Elongational Flow and Melt-Spinning Instability of Concentrated Suspensions of Small Particles in Polymer Melts

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Synopsis

It is suggested that the existence of yield values in the elongational viscosity of concentrated suspensions of small particles in polymer melts leads to enhanced instability of uniaxial stretching and melt-spinning behavior. This is supported by analyses of filament stability. Severe instabilities are found in experiments on both simple stretching and melt spinning of filaments of suspensions of carbon black, titanium dioxide, and calcium carbonate in polystyrene. Necking and low elongations to break are observed in the former case. The melt-spinning results show "draw resonance" occurring at low drawdown ratios and high amplitudes of disturbances in the unstable region.

INTRODUCTION

It has been shown by various investigators over the years that polymer melts filled with high loadings of small particles such as carbon black,[1-4] titanium dioxide,[4,5] talc,[6] and calcium carbonate[4] exhibit yield values in their shear viscosity characteristics. Only recently, articles by Lobe and White[3] and Tanaka and White[4] have shown that yield values also exist in these systems in elongational flow. It was found that through the presence of a yield value, the elongational viscosity of a polymer melt system can be transformed from an increasing function to a decreasing function of stretch rate.

In recent years, investigators from our laboratories[7-12] have made extensive studies of elongational flow characteristics and processing of homogeneous polymer melts. The results of these studies show that the deformation rate dependence of the elongational viscosity or rheological characteristics leading to such behavior (deformation rate softening of the relaxation spectrum) strongly affects filament stability. A decreasing elongational viscosity gives rise to increased instability of uniaxial stretching flows including necking in simple filament stretching and draw resonance in melt spinning. A similar view is implicit in studies of the onset of draw resonance for non-Newtonian fluids by Shah and Pearson,[13] Han, Lamonte, and Shah,[14] and Ishihara and Kase.[15]

The results described in the preceding paragraph suggest that highly filled compounds should exhibit enhanced instability in elongational flow. It is our purpose in this article to develop this idea and investigate the elongational flow and melt-spinning stability of particle filled polymer melts and compare it to the behavior of the melt matrix.

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THEORETICAL

General

We shall attempt to develop the ideas on filament stability described in the introduction. We are concerned with both the problem of stability of filaments in elongational flow and in melt-spinning operations (see Fig. 1) for fluids with yield values. In the Appendix we describe three-dimensional tensor constitutive equations for fluids with yield values. Our considerations in this paper are one-dimensional in character, and we need only to treat the uniaxial tensile stress σ_{11}, for which we write

$$\sigma_{11} = Y_e + \nu(t)\frac{dv_1}{dx_1} \tag{1}$$

where Y_e is the tensile yield value and $\nu(t)$ is the effective Bingham differential viscosity. (The theory of fluids with yield values largely dates to Bingham[16]; compare Prager.[17]) For a Bingham plastic fluid (see Appendix),

$$\nu(t) = 3\eta \tag{2}$$

In succeeding subsections, we develop some special theories of filament stability and show how it decreases by the presence of a yield value.

Simple Theory of Filament Stability

In this subsection we develop an oversimplified theory of filament stability based on the model of Figure 2. This is suggested by the studies of Orowan[18] and Chang and Lodge.[19] For a uniaxial elongational flow, the tension F in the filament is related to the tensile stress σ_{11} through the expression

$$F = A\sigma_{11} \tag{3}$$

where A is the cross-sectional area of the filament.

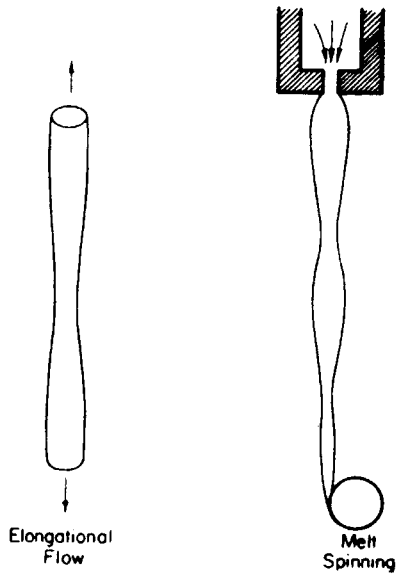

Fig. 1. Unstable elor gational flow and melt spinning.

