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The Spinnability of Polymer Fluid Filaments

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Synopsis

A theoretical study of the stability of extending liquid filaments has been carried out. The interaction of surface tension and different fluid rheological properties is investigated. It is also hypothesized that cohesive failure or fracture will occur if a critical stress level is reached. It is predicted that viscosity and viscoelasticity tend to stabilize the filaments. However, even extremely high viscosity filaments will neck and exhibit ductile failure. In highly viscoelastic fluids, defects tend to heal during stretch. Highly viscoelastic fluid filaments fail by fracture. The theory is used to predict the failure of molten polymer filaments as a function of molecular weight. The extensibility or spinnability of filaments is predicted to exhibit a maximum at intermediate molecular weights with capillarity-ductile failure occurring at low molecular weights and cohesive fracture, at high molecular weights. The results are compared to experiments on polyethylenes. There is general qualitative agreement especially with the behavior of low and high molecular weights where capillarity and fracture occur. The tendency to necking and ductile failure differs considerably among melts and is more pronounced in high-density than in low-density polyethylenes. The application to continuous spinline behavior is discussed, and draw resonance is suggested to be the continuous process analogue of ductile failure.

INTRODUCTION

No problem is more fundamental to polymer rheology or to the fiber industry than the factors determining the ability to form threads from polymer solutions and melts. The problem dates to the very beginnings of the polymer industry, with the melt spinning of thread from gutta percha being described in the patent literature as early as 1845.[1] A decade later, Audemars proposed the manufacture of fiber from solutions of cellulose nitrate plus rubber in ether–alcohol solutions; and in the 1880's and 1890's, Chardonnet and others commercially spun cellulosic fibers from solution.[2] In the present century, Carothers and Hill[3] have suggested and described the formation of synthetic fibers from both synthetic polymer melts and their solutions. A great industry has been built on these processes.

One cannot easily form fibers from all polymer melts nor from all solutions; and as far back as 1933, Carothers and Van Natta[4] studied the influence of molecular weight on fiber formation. It is our purpose here to consider this ability of fluids to be stretched out into filaments of small diameter. We shall refer to it as the *spinnability* of the fluid. It was not until the postwar

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period that studies of the mechanism of spinnability of polymer fluid filaments began to appear. Nitschmann and Schrade[5] called attention to ductile failure mechanisms and noted that an elongational viscosity that increased with extension rate would stabilize the filament. The existence of such an effect in the theory of viscoelastic fluids and its stabilizing influence were noted by Lodge,[6] White,[7] and Chang and Lodge,[8,9] among others. Hirai[10] suggested that filament instability was due rather to capillarity. Ziabicki and Takserman-Krozer[11–13] have argued against the ductile failure mechanism and proposed instead that filaments fail according to either capillarity or a "cohesive" fracture mechanism depending upon the rheological properties of the fluid, with the former mechanism dominating in low-viscosity systems. More recently, Onogi, Matsumoto, and Kamei[14] have initiated a comprehensive experimental study of the tensile failure of molten polymer filaments as a function of molecular weight. White and Tokita[15] and Cogswell and Hubbard[16] have given general discussions of various types of failure phenomena during polymer processing.

It is the authors' view that each of the above views on spinnability is, in some respects, correct. However, no generally consistent theory which includes and properly integrates all of these effects has been developed. This is the purpose of the present paper. We believe that each of three mechanisms—*capillarity, ductile failure,* and *fracture*—must be considered in any self-consistent theory. To be specific, by *capillarity* we mean the surface tension-induced breakup of filaments into drops or ligaments (see Fig. 1a). The action of surface tension to propagate disturbances and cause the breakup of a liquid column[17,18] was first proposed by Plateau about one hundred years ago and was then considered by Rayleigh[19–22] in some detail using the methods of linear stability analysis. There have been numerous variations and attempts at extension[23–28] of Rayleigh's analysis including studies of nonlinear stability.[26–28] The capillarity instability in viscoelastic fluid jets has been considered by Middleman[29] and by Yerushalmi, Shinnar, and their co-workers.[30,31]

By *ductile failure* we mean a 100% reduction in cross section within a neck caused by the high local stress level (see Fig. 1b). The problem of ductile failure of filaments, i.e., failure due to the growth of a neck, was first considered by metallurgists investigating the failure of steel and other metals. The concept is implicit in much of the early literature,[33,34] but the first analysis of stress concentrations leading to neck development is due to Nadai and Manjoine.[34] This was later reformulated and elaborated on by Orowan.[35] A careful discussion of necking in solid polymers was given by Vincent.[36] Recently, Chang and Lodge[8] have analyzed neck development in a nonlinear viscoelastic fluid using a formulation similar to Orowan's[35] and found viscoelasticity to be stabilizing. Detailed stress analyses in a necked region of a plastic material described by a von Mises criterion have been given by Bridgman.[37]

The interaction between ductile and surface tension instabilities has received little attention but is implicit in work of Tomotika[25] and Flumerfelt.[32]

By *fracture* we mean a cohesive failure involving the instantaneous reduction of a finite cross section, i.e., a break (see Fig. 1c). Theories of fracture based on critical stresses and energies date to the 19th century.[33,38] The sit-

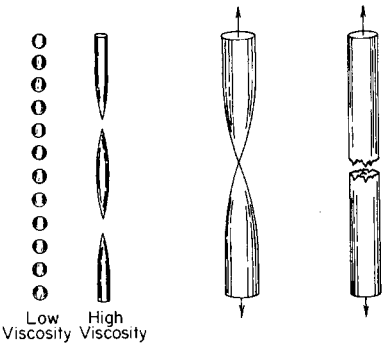

Fig. 1. Mechanisms of filament instability: (a) capillarity; (b) ductile failure; (c) fracture.

uation is, however, complex for, as shown by Griffith,[39] fracture is generally associated with the presence of microscopic defects. In metals, fracture often occurs in a developing neck as discussed by Orowan[35] and Nadai[33,34] and others so that the ductile failure and fracture mechanisms are combined. Most studies of the catastrophic failure of solids deal with materials which exhibit elastic or elastic-plastic response. In working with polymer melts, we are dealing, however, with viscoelastic fluids and not solids, and there are very characteristic differences in response. Most importantly, a viscoelastic fluid may exhibit large deformations when stretched at small rates and "fracture" only with rapid deformations. Reiner and Freudenthal[38,40] and Reiner and Weissenberg[38] view this in terms of the energetic theory of strength and propose that we must divide the energy of deformation or stress work into dissipative and recoverable parts—and that only the recoverable deformation energy contributes to failure. For a simple Maxwell fluid, this leads to a critical stress criterion. While Reiner et al. do not consider the influence of defects, it would seem that the appropriate modification of the essence of Griffith's theory would be the use of the recoverable energy.

