}\right]\left(\frac{1}{r^4}\right)$$

$$- \left[\frac{\rho\Omega^2R^4}{2[(1/\kappa^2) - 1]^2}\right]\left[\left(\frac{r}{R}\right)^2 - \left(\frac{R}{r}\right)^2 + 4\ln\left(\frac{r}{R}\right)\right] + c(z) \quad (34)$$

The upward stress is seen to be divided into two parts, a contribution due to viscoelasticity which would cause surface elevation and a contribution of centrifugal force tending to throw the fluid radially outwards. Equation (34) not only shows how the Weissenberg "stirring rod" effect is caused by viscoelasticity, but it enables us to see that the viscoelastic ratio number is always less than one half.

Turning now to an oversimplified picture of thread formation from a polymer solution, that of steady extension of a fluid filament having a circular cross section, we will derive an expression for the Trouton viscosity. The flow field is

$$\mathbf{V} = az\, \mathbf{e}_z \quad - (az/2)\, \mathbf{e}_x \quad - (az/2)\, \mathbf{e}_y \quad (35)$$

The stress tensor is given by eq. (35) in our earlier paper.[97] Making use of the boundary condition that the normal stress in the radial direction in the filament must equal atmospheric pressure on the fluid surface, we may express the axial tension as

$$\tau_{zz} = (3/2)\omega_1 \left\{1 + J_e\omega_1a \left[1 - (\omega_2/\omega_3)\right]\right\}a \quad (36)$$

and the Trouton viscosity is

$$\eta_T = (3/2)\omega_1 \left[1 + J_e\omega_1a \left(1 - N_{VR}\right)\right] \quad (37)$$

Now the shear viscosity of a second-order fluid is independent of shear rate and is a decreasing function of shear rate in third and higher order fluids. The opposite effect is found above for the Trouton viscosity; it increases with stretching rate, and the increase is due to the viscoelastic properties through the steady state shear compliance (or Weissenberg number).

Spinnbarkeit, like the Weissenberg effect, is seemingly due to the viscoelas-tic properties of the spinning solution.

No satisfactory theoretical analysis or experimental study would appear to exist for the effect of viscoelasticity upon the stability of cylindrical fluid filaments. Other studies of the relationship of viscoelasticity to flow stability and turbulence have appeared in recent years. The petroleum industry is making use of the *Dodge-Metzner effect*[19,50] in which the fric-tional drag in pipeline flow is significantly reduced at high Reynolds num-bers, indicating perhaps that viscoelasticity enhances stability in Poiseuille flow. More extensive experiments of the effect of viscoelasticity upon drag reduction have been made by Sailor, Park, and Metzner.[75] On the other hand, Thomas and Walters[85] have shown theoretically that viscoelasticity decreases the hydrodynamic stability of flow in curved pipes. The latter flow instability however is due to centrifugal forces (as in the Taylor co-axial cylinder problem) and is to some extent in a different category from the cylindrical filament and Poiseuille flow problems.

We may conjecture that in spinning fibers one must choose systems of intermediate viscoelastic properties. Spinning solutions with negligible viscoelasticity cannot be spun, while highly viscoelastic polymer melts will fracture at moderate output rates.[103]

Finally, we shall discuss the behavior of polymer solutions and melts flowing through the holes of a spinneret and the resulting properties of the emerging filament. Consider a viscoelastic fluid in fully developed laminar shear flow moving axially through a cylindrical duct. Though rig-orous analyses of the shear stress–shear rate–slippage relationships and pressure gradient–flow rate behavior of non-Newtonian fluids in tubes date to Mooney's 1931 paper,[56] the significance of viscoelastic properties in this geometry were not fully realized until the work of Philippoff and Gas-kins[25,63,65] in the last decade. Rigorous studies including viscoelastic ef-fects are given by Coleman and Noll[13] and by Metzner and his co-work-ers.[52,78,99] Calculating the axial normal stress in the manner used in the papers by Metzner et al. for a second-order fluid yields

$$\tau_{zz} = -p(0,z) + 128\, J_e\omega_1{}^2\, [1 + (2/3)\, N_{VR}]\, (V/D)^2(r/R)^2 \quad (38)$$

where z is the axial direction, D the duct diameter, R the radius, and V the average velocity. Derivation of the velocity profile for a second order fluid shows it to be parabolic and the pressure gradient to be linear with the flow rate obeying Poiseuille's law. However the total pressure built up in the spinneret is not only used in overcoming friction, but in the elastic and kinetic energy fluxes of the fluid. In polymer melts the elastic energy flux will dominate the kinetic energy. Calculation of the fiber efflux rate from the pressure built up in the spinneret will lead to abnormally large values unless elastic energy be considered. This is the same phe-nomena as that upon which the Philippoff-Gaskins end effect experiment[65] is based. While discussing the flow of a viscoelastic fluid through a cylin-

drical duct, it should be noted that some controversy exists as to the die length necessary to obtain fully developed flow.[77,96]