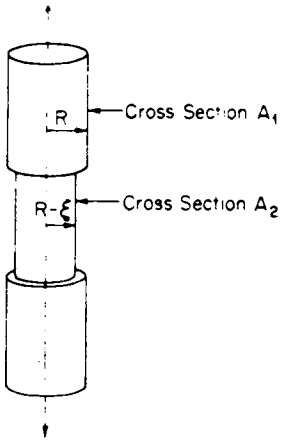

Fig. 2. Model for analysis filament instability.

The elongation rate in uniaxial extension in an undisturbed flow may be expressed in terms of the area A of the filament through

$$\frac{dv_1}{dx_1} = \frac{1}{L}\frac{dL}{dt} = \frac{1}{(V/A)}\frac{d(V/A)}{dt} = -\frac{1}{A}\frac{dA}{dt} \tag{4}$$

where V is the volume of the filament and L is the filament length.

The steady-state stress field in a fluid with a yield value may be expressed as follows:

$$\sigma_{11} = Y_e + \nu\frac{d}{d}\frac{v_1}{x_1} = Y_e + \nu\left(-\frac{1}{A}\frac{dA}{dt}\right) \tag{5}$$

During the uniaxial stretching process, necks develop in the filament. Let the filament be divided into two regions, 1 and 2. Region 2 with radius $(R - \xi)$ represents the necked region whose cross section is less than the major homogeneous 1 portion. From eq. (5), we may write the force balance of eq. (3) as

$$F = A_1\left[Y_e + \nu\left(\frac{-1}{A_1}\frac{dA_1}{dt}\right)\right] = A_2\left[Y_e + \nu\left(\frac{-1}{A_2}\frac{dA_2}{dt}\right)\right] \tag{6}$$

This may be rewritten as

$$\frac{d}{dt}(A_1 - A_2) = \frac{Y_e}{\nu}(A_1 - A_2) \tag{7}$$

where $(A_1 - A_2)$ represents the defect size. This may be integrated to give

$$(A_1 - A_2)(t) = (A_1 - A_2)(0)\, e^{\int^t Y_e/\nu dt} \tag{8}$$

The defect grows approximately exponential in time depending upon the character of ν. If ν is constant and is given by eq. (2), we have

$$(A_1 - A_2)(t) = (A_1 - A_2)(0)e^{Y_e t/3\eta} \tag{9}$$

The character of defect growth depends upon the dimensionless group:

$$\frac{Y_e t}{\eta} = \frac{Y_e L}{\eta V} \tag{10}$$

where the t has been converted to filament length L divided by the velocity. This dimensionless group has been used by Oldroyd[20] and Prager[17] in studies of shear flow and has been called the Bingham number.

Linearized Stability Model

In this subsection we present a linearized stability analysis based on the approach taken by Ide and White[7,9,21] for viscoelastic fluids. Consider again the force balance of eq. (3). We may rewrite this in terms of a disturbance ξ:

$$F = \pi(R + \xi)^2(\bar{\sigma}_{11} + \sigma'_{11}) \tag{11}$$

Linearizing and subtracting out the expression for the unperturbed filament yields

$$2\pi R\xi\bar{\sigma}_{11} + \pi R^2\sigma'_{11} = 0 \tag{12}$$

We may write for the stresses $\bar{\sigma}_{11}$ and σ'_{11} for a filament

$$\bar{\sigma}_{11} = Y_e + \nu E \tag{13c}$$

where E is the steady-state extension rate and

$$\sigma'_{11} = \nu\frac{dv'_1}{dx_1} + \nu' E = -2\frac{\nu}{R}\left[\frac{d\epsilon}{dt} + \frac{E}{2}\xi\right] + \nu' E \tag{13b}$$

From eqs. (12) and (13),

$$2\pi R(Y_e + \nu E)\xi - 2\pi\nu R\left(\frac{d\xi}{dt} + \frac{E}{2}\xi\right) + \nu' E = 0 \tag{14}$$

which may be rewritten

$$\frac{1}{\xi}\frac{d\xi}{dt} = \frac{E}{2} + \frac{Y_e}{\nu} - \frac{1}{2\pi R}\frac{\nu'}{\nu}E \tag{15}$$

$$\ln\frac{\xi(t)}{\xi(0)} = \left(1 + \frac{2Y_3}{\nu E}\right)\frac{Et}{2} - \int_0^t \frac{E}{2\pi R}\frac{\nu'}{\nu}dt \tag{16}$$

For the case of a Bingham plastic fluid (constant ν), eq. (16) becomes

$$\ln\frac{\xi(t)}{\xi(0)} = \left(1 + \frac{2}{3}\frac{Y_e}{\eta E}\right)\frac{Et}{2} \tag{17}$$

Again we see the stability of a filament is decreased by the presence of the yield value. The extent of decrease is determined by the Bingham number, which has the form $Y_e/\eta E$.