We will specifically investigate the question of how this ability to form fibers by extending a fluid filament would vary in a homologous series of organic compounds ranging from low molecular weights to polymers. This theory of spinnability will be constructed using the methods of linear stability analysis. We will also look at comparisons to experiment. In the final part of the paper, we will relate our results to continuous melt-spinning operations. This paper is a continuation of earlier studies at the University of Tennessee on the rheology and development of structure during fiber formation[41–47] and, most specifically, the papers of Chen, Hagler, Abbott, Bogue, and White[42] and Takaki and Bogue[46] which study the stretching of molten polymer filaments.

HOMOGENEOUS DEFORMATION OF FLUID FILAMENTS

For a fluid filament of radius R and length L in uniaxial extension (see Fig. 2),

$$\mathbf{v} = v_1(x_1)\mathbf{e}_1 + v_2(x_2)\mathbf{e}_2 + v_3(x_3)\mathbf{e}_3 \tag{1}$$

with v_2 equal to v_3. Here, the rate of deformation tensor $\mathbf{d}$ is

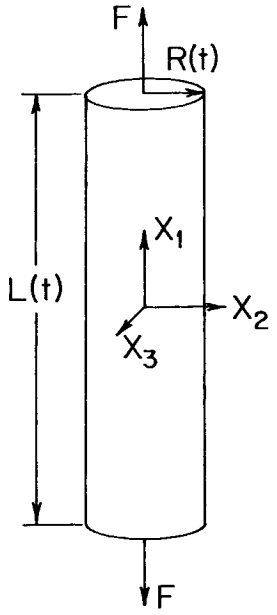

Fig. 2. A fluid filament in uniaxial extension.

$$\mathbf{d} = \tfrac{1}{2}[(\nabla \mathbf{v}) + (\nabla \mathbf{v})^T] = \begin{vmatrix} E & 0 & 0 \\ 0 & -\tfrac{1}{2}E & 0 \\ 0 & 0 & -\tfrac{1}{2}E \end{vmatrix} \tag{2a}$$

where

$$E = \frac{\partial v_1}{\partial x_1} \tag{2b}$$

and for constant E, the filament deforms according to

$$L = L(0)e^{Et} \qquad R = R(0)e^{-Et/2} \tag{3}$$

The rheological properties of fluids vary considerably with molecular structure, and this variation would seem to have a very strong influence on spinnability. Nowhere is this variation as striking in organic compounds, especially in homologous series varying from low molecular weights to polymers.[14,48–57] Low molecular weight compounds behave as Newtonian fluids, while high molecular weight polymers are viscoelastic.

For Newtonian fluids, the stress tensor σ may be represented as[17,18,58]

$$\sigma = -p\mathbf{I} + 2\eta\mathbf{d} \tag{4}$$

The stress in a Newtonian fluid filament is

$$\sigma = -\gamma/R\ \mathbf{I} + \begin{vmatrix} \chi E & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \tag{5a}$$

with

$$\chi = 3\eta \tag{5b}$$

where γ is the surface tension and σ_{22} and σ_{33} equal to $(-\gamma/R)$ follows from the boundary conditions on the surface of the cylinder.[17,18,59] The quantity χ is known as the elongational viscosity and, its equality to 3η is due to Trouton.[60]

We will to a large extent be concerned with polymeric fluids which possess viscoelastic rather than simple viscous properties. For viscoelastic fluids, the stress depends upon the entire deformation history of the fluid. The simplest type of viscoelastic fluid model is the one-dimensional equation of Clerk Maxwell.[38,61] The generalization of Maxwell's constitutive equation to a three-dimensional form valid for large deformations is not unique, but the most useful such generalization is White and Metzner's[62,63]:

$$\sigma = -p\mathbf{I} + \mathbf{P} \tag{6a}$$

$$\mathbf{P} + \tau \frac{\delta \mathbf{P}}{\delta t} = 2\eta \mathbf{d} \tag{6b}$$

where

$$\frac{\delta P_{ij}}{\delta t} = \left(\frac{\partial}{\partial t} + v_m \frac{\partial}{\partial x_m}\right) P_{ij} - \frac{\partial v_i}{\partial x_m} P_{mj} - \frac{\partial v_j}{\partial x_m} P_{im} \tag{6c}$$

is Oldroyd's contravariant convected derivative[64] and τ is a relaxation time. The asymptote of τ being equal to zero is the Newtonian fluid case. In simple shear flow,

$$\mathbf{v} = \dot{\gamma} x_2 \mathbf{e}_1 + 0\mathbf{e}_2 + 0\mathbf{e}_3 \tag{7}$$

where $\dot{\gamma}$ is the shear rate. Equation (6) leads to a shear viscosity η and a first normal stress difference of $2\eta\tau\dot{\gamma}^2$ with a *zero* second normal stress difference. This is in reasonable agreement with experiment,[63,65] especially if we take τ to be a function of deformation rate.[62] In small deformation oscillatory experiments, the agreement of eq. (6) with experimental data is only qualitative.[66]

The rheological response of a viscoelastic fluid of the type described by eq. (6) to a uniform uniaxial extension has been nicely treated by Denn and Marrucci.[67] Modifying their result to include surface tension gives the transient stress

$$\sigma_{11}(t) = -\frac{\gamma}{R} + P_{11} - P_{22} = -\frac{\gamma}{R} + \frac{2\eta E}{1 - 2\tau E}\left[1 - e^{-(1-2\tau E)t/\tau}\right] + \frac{\eta E}{1 + \tau E}\left[1 - e^{-(1+\tau E)t/\tau}\right] \tag{8a}$$

$$\sigma_{22} = \sigma_{33} = -\frac{\gamma}{R} \tag{8b}$$

where the deformation begins at time zero. For small E, the response is linear viscoelastic.[66] When E is greater than $1/2\tau$, the stress grows in an unbounded manner. For long duration times when E is less than $1/2\tau$, eq. (5a) is valid, but with χ a function of τE. Specifically,

$$\chi = \frac{3\eta}{(1 + E\tau)(1 - 2E\tau)} \tag{8c}$$

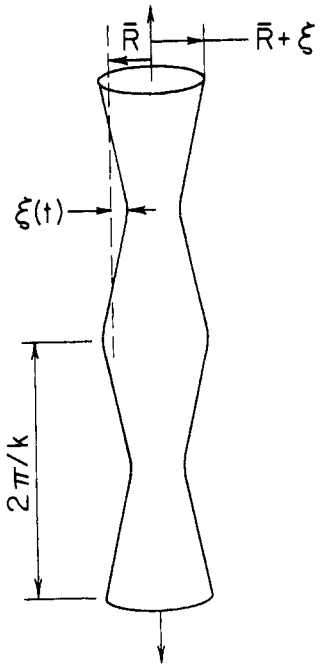

Fig. 3. Filament containing a periodic disturbance in its diameter.