Metzner and his co-workers[50-54,78] have shown that the diameter of a horizontal fluid jet leaving a cylindrical tube (or parallel plate channel[99]) may be related to the momentum flux of the fluid and the axial normal stress. Middleman and Gavis[26,55] have shown that at low Reynolds numbers, horizontal jets of Newtonian fluids expand to a diameter far greater than that predicted from a momentum flux balance and point out that undoubtedly a similar effect exists in viscoelastic fluids. The experiments of Middleman and Gavis have been verified in Metzner's laboratory.[53] Use of the theoretical development we shall give will be limited to flux rates higher than the Middleman-Gavis range. A second limitation also exists to the technique of Metzner et al., this being that extrudate expansion is a strong function of length/diameter ratio of tubes[4,52] and what we are considering is a large L/D asymptote. It is this effect of extrudate diameter on L/D which has lead to the question of at what point the flow is fully developed.[96]

Considering a fiber filament emerging downward from the spinneret, we make macroscopic momentum and mass flux balances between the exit of a spinneret hole and the filament

$$\int_0^R 2\pi r \rho u^2 dr - \int_0^R 2\pi r \tau_{zz} dr = \int_0^{d_f/2} 2\pi r \rho v_f^2 dr$$

$$- \int_0^{d_f/2} 2\pi r \tau_f dr - \int_0^{d_f}\int_0^{d_f/2} 2\pi r \varphi g dr dz \quad (39)$$

$$\pi D^2 V/.4 = \int_0^{d_f} 2\pi r v_f dr \quad (40)$$

where v_f is the filament velocity and τ_f the stretching tension in the descending fiber. The integrals on the left-hand side of eq. (40) may immediately be integrated from consideration of the parabolic velocity profile and eq. (38). If we introduce the simplifying conjecture that the velocity profile in the descending filament is uniform, we may eliminate the filament velocity between eqs. (39) and (40) and obtain an expression for the filament diameter d_f

$$\frac{D^2}{(d_f)} = 4/3 - \frac{32 N_{We} (1 + (2/3) N_{Vr})}{N_{Re}} + \frac{\tau_f}{\rho V^2}$$

$$+ \frac{\int_0^{d_f}\int_0^1 \rho g(r/R) d(r/R) dz}{\rho V^2} \quad (41)$$

If we were considering a horizontal viscoelastic jet rather than a vertically descending fiber filament, the last two terms in the above equation would not appear, the jet would expand to a diameter greater than that for a Newtonian fluid, and the diameter would remain constant. In the vertical

filament, we must consider in addition the final two terms representing, respectively, axial stretching and gravitation. The net effect on the descending filament is that the second term on the right-hand side of eq. (41) causes an immediate expansion upon emergence from the spinneret and as the fiber continues to descend the gravitational forces and axial filament tension causes an increasing contraction.

In the above analysis we have neglected the effect of the aerodynamic drag by surrounding gases upon the moving fiber. This problem has recently received serious study by Sakiadis.[76]

6. Conclusions

In this paper, we have made a serious study of the constitutive and hydrodynamic theory of viscoelastic fluids, in particular for slow flows. We have also shown the significance of our theoretical results to the important industrial problems of melt fracture in extrusion and to melt and dry spinning of fibers.

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Résumé

On a développé une théorie hydrodynamique pour l'écoulement de fluides visco-élastiques non-linéaires. Il faut introduire deux nouveaux groupes sans dimensions dans

la correction du second ordre de l'écoulement viscoélastique. Ces groupes s'appellent les rapports numériques de Weissenberg et de viscoélasticité. On en a discuté les applications importantes du pont de vue industriel. On suggère que le rapport de Weissenberg détermine le début de fracture lors de la fusion.

Zusammenfassung

Die hydrodynamische Theorie für das Fliessen von nichtlinear viscoelastischen Flüssigkeiten wird entwickelt. Zwei neue dimensionslose Gruppen müssen in die vollständige zweite Näherung der Theorie des viscoelastischen Fliessens eingeführt werden. Diese Aggregate werden die Weissenberg'sche und die viscoelastische Verhältniszahl genannt. Die Anwendung auf industriell wichtige Probleme wird diskutiert. Es wird angenommen, dass die Weissenbergzahl den Eintritt des Schmelzbruches bestimmt.