Melt-Spinning Instability

The force balance and continuity equation for melt spinning is[9,13–15]

$$F = A\sigma_{11} \tag{18a}$$

$$\frac{\partial A}{\partial t} + \frac{\partial}{\partial x_1}(Av_1) = 0 \tag{18b}$$

Introducing eq. (1) and combining these expressions gives

$$F = A\left(Y_e + \nu\frac{dv_1}{dx_1}\right) \tag{19a}$$

$$= A\left[Y_e + \nu\left(-\frac{1}{A}\frac{\partial A}{\partial t} - \frac{v_1}{A}\frac{\partial A}{\partial x_1}\right)\right] \tag{19b}$$

$$= AY_e - \nu\left(\frac{\partial A}{\partial t} + v_1\frac{\partial A}{\partial x_1}\right) \tag{19c}$$

We must simultaneously solve eqs. (18b) and (19). If we introduce a characteristic velocity v_1 of fiber radius R and length L, we may write

$$A^* = \frac{1}{R^2}A, \quad v_1^* = \frac{1}{v}v_1, \qquad t^* = \frac{t}{L/U}, \qquad x_1^* = \frac{x_1}{L} \tag{20}$$

and transform eqs. (18b) and (19) to

$$\frac{\partial A^*}{\partial t^*} + \frac{\partial}{\partial x_1^*}(A^* v_1^*) = 0 \tag{21a}$$

$$\frac{FL}{\nu R^2 U} = \left(\frac{Y_e L}{\nu U}\right)A^* - \left(\frac{\partial A^*}{\partial t^*} + v_1^*\frac{\partial A^*}{\partial x_1^*}\right) \tag{21b}$$

There are clearly two dimensionless groups which characterize this problem. The first dimensionless group, $FL/\nu R^2 U$, also arises for Newtonian fluids. The second group, $Y_e L/\nu U$, is the Bingham number.

It is our expectation that the Bingham number will act to destabilize the spinline. It should be equivalent to lowering the power law exponent in the work of Shah and Pearson,[13] Han et al.,[14] and Ishihara and Kase.[16] These authors find that this destabilizes the spinline.

A general view of the relationship between the two stability problems in elongational flow which we treat here is given by White and Ide.[9] Interpretations for convected Maxwell (White–Metzner) viscoelastic models are given by these authors and Minoshima et al.[11] Instabilities in stretching filaments and in melt spinning order in severity in the same manner. A similar effect seems to occur here with the Bingham number as the order parameter. We develop the theory of spinning in detail for fluids with yield values in a future article.

EXPERIMENTAL

Materials

Compounds of polystyrene with carbon black, titanium dioxide, and calcium carbonate: the polystyrene was a Dow Styron 678U. The carbon black was a Columbian Carbon FEF-LS N542, the titanium dioxide was du Pont R101, the calcium carbonate was Pfizer Super-flex 200. Compounds with 10, 20, and 30 vol % particulates were prepared on a two-roll mill at 150°C. The shear viscosity, principal normal stress difference, and elongational viscosity of the compounds at 180°C were given in an earlier paper.[4] We show the steady-state elongational viscosity of the carbon black and titanium dioxide compounds in Figures 3 and 4.

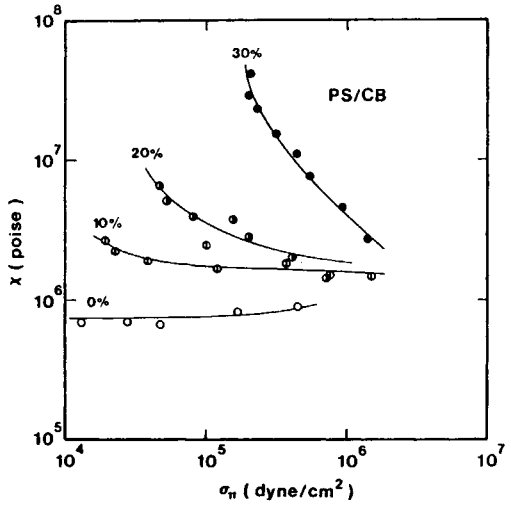

Fig. 3. Elongational viscosity of carbon black-filled polystyrene melts.