For small τE, χ is simply 3η, or three times the shear viscosity.

More general useful constitutive equations may be developed for viscoelastic fluids which can be applied to analyze flow problems. The authors have found constitutive equations[42,63,68–77] of form

$$\mathbf{P} = \int_0^\infty [m_1(z)\mathbf{c}^{-1} - m_2(z)\mathbf{c}]dz \tag{9}$$

of great use, where $\mathbf{c}^{-1}$ is the Finger deformation tensor and $\mathbf{c}$ the Cauchy deformation tensor, and $m_1(z)$ and $m_2(z)$ are relaxation modulus functions dependent upon deformation invariants. Generally, eq. (6) is equivalent to the special case of eq. (9) for which $m_2(z)$ is zero and $m_1(z)$ is a single exponential term. Transient stress development in uniaxial extension of single integral constitutive equations has received attention in the literature.[42,71]

Experimental studies of stress development in molten polymer filaments undergoing constant stretch rate have been made by Ballman,[72] Meissner,[73] Vinogradov et al.,[74] and Everage and Ballman.[75] The latter authors[73–75] have observed the unbounded growth of stress at high deformation rates. At low deformation rates, the χ–E function is obtained. The χ function has also been obtained by Cogswell[76] using constant stress experiments.

ANALYSIS OF NONHOMOGENEOUS DEFORMATION

Dynamics

The basis of our analysis is Cauchy's[77] law of motion:

$$\rho\left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{v}\right] = \nabla\cdot\sigma \tag{10}$$

As we are treating thin cylindrical filaments, we will use Cauchy's law integrated across the filament cross section. Matovich and Pearson[78] have carried out such an integration for the steady-state case including consideration of the influence of surface tension on the filament periphery. Generalizing this to the unsteady-state gives

$$\pi R^2\rho\left[\frac{\partial v_1}{\partial t} + v_1\frac{\partial v_1}{\partial x_1}\right] = \frac{\partial}{\partial x_1}[\pi R^2\sigma_{11}] + \frac{\partial}{\partial x_1}[2\pi R\gamma] \tag{11}$$

where R is the filament diameter. Note that the special case of the above equation where inertia and surface tension are neglected is

$$\frac{\partial}{\partial x_1}[\pi R^2\sigma_{11}] = \frac{\partial F}{\partial x_1} = 0 \tag{12}$$

where F is the tensile force acting on the filament cross section.

Disturbances and Linearized Disturbance Equations

We presume that the periphery of a filament of a fluid is perturbed by an amount ξ (see Fig. 3):

$$R = \bar{R} + \xi \tag{13}$$

which results in the velocity components v_1, v_2, and v_3 being perturbed according to

$$v_1 = \bar{v}_1 + v'_1 \tag{14a}$$

$$v_2\Big|_{x_2=R} = \bar{v}_R + v'_R = \frac{d\bar{R}}{dt} + \frac{D\xi}{Dt} \tag{14b}$$

where $D\xi/Dt$ is the time derivative following the fluid. These components are interrelated through continuity

$$\frac{\partial v_1}{\partial x_1} = -\left(\frac{\partial v_2}{\partial x_2} + \frac{\partial v_3}{\partial x_3}\right) \tag{15a}$$

$$\frac{\partial v_1}{\partial x_1} = -\frac{2}{R}v_R \tag{15b}$$

Noting that $\bar{v}_1$ and $\bar{v}_R$ satisfy continuity, we may rewrite eq. (15) as follows:

$$\frac{\partial v'_1}{\partial x_1} = \frac{\partial v_1}{\partial x_1} - \frac{\partial \bar{v}_1}{\partial x_1} = -2\left[\frac{\bar{v}_R + v'_R}{\bar{R}+\xi} - \frac{\bar{v}_R}{\bar{R}}\right] = -\frac{2}{\bar{R}}\left[\frac{D\xi}{Dt} - \frac{\bar{v}_R}{\bar{R}}\xi\right] \tag{16}$$

For uniaxial extension, as specified in eq. (3), we have from eq. (14) and eq. (15)

$$\bar{v}_1 = Ex_1, \quad \bar{v}_R = -\frac{E}{2}\bar{R} \tag{17}$$

$$\frac{\partial v'_1}{\partial x_1} = -\frac{2}{\bar{R}}\left[\frac{D\xi}{Dt} + \frac{E}{2}\xi\right] \tag{18}$$

We will presume that the disturbance ξ varies periodically along the length of the filament, i.e. (see Fig. 3),

$$\xi(t,x_1) = \hat{\xi}(t)e^{ikx_1} \tag{19}$$

As the filament is being steadily elongated, the periodicity of the disturbance changes. For an incompressible fluid, the wavelength λ and wave number k vary according to

$$\lambda = \lambda(0)e^{Et} \tag{20a}$$

$$k = \frac{2\pi}{\lambda} = k(0)e^{-Et} \tag{20b}$$

A filament fails when $\xi(t)$ becomes equal to $\bar{R}(t)$.