Elongational Flow Stability

Filaments of compounds of polymer melts with small particles were prepared in an Instron capillary rheometer using a die of diameter 0.058 in. The filaments were annealed and then stretched horizontally on a layer of silicone oil at 180°C in an elongational rheometer developed in our laboratories.[8]

Melt Spinning

The fibers were melt spun from an Instron capillary rheometer using a die of diameter 0.058 in. The throughput was 0.09 cm^3/min. An ice water quench was kept at 19.5 cm below the die. The fiber was spun through the bath and taken up on a 6.35-cm roll driven by $1/15$ horsepower B and B motor.

The diameter of the measured along its length using a thickness gauge. From

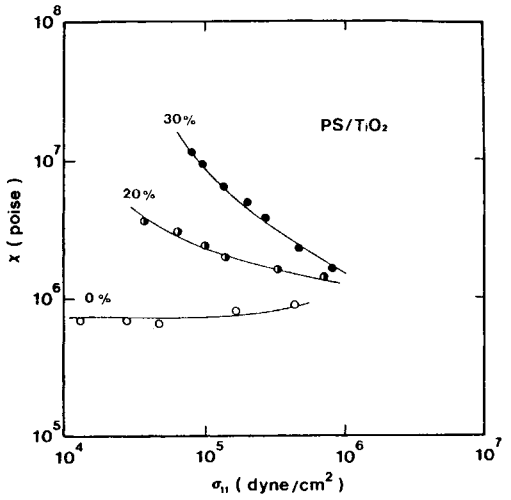

Fig. 4. Elongational viscosity of titanium dioxide-filled polystyrene melts.

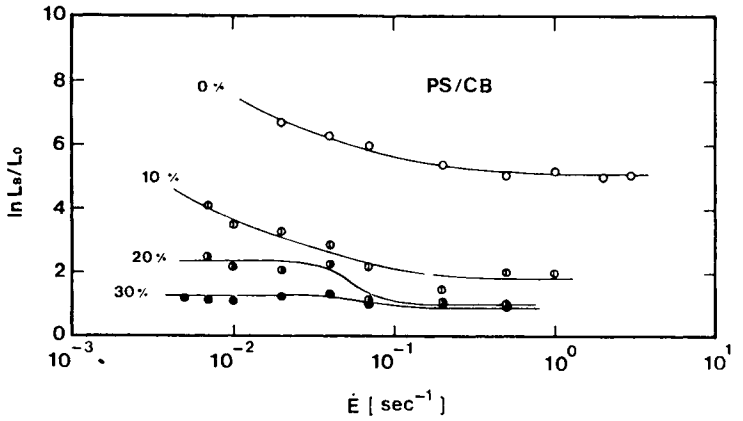

Fig. 5. Elongation to break of polystyrene filaments containing carbon black.

the diameter variation along the fiber, the ratio of the maximum diameter to the minimum one, D_{max}/D_0, was determined. The wavelength λ of the disturbance was measured when a periodic fluctuation was found. The period of the fluctuation was determined from

$$T = \lambda/V_L \tag{22}$$

This was evaluated as a function of draw ratio V_L/V_0.

RESULTS

In Figures 5 and 6 we show the influence of carbon black, titanium dioxide, and calcium carbonate on the elongation ratio L/L_0 at break of the initial polystyrene resins. In each case the addition of particles significantly reduces the elongation to break. Visual observation shows neck development and apparent ductile failure in the sense of Ide and White.[7-9,21]

At low drawdown ratios in the melt-spinning experiment, diameter fluctuations were observed but were small in magnitude and random in period. At a critical drawdown ratio, the fluctuations became greatly increased in amplitude and periodic. The critical draw ratios V_L/V_0 for the onset of this amplified regular

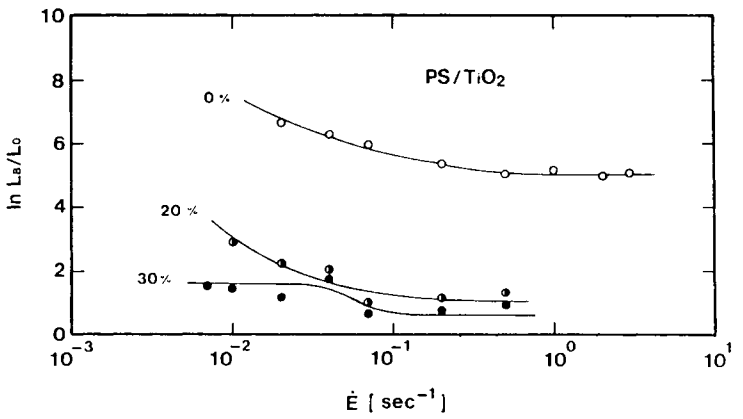

Fig. 6. Elongation to break of polystyrene filaments containing titanium dioxide.