Newtonian Fluid Filaments

In extending Newtonian fluid filaments, breakup results from the interaction of capillarity and ductile failure. For low-viscosity fluids, we may neglect extension since they break rapidly by capillarity, while for high viscosity, we may neglect inertia. Let us look at each of these cases in turn. First, the low-viscosity case where we neglect extension so that the filament is originally stationary. Substitution of eq. (5) into eq. (11) gives

$$\pi R^2 \rho \frac{\partial v_1}{\partial t} = \frac{\partial}{\partial x_1}\left[\pi R^2\left(-p_\gamma + 3\eta\frac{\partial v_1}{\partial x_1}\right)\right] + \frac{\partial}{\partial x_1}[2\pi R\gamma] \tag{21}$$

We now introduce eqs. (13), (18), and (19) with

$$\bar{p}_\gamma = \frac{\gamma}{R},\ p'_\gamma = -\gamma\left(\frac{\xi}{R^2} + \frac{\partial^2\xi}{\partial {x_1}^2}\right) = -\frac{\gamma}{R^2}(1 - k^2R^2)\hat{\xi} \tag{22a,b}$$

where in obtaining eq. (22b) we follow Rayleigh[19–21] and Weber[23] (see Levich[18] for a detailed development). This allows us to transform eq. (21) into

$$\frac{d^2\hat{\xi}}{dt^2} = -\frac{3\eta k^2}{\rho}\frac{d\hat{\xi}}{dt} + \frac{\gamma k^2}{2\rho R}(1 - k^2R^2)\hat{\xi} \tag{23}$$

This clearly has an exponential solution

$$\hat{\xi}(t) = \hat{\xi}(0)e^{\alpha t} \tag{24}$$

where

$$\alpha^2 + \frac{3\eta k^2}{\rho}\alpha - \frac{\gamma k^2}{2\rho R}(1 - k^2R^2) = 0 \tag{25}$$

which may be readily seen to be Weber's[23] asymptotic solution of Rayleigh's analysis. The asymptotes for low and high viscosity are

$$\lim_{\rho/\eta\to\infty} \alpha = \sqrt{\gamma k^2/2\rho R\,(1 - k^2R^2)} \tag{26}$$

$$\lim_{\rho/\eta\to 0} \alpha = \frac{\gamma}{6\eta R}(1 - k^2R^2) \tag{27}$$

where for eq. (26) kR would be 0.7, and in eq. (27) kR would be zero to give

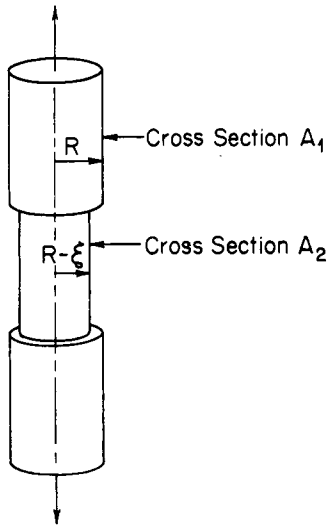

Fig. 4. Orowan-Chang-Lodge model of disturbance in a filament being stretched.

the maximum growth rate. Thus, the corresponding wavelength increases with viscosity.

Let us now turn to the problem of the very viscous filament. Here, we consider the interaction of surface tension and ductility in the absence of inertial effects. The equation of motion is

$$0 = \frac{\partial}{\partial x_1}\left[\pi R^2\left(-p_\gamma + 3\eta\frac{\partial v_1}{\partial x_1}\right)\right] + \frac{\partial}{\partial x_1}[2\pi R\gamma] \tag{28}$$

Equation (28) with the aid of eqs. (13), (14), (16), (19), and (22) reduces to

$$\frac{1}{\hat{\xi}}\frac{d\hat{\xi}}{dt} = -\frac{1}{R}\frac{dR}{dt} + \frac{\gamma}{6\eta R}(1 - k^2R^2) \tag{29}$$

The maximum growth rate is for k equal to zero, and for stretching with constant rate E, we obtain

$$\ln\frac{\xi(t)}{\xi(0)} = \frac{\gamma}{3\eta R(0)E}(e^{(E/2)t} - 1) + \frac{E}{2}t \tag{30}$$

This shows an additive effect of ductility and capillarity on disturbance growth.

For the case of very high viscosity so that capillarity can be neglected,

$$\frac{1}{\xi}\frac{d\xi}{dt} = -\frac{1}{R}\frac{dR}{dt}\left(=\frac{E}{2}\right) \rightarrow \frac{d}{dt}(R\xi) = 0 \tag{31}$$

Equation (31) may also be obtained as a linearized form from the original analysis of ductile failure due to Orowan,[34] which is based on the model shown in Figure 4. Orowan showed that the cross-sectional area of a defect in a Newtonian fluid filament remained constant in time, that is,

$$\frac{dA'}{dt} = \frac{d}{dt}[\pi R^2 - \pi(R - \xi)^2] = \frac{d}{dt}(R\xi) = 0 \tag{32}$$

where A' is the perturbed cross section.

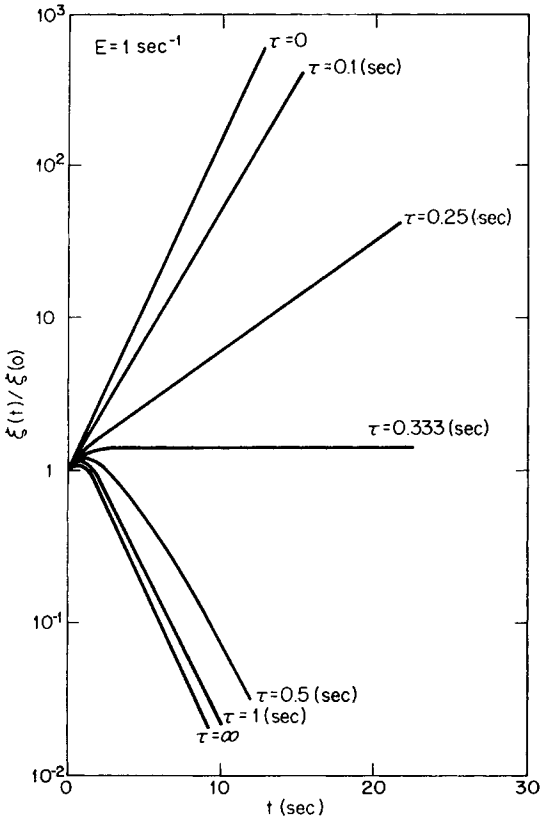

Fig. 5. Development of disturbance as a function of relaxation time τ. Prediction of eq. (35) at E = 1/sec.