TABLE I
Critical Drawdown Ratios for the Onset of Draw Resonance in Melt Spinning

System	V_L/V_0
PS	40
PS/carbon black (10%)	7
PS/carbon black (20%)	5
PS/TiO_2 (10%)	10
PS/TiO_2 (20%)	10
PS/$CaCO_3$ (10%)	10
PS/$CaCO_3$ (20%)	6

disturbance are shown in Table I. These show that the presence of the particles greatly reduces the stability of the spinline. In Figure 7 we plot D_{max}/D_0 as a function of V_L/V_0. The amplitude of the disturbances are considerably higher for the particle-filled melts than for the base polystyrene for all V_L/V_0. The ratio of wavelength λ to spinline length L, shown in Figure 8, increases with drawdown. In Figure 9 the period P is plotted as a function of drawdown V_L/V_0. It is seen to decrease almost inversely with V_L/V_0.

INTERPRETATION

The results of the preceding section show the destabilization of elongational flow for both simple stretching of filaments and melt spinning by the presence of high volume loadings of solid particles. This would seem to bear out the initial premise and theoretical arguments of this article.

There are few studies in the literature of the elongational flow properties of filled polymer melts. Indeed only Han and Kim[22] have discussed the spinning of such a system (polypropylene filled with calcium carbonate). Adding the filler increases the spinline elongational viscosity χ_{sp} and causes it to fall off more

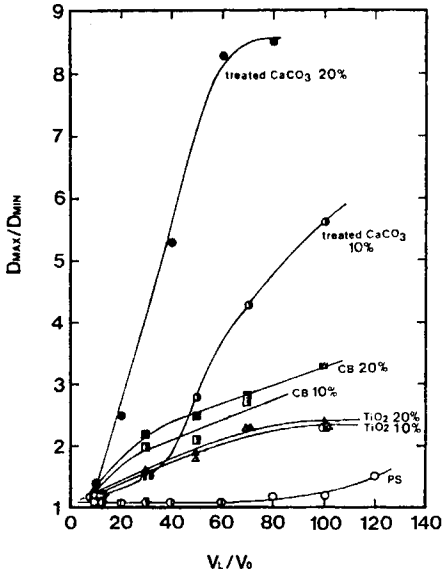

Fig. 7. D_{max}/D_0 as a function of drawdown V_L/V_0 for melt-spun filaments.

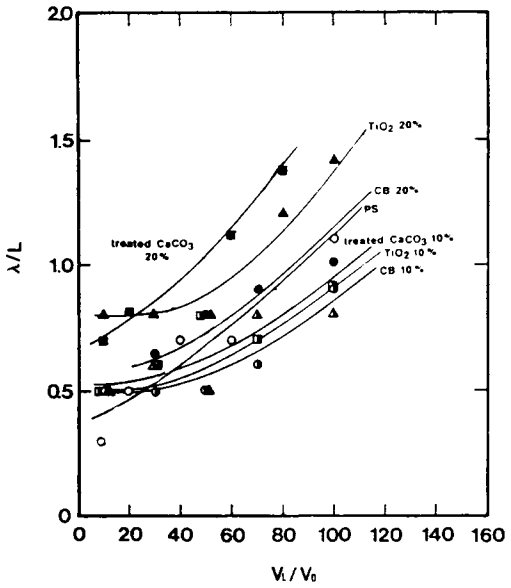

Fig. 8. Draw resonance wavelength as a function of drawdown ratio for melt-spun filaments.

rapidly with deformation rate. This suggests greater spinline instability. However, this is not investigated by Han and Kim.

It might be conjectured that the observations of this paper should be interpreted as hydrodynamic particle effects. Segregated groups of particles could be a "stress concentrator" which would lead to premature failure. However, the extensive mill mixing of the samples and visual observations make this interpretation doubtful.

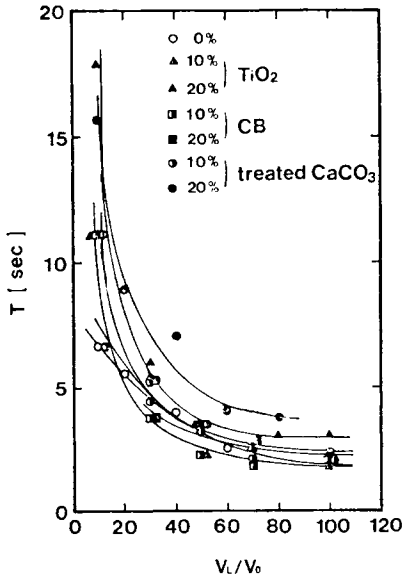

Fig. 9. Draw resonance period as a function of drawdown ratio for melt-spun filaments.