Viscoelastic Fluid Filaments

With viscoelastic fluids, we are generally treating high-viscosity liquids and may neglect inertia and capillarity. If we consider long-duration stretching for highly viscoelastic fluid, we note from eq. (8a) that $P_{11} \gg P_{22}$ for large τE. If we neglect P_{22}, we can obtain an analytical solution. Introduction of eqs. (6), (13), (14), (17), (18), and (19) into eq. (11) gives (after considerable manipulation)

$$\frac{1}{\xi}\frac{d\xi}{dt} = \frac{E\left(-\bar{P}_{11} + \dfrac{2\eta}{\tau}\right)}{2\bar{P}_{11} + 4\dfrac{\eta}{\tau}} \tag{33}$$

where

$$\bar{P}_{11} = \frac{2\eta E}{1 - 2\tau E}\left[1 - e^{-(1-2\tau E)t/\tau}\right] \tag{34}$$

The integrated form is

$$\ln\frac{\xi(t)}{\xi(0)} = -\frac{E}{2}t - \frac{\tau E}{1 - \tau E}Et$$

$$-\frac{(\tau E)^2}{(1-2\tau E)(1-\tau E)}\ln\frac{(1-\tau E)-\tau E e^{-(1-2\tau E)t/\tau}}{1-2\tau E} + \frac{\tau E}{1-2\tau E}\ln\frac{(1-\tau E)e^{(1-2\tau E)t/\tau}-\tau E}{1-2\tau E} \quad (35)$$

The predictions of the above expression are shown in Figure 5 for varying τ at $E = 1(1/\text{sec})$.

If we consider long-duration growth of disturbances, the logarithmic terms of the above equation may be simplified to yield

$$\ln\frac{\xi(t)}{\xi(0)} = \frac{E(1-3\tau E)}{2(1-\tau E)}t + \frac{\tau E}{1-\tau E}\ln\frac{1-\tau E}{1-2\tau E} \qquad \left(\text{for } \tau E < \frac{1}{2}\right) \quad (36a)$$

$$\ln\frac{\xi(t)}{\xi(0)} = -\frac{E}{2}t + \ln(Et+1) \qquad \left(\text{for } \tau E = \frac{1}{2}\right) \quad (36b)$$

$$\ln\frac{\xi(t)}{\xi(0)} = -\frac{E}{2}t + \frac{\tau E}{1-\tau E}\ln\frac{\tau E}{2\tau E - 1} \qquad \left(\text{for } \tau E > \frac{1}{2}\right) \quad (36c)$$

For small values of τE, the disturbance grows with time and when $\tau \to 0$, this reduces to the Newtonian result eq. (31). When τE increases to a value of $\frac{1}{3}$, disturbances cease to grow; and when τE is greater than $\frac{1}{3}$, the disturbances are indeed damping out.

This enhanced stability of filaments to disturbances may be traced to the unbounded development of stress in nonlinear viscoelastic fluids at large values of τE as shown by Denn and Marrucci[67] and represented in eq. (8). Because of this effect, the deformation response to the high stresses in regions of minimal cross section is small and disturbances do not grow. It is of interest that the criterion of disturbance growth of τE equal to $\frac{1}{3}$ is more severe than the one of stress growth of τE being equal to $\frac{1}{2}$.

Just as the Newtonian fluid ductile failure asymptote is equivalent to the simple Orowan model, so the present analysis is equivalent to that of Chang and Lodge.[8] An exact comparison is possible but would generally require a numerical solution to the Chang-Lodge nonlinear integral equation. It is, however, possible to obtain an analytical solution for the asymptote of $\tau \to \infty$. This would be the case for a material like vulcanized rubber.[79]

Referring to Figure 4, the stress can be expressed as

$$\sigma_{11}(t) = P_{11} - P_{22} = G(c_{11}^{-1} - c_{22}^{-1}) = G\left[\left(\frac{A(0)}{A(t)}\right)^2 - \frac{A(t)}{A(0)}\right] \quad (37)$$

A simple force balance of two cylinders of different cross-sectional area A_1, A_2 gives, after neglecting P_{22},

$$\frac{A_2(t)}{A_1(t)} = \left(\frac{A_2(0)}{A_1(0)}\right)^2 \quad (38)$$

The above expression seems to be able to approximate their result for the material parameters and conditions they employed. In terms of radius, we obtain from the above equation

$$\frac{\xi(t)}{\xi(0)} = 2\frac{R(t)}{R(0)} \quad (39)$$

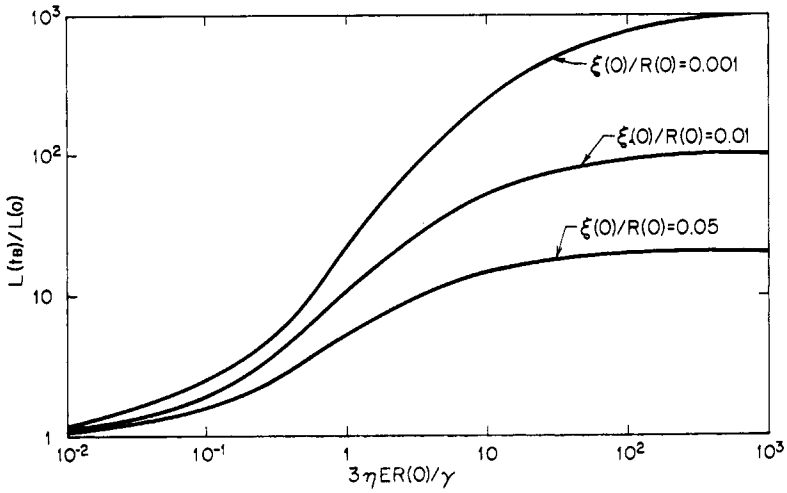

Fig 6. Elongation to break $L(t_B)/L(0)$ as a function of $3\eta ER(0)/\gamma$ with $\xi(0)/R(0)$ as a parameter.

For constant stretching rate, the above ratio becomes $2e^{-Et/2}$, which is the asymptotic value of eq. (36c) for $\tau \to \infty$.

We can also obtain an analytical result without neglecting P_{22} for this asymptotic case:

$$\frac{\xi(t)}{\xi(0)} = \frac{R(R^6 + 2R(0)^6)}{R(0)[R(0)^6 + 2R^6]} = \frac{(2e^{2Et} + e^{-Et})}{(e^{2Et} + 2e^{-Et})} e^{-Et/2} \to 2e^{-Et/2} \tag{40}$$

We note that neglecting P_{22} does not affect our result if we are concerned with the long-time asymptote.

PREDICTION OF SPINNABILITY

Interpretation from Theory

It is possible to use the results of the previous section to predict the length of a thread which may be formed by extending a cylinder. This is done by determining the time t_B required for the disturbance to grow to the size of the cylinder radius, i.e.,

$$\xi(t_B) = R(t_B) = R(0)e^{-Et_B/2} \tag{41}$$

and then to compute the elongation to break:

$$\ln \frac{L(t_B)}{L(0)} = Et_B. \tag{42}$$

For Newtonian ductile and capillarity failure, introducing eq. (30) into eq. (41) gives

$$\ln \frac{L(t_B)}{L(0)} = \ln \frac{R0)}{\xi(0)} - \frac{\gamma}{3\eta ER(0)} \left(\sqrt{\frac{L(t_B)}{L(0)}} - 1 \right) \tag{43}$$

We note $L(t_B)/L(0)$ becomes equal to $R(0)/\xi(0)$ in the absence of surface tension. The elongation to break $L(t_B)/L(0)$ was determined as a function of

$3\eta ER(0)/\gamma$ taking $\xi(0)/R(0)$ as parameter and plotted in Figure 6. The dimensionless number $\gamma/3\eta ER(0)$ is the ratio of surface tension to elongational viscous stress (a capillarity number).

For the convected Maxwell fluid with $\tau E < \frac{1}{2}$ and no surface tension, substituting eq. (36a) into eq. (41) gives the elongation to break:

$$\ln \frac{L(t_B)}{L(0)} = \frac{1}{1-2\tau E}\left\{(1-\tau E)\ln\frac{R(0)}{\xi(0)} - \tau E \ln\frac{1-\tau E}{1-2\tau E}\right\} \tag{44}$$

This is the expression for purely ductile failure of a viscoelastic fluid. We note the spinnability is completely characterized by the defect size $\xi(0)/R(0)$ and a dimensionless number τE, the Weissenberg number[7,63] appropriate to this type of deformation. As τE increases, so will $L(t_B)$ so that viscoelasticity increases spinnability. When $\tau E > \frac{1}{2}$, the filaments may be stretched out indefinitely according to our theory. When the elongation rate E goes to zero, it is found that viscoelasticity destabilizes the capillarity breakup of a liquid cylinder.[29,30] For finite E, however, viscoelasticity acts to stabilize the cylinder. For disturbances introduced into stationary fluids, viscoelastic constitutive equations reduce to linear viscoelasticity which is always "softening" rather than "strain hardening." It is possible that linear viscoelastic stability analyses may generally mispredict the growth characteristics of disturbances when these reach finite amplitudes. This would be especially the case in a problem like the growth of disturbances propagated by surface tension on a filament which involves large deformation rates when the amplitude become large. Similar views are expressed by Gordon, Yerushalmi, and Shinnar.[31] When steady flows exist, the nonlinearities directly appear in the linearized analysis, and this problem does not arise.

In the above discussions, we have only considered tensile failure resulting from ductility and surface tension. For a real material, we need also consider cohesive fracture resulting from high tensile stresses and strain energies. Indeed, there may be no true ductile failure because as the neck thins down, a critical stress may always be exceeded. We shall presume that cohesive failure will always follow if the total applied stress exceeds some critical stress σ_{cr}. Returning now to our extending viscoelastic fluid filament, we see that when $\tau E > \frac{1}{2}$, the stress increases exponentially with time so that in practice the stress reaches the critical value which leads the material to fracture. In this asymptote, P_{22} is negligible and the spinnability may be expressed as

$$\ln \frac{L(t_B)}{L(0)} = \frac{\tau E}{2\tau E - 1}\ln\left\{1 + \frac{\sigma_{cr}(2\tau E - 1)}{2\eta E}\right\} \tag{45}$$

When $\tau E = \frac{1}{2}$, the predictions of the ductility and fracture mechanisms are

$$\ln \frac{L(t_B)}{L(0)} = \frac{R(0)}{\xi(0)} - 1 \tag{46a}$$

$$\ln \frac{L(t_B)}{L(0)} = \frac{\tau}{2\eta}\sigma_{cr} \tag{46b}$$

which are unrealistically large. This is because the stress is predicted to increase linearly with time when $\tau E = \frac{1}{2}$. We can probably improve this by using more realistic constitutive equations of the form of eq. (9) in which the

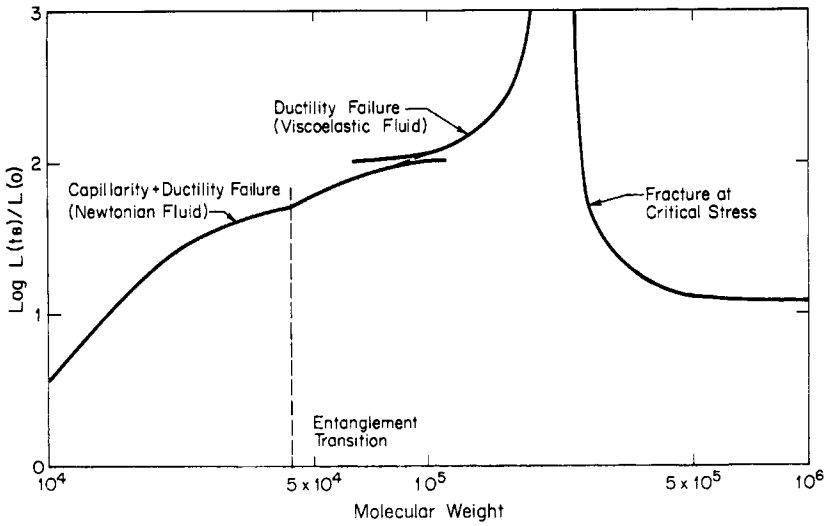

Fig. 7. Predicted elongation to break $L(t_B)/L(0)$ as a function of molecular weight for polystyrene at 160°C based on eqs. (43), (44), and (45) using the rheological data of Onogi, Masuda, and Kitagawa[54] and $\xi(0)/R(0) = 0.01$, $R(0) = 0.1$ cm, $\gamma = 30$ dynes/cm, $\sigma_{cr} = 10^8$dynes/cm^2, and $E = 0.01$ 1/sec.

dependence of τ upon E is included. In this case, the stress would be predicted to increase exponentially or reach steady-state value but no linear increase with time for any stretch condition.