If one applies an analysis similar to Goddard's[23] study of elongational flow of fiber-filled melts, one would expect that in concentrated suspensions in general the elongational viscosity function should more closely resemble the shear viscosity function.[24] This would tend to make elongational viscosity of all suspensions an amplified decreasing function like the shear viscosity. This argument has merit but in the present case where the shear viscosity has a yield value and the high low deformation rate viscosity is caused by interparticle forces, it is probably of secondary importance. It would seem more pertinent to suspensions of larger particles such as glass beads where interparticle interaction is much smaller. In any case, it should be examined in greater detail.

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APPENDIX A

Constitutive Equations of Plastic Fluids and Elongational Flow

Formulation of constitutive equations for fluids with yield values dates to the work of Schwedoff and Bingham 60 years and more ago. These analyses were however one-dimensional in form and directed to shear flow. Three-dimensional tensor formulation of constitutive equations which respond as differentially linear fluids above the yield value date to the work of Hohenemser and Prager[25] and later Oldroyd.[26] This involved combining the von Mises yield surface and the Navier–Stokes Newtonian fluid. The Bingham–Hohenemser–Prager–Oldroyd (BHPO) constitutive equation is of form

$$\mathbf{d} = 0 \qquad tr\ \mathbf{P}^2 < 2Y^2 \tag{A-1a}$$

$$\mathbf{P}\left(1 - \frac{Y}{\Pi_p^{1/2}}\right) = \mathbf{H} \qquad tr\ \mathbf{P}^2 > 2Y^2 \tag{A-1b}$$

where $\mathbf{P}$ is the deviatoric stress tensor defined through

$$\mathbf{P} = \boldsymbol{\sigma} - \frac{1}{3}(tr\ \boldsymbol{\sigma})\mathbf{I} \tag{A-1c}$$

and $\mathbf{H}$ is

$$\mathbf{H} = 2\eta\mathbf{d} \tag{A-2}$$

Oldroyd[25] later proposed using the same formulation with $\mathbf{H}$ representing the behavior of a viscous non-Newtonian fluid. This is accomplished through use of eq. (A-2) with η depending upon the invariants of the deformation rate tensor.

The characteristics of materials which respond as viscoelastic fluids above a yield value were first considered by Hutton[28] and later in more detail by White,[29] Lobe and White[3] and by Tanaka and White.[4,30,31] White[29] presumes the constitutive equation is again of the form of eq. (A-1) only with $\mathbf{H}$ a memory functional equation of form

$$\mathbf{H} = \int_0^\infty \left\{\mu_1(z)\left[\mathbf{c}^{-1} - \frac{1}{3}(tr\ \mathbf{c}^{-1})\mathbf{I}\right] - \mu_2(z)\left[\mathbf{c} - \frac{1}{3}(tr\ \mathbf{c})\mathbf{I}\right]\right\}dz \tag{A-3}$$

In uniaxial extension,

$$v_1 = v_1(x_1) \qquad v_2(x_2) = v_3(x_3)$$

$$\frac{\partial v_1}{\partial x_1} = -2\,(\partial v_2/\partial x_2) \tag{A-4}$$

For the BHPO fluid,

$$\sigma_{11} = \chi(dv_1/dx_1) = Y_e + 3\eta E \tag{A-5}$$

where Y_e, the yield value in uniaxial elongational flow, is

$$Y_e = \sqrt{3}\,Y \tag{A-6}$$

E is the elongation rate dv_1/dx_1, and χ, the elongational viscosity, is

$$\chi = (Y_e/E) + 3\eta \tag{A-7}$$

For the plastic viscoelastic fluid, χ depends upon the forms of $\mu_1(z)$ and $\mu_2(z)$. If we take

$$\mu_1(z) = (G/\tau)e^{-z/\tau} \quad \mu_2(z) = 0 \tag{A-8}$$

it follows that

$$\sigma_{11} = Y_e + \frac{3G\tau E}{(1 - 2\tau E)(1 + \tau E)} \tag{A-9}$$

$$\chi = \frac{Y_e}{E} + \frac{3G\tau}{(1 - 2\tau E)(1 + \tau E)} \tag{A-10}$$

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