Response of Homologous Series of Polymer Melts

By knowledge of the dependence of rheological properties upon molecular weight of homologous series of molten polymers, we may use the results of the previous section to compute the dependence of fiber spinnability upon molecular weight. Substantial data on polystyrene melts with narrow molecular weight distributions are available, largely due to the efforts of Kyoto and Nagoya researchers.[14,52,54–57] Less extensive but significant data exist on other systems such as polyisobutylene[49,51] and poly(vinyl acetate).[53,57] Using these data, we can determine η and τ as a function of molecular weight, neglecting non-Newtonian viscosity in the approximation of the convected Maxwell model. At low molecular weights, polymer melts are Newtonian fluids, with the viscosity increasing approximately as the first power of the molecular weight. As molecular weight increases, they reach a transition region in which viscoelasticity develops, the viscosity function becomes non-Newtonian, and the zero shear viscosity changes to about a 3.5 power dependence upon molecular weight.[49,51,56,57]

In Figure 7, we plot $L(t_B)/L(0)$ versus molecular weight for polystyrene at 160°C for filaments with elongation rates of 0.01 sec^{-1} using eqs. (43) and (44). The rheological properties τ and η are taken from the work of Onogi, Masuda, and Kitagawa.[54] Initial defect size $\xi(0)/R(0) = 0.01$, initial radius $R(0) = 0.1$ cm and surface tension $\gamma = 30$ dynes/cm are used. It can be seen that the "spinnability" $L(t_B)/L(0)$ is predicted to increase with molecular weight and to eventually go to very large values when τE is greater than $\frac{1}{3}$

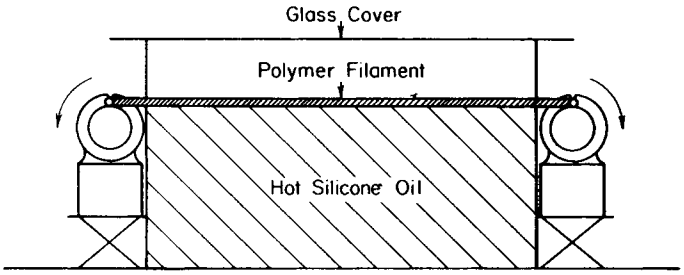

Fig. 8. Experimental apparatus for study of extension of molten polymer filaments.

and approaching ½. This would be at a value of τ of 50 sec for E equal to 0.01 sec^{-1}. This is, of course, unrealistic as infinite stresses would develop in the filament as it is so extended. We now invoke a critical stress leading to cohesive failure. The value of $L(t_B)/L(0)$ may be computed from eq. (45). As η and τ increase rapidly with molecular weight, $L(t_B)/L(0)$ rapidly approaches the asymptote $\sqrt{\sigma_{cr}\tau/\eta}$ or $\sqrt{\sigma_{cr}/G}$. This is shown in Figure 7 using a critical stress σ_{cr} of 10^8 dynes/cm^2.

The transition between the surface tension–ductility curve and the cohesive failure predictions in Figure 7 seems abrupt. We can probably improve this by using better constitutive equations in which the dependence of τ upon E is included.

EXPERIMENTAL

Apparatus and Materials

We have carried out various experiments in our laboratories on the stability of molten polymer filaments using apparatus of the type shown in Figure 8. The polymer filament floats near the surface of the silicone oil and is taken up by two drums. The oil bath is 30 cm long and 11 cm wide, and the silicone oil is about 11 cm deep. The temperature is controlled within ±1°C. The apparatus is similar to that of Meissner[73] and, to a lesser extent, Cogswell.[76] The apparatus enables one to perform and observe constant elongation rate experiments and has been most useful in studying the mechanism of breakup of filaments.

Our studies thus far have emphasized polyethylenes. Several of the polymers investigated and their behavior are summarized in Table I. The series of polymers were so chosen as to represent a wide range of molecular weights and rheological properties as well as include both low-density and high-density varieties.

Results

The experimental results are summarized in Table I. Low molecular weight polyethylene wax showed an obvious capillarity breakup.

High molecular weight low-density polyethylene filaments generally exhibit cohesive fracture at high extension rates but can be extended almost indefinitely at low rates. At constant elongation rate E, as melt index decreases

TABLE I
Polyethylene Melt Filament Breakup Characteristics at 160°C

Material	Melt index	Zero shear viscosity η_0, poise	Elongation to break $\ln L(t_B)/L(0)$ (E = 0.1 sec^{-1})	Remarks on failure	Reference to rheological characterization study
A. Low-Density Polyethylene					
Union Carbide DYDT	polymer wax (>2000)	small	0	capillarity failure	—
Union Carbide DNDA0455	60	—	very large	large extension before ductile failure	—
Union Carbide DADA0917	23	8×10^3 (180°C)	13.5	stretches almost indefinitely at low stretch rate	80
Dow TYON 610M	5.0	5×10^4 (180°C)	9.5	stretches almost indefinitely at low stretch rate	80
Dow TYON 560E	2.1	9×10^4 (160°C)	4.5 (130°C)	cohesive fracture at high stretch rate	41
Tennessee Eastman Tenite 800	1.7	2.6×10^5 (160°C)	4.5	cohesive fracture at high stretch rate	69
B. High-Density Polyethylene					
Phillips Marlex EMB6050	5.0	5×10^4 (180°C)	3.0	ductile failure	47, 80
Tennessee Eastman Tenite 3340	2.6	1.65×10^5 (160°C)	2.5	ductile failure	69
Phillips Marlex EHM6001	0.1	2×10^6 (180°C)	1.5	ductile failure	47, 80

(molecular weight increases), the elongation to break decreases. The trends are in agreement with Figure 7.

We also studied high-density linear polyethylenes. These melts exhibited ductile failure on being stretched, and only small elongations to break were found possible.

Comparison with Other Experimental Studies

Our experimental results are similar to those of other researchers. Ziabicki[11] has examined experimental data from the literature and found that the thread length L may be represented as a function of the product of viscosity η and applied velocity V. The data are similar to Figure 6 at low ηV but decrease at high ηV. This is presumably due to fracture. If one interprets η as related to molecular weight, the Ziabicki data summary has the same form as Figure 7.

Experimental studies by Chen, Hagler, Abbott, Bogue, and White[42] in their weight-dropping elongational flow apparatus found that low-density polyethylene filaments could readily be deformed, but high-density polyethylene exhibited ductile failure. Presumably, the reason our analysis is unable to cope with observations of this sort is that it is based upon a simple Maxwell model, and one would probably need to use more sophisticated constitutive equations similar to eq. (9).

Various researchers[14,15,46] have considered the influence of molecular weight distribution on tensile failure of filaments. Broadening molecular weight distribution enhances filament stability and increases elongation to break. This is not readily interpretable in terms of our theory. A more sophisticated constitutive equation is needed. The approach of Takaki and Bogue[46] does suggest how the necessary constitutive equations might be formulated.

APPLICABILITY TO CONTINUOUS SPINLINE

The application of the above analysis to continuous fiber spinline (see Fig. 9) must now be discussed. The problem we are basically concerned with is whether the filament formed from the extruder can be successfully taken up on a bobbin. Clearly, capillarity, ductile failure, fracture, or their combination can prevent this. To analyze this, one may consider to some extent the motion of an initial disturbance with distance or residence time along the length of a spinline and cohesive failure or fracture occurring at distances from the spinneret where the tensile stress in the descending fiber equals the critical stress. However, one must be careful as there are differences. Most obviously, (i) the deformation rate E varies with position so as to make the applied force F almost constant, (ii) the initial conditions at the spinneret are complex and involve extrudate swell recovery from flow within the capillary, and (iii) there are enormous temperature gradients along the spinline with resulting positional variations in rheological properties.

More subtly, there are basic differences in the dynamic equations of extending a filament and a continuous spinline because of the form of the continuity equation. Analyses of the unsteady state dynamics of moving threa-

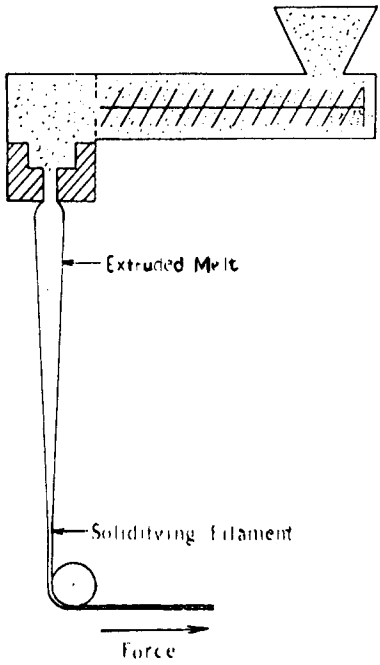

Fig. 9. Continuous spinline.

dlines have been carried out by Kase and Matsuo,[81–83] Pearson, Matovich, and Shah,[84,85] Gelder,[85] Han, Lamonte, and Shah,[87] and Zeichner,[88] among others. The appropriate balance equations should be seen to be

$$\frac{\partial}{\partial t}(\pi R^2) + \frac{\partial}{\partial x_1}(\pi R^2 v_1) = 0 \tag{47}$$

$$\pi R^2 \rho \left[\frac{\partial v_1}{\partial t} + v_1 \frac{\partial v_1}{\partial x_1}\right] = \frac{\partial}{\partial x_1}(\pi R^2 \sigma_{11}) + \frac{\partial}{\partial x_1}(2\pi R\gamma) + \pi R^2 \rho g \tag{48}$$

$$\pi R^2 \rho c \left[\frac{\partial T}{\partial t} + v_1 \frac{\partial T}{\partial x_1}\right] = -2\pi R h(T - T_s) \tag{49}$$

Equation (48) is the same as eq. (13) and represents a force balance, while eq. (47) is continuity and eq. (49) is a heat balance where T is temperature, c is heat capacity, h is a heat transfer coefficient, and the subscript s refers to the surroundings. An important and different role is played by continuity in the case of a continuous threadline as opposed to uniaxial stretching of a filament.

The basic question that we must ask is: In the residence time of the threadline, will disturbances entering just below the spinneret cause failure or will the stress rise above a critical value as the filament was forced to draw down? Low-viscosity Newtonian fluids (and thus low molecular weight organic compounds) will exhibit capillarity breakup into drops or ligaments well before the take-up roll is reached. In a slightly more viscous (and thus slightly higher molecular weight) fluid, the rise in viscosity begins to stabilize the filament but gravitation forces induce a breakup of the thread due to a combined capillarity-ductile failure mechanism. This again occurs before it

reaches the bobbin. At still higher viscosity levels, continuous spinlines should be possible.

Let us now turn our attention to very high molecular weight "elastic" polymer melts and the limitations on their spinline behavior. These filaments will fracture at low take-up velocities due to the stresses required to draw down the spinline diameter. The higher the characteristic time, the lower the elongation rates and the take-up velocity required to achieve the critical stress.

The conclusions of the above paragraphs are in general agreement with spinline experiments performed in our laboratories. It was found impossible to melt spin low molecular weight paraffins because of capillarity, but among commercial polyethylene melts, spinnability decreases with increasing molecular weight because of fracture.[45] Nadella[89] has found a similar decrease in spinnability with increasing molecular weight for polypropylenes.

We now inquire about the intermediate region of spinning conditions where capillarity instabilities are damped out by viscosity and the spinline stresses are too small to cause cohesive fracture. This is the region where instabilities and ultimate spinline breakdown must be due to the analogue of ductile failure. The formulation of this problem is straightforward and is equivalent to that first given and solved by Kase, Matsuo, and Yoshimoto[82] and later by Pearson and Matovich[84] and Gelder.[86] These authors predict the development of an instability at a critical draw-down ratio consisting of a periodic variation of filament diameter. Such an instability has been observed by several researchers and is known as *draw resonance*.[87,90,91] Draw resonance is a continuous threadline analogue of ductile failure. The reason for the different appearance of the ductile failure phenomenon in the continuous threadline is probably that the different form of the continuity equation leads to stability equations of higher order. This would seem most apparent by comparing the Pearson-Matovich[84] paper to the present one.

CONCLUSIONS

1. A theory of maximum extensibility of polymer fluid filaments is developed as a function of the rheological properties of the fluid. Three mechanisms of failure—*capillarity, ductile failure,* and *fracture*—are proposed. A mathematical theory has been developed using the methods of linear stability theory. It shows that high viscosity prevents capillarity failure and that high levels of viscoelasticity (as represented by a convected Maxwell model with a constant relaxation time) prevents ductile failure as well, but stress develops indefinitely. These highly elastic melts fail by fracture.

2. The theory developed can be applied to polymer melts and is equivalent to low molecular weight fluids failing by capillarity and high molecular weight melts by ductile failure and fracture. The theory predicts a maximum in spinnability with respect to molecular weight.

3. An experimental study of the failure of polyethylene melt filaments in tension is reported. Waxes fail by capillarity, low-density polyethylene melts, by fracture, and high-density polyethylene, by ductile failure. The higher the molecular weight of the melts, generally, the smaller the elongation to break.

4. The concepts developed for simple elongational flow may be applied to a continuous spinline. Failure can occur by capillarity and fracture, and draw resonance appears to be the analog of ductile failure.

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