

# Studies on Melt Spinning. VIII. The Effects of Molecular Structure and Cooling Conditions on the Severity of Draw Resonance

CHANG DAE HAN and SUHAS M. APTE, *Department of Chemical Engineering, Polytechnic Institute of New York, Brooklyn, New York 11201*

## Synopsis

The effects of molecular structure and cooling conditions on the severity of draw resonance was investigated by carrying out carefully controlled melt spinning experiments. For the study, two types of polymeric materials were used: one which exhibits viscoelastic behavior (high-density polyethylene, polypropylene, and polystyrene), and the other which exhibits almost Newtonian behavior [nylon-6 and poly(ethylene terephthalate)]. In order to investigate the effect of cooling on the severity of draw resonance, different methods of cooling the molten threadline were employed. In one set of experiments, isothermal chambers of various lengths (3, 6, and 12 in.) were attached to the spinnerette face, so that the molten threadline, upon exiting from the spinnerette, began to cool in the ambient air only after it had passed through the isothermal chamber. This method of cooling is called "delayed cooling," providing both an isothermal region (inside the isothermal chamber) where only stretching occurs, and a nonisothermal region (outside the isothermal chamber) where both stretching and cooling occur simultaneously. In other experiments, the temperature profile of the molten threadline was controlled by adjusting the temperature of the heated chamber. This method of cooling provides a gradual drop of the threadline temperature, compared to the more sudden drop when spinning into a cold environment provided at the spinnerette exit. The severity of draw resonance was recorded on movie film, and the thread tension was measured with a low-force load cell transducer and recorded on a chart recorder. The temperature of the threadline along the spin direction was measured using a fiber optical probe attached to a Vanzetti Infrared Thermal Monitoring System (Model TM-1). It was found that the severity of draw resonance depended on the molecular structure and the way the molten threadline was cooled. Of particular interest is the observation that, for the viscoelastic materials investigated, cooling destabilized the molten threadline outside the isothermal chamber. This gave rise to more severe resonant behavior, at and above the critical draw-down ratio, in contradiction to the theoretical prediction by Fisher and Denn. It was observed, also, that the elasticity of the materials tended to destabilize the molten threadline (i.e., it increased the severity of draw resonance), again in contradiction to the theoretical prediction of Fisher and Denn. It is believed that morphological changes of polymers may play an important role in the occurrence of draw resonance when a melt threadline is stretched under cooling. Our study indicated that a good understanding of draw resonance of viscoelastic fluids requires more careful study than the classical hydrodynamic stability analysis reported by Fisher and Denn. They based their analysis on several convenient and yet unjustified assumptions, and solely on phenomenological considerations. We suggest that future theoretical analysis of draw resonance be carried out by considering a fluid model with a nonlinear memory function in order to properly account for the deformation history of the fluid, and the relaxation and cooling processes in the die swell region and the region below it.

## INTRODUCTION

In recent years, the phenomenon of draw resonance occurring in melt spinning has attracted the attention of many researchers, both experimental and theoretical. In the 1960s, a few experimental studies of draw resonance were reported by Miller,<sup>1</sup> Freeman and Coplan,<sup>2</sup> and Bergonzoni and DiCresce.<sup>3</sup> More recently,

in the 1970s, further experimental studies were carried out by Han and co-workers,<sup>4-6</sup> Vassilatos,<sup>7</sup> Weinberger and co-workers,<sup>8-10</sup> Blyler and Gieniewski,<sup>11</sup> and Matsumoto and Bogue.<sup>12</sup>

Theoretical analyses of draw resonance were carried out by Kase et al.,<sup>13</sup> Pearson and Matovich,<sup>14</sup> and Gelder,<sup>15</sup> who considered the isothermal spinning of Newtonian fluids. Shah and Pearson<sup>16,17</sup> and Ishihara and Kase<sup>18</sup> considered draw resonance of power-law fluids. More recently, Fisher and Denn<sup>19,20</sup> also carried out theoretical analyses of draw resonance in isothermal and nonisothermal spinning operations, using a convected Maxwell fluid. Some researchers<sup>14,16</sup> used a perturbation approach and others<sup>15,18-20</sup> used an eigenvalue approach.

Very recently, using the theory of the kinematic throughput wave, Hyun<sup>21</sup> introduced a new concept for analyzing the phenomenon of draw resonance in isothermal melt spinning.

At present, there are two major issues which have yet to be resolved by researchers. One is the role that the fluid elasticity plays in the occurrence of draw resonance, and the other is the effect of cooling conditions on the severity of draw resonance of viscoelastic fluids. Whereas the theoretical study of Fisher and Denn<sup>19</sup> claims that the fluid elasticity stabilizes the flow (i.e., suppresses the severity of draw resonance), the experimental studies of Han and co-workers,<sup>4-6</sup> Vassilatos,<sup>7</sup> and Weinberger and co-workers<sup>8,9</sup> show that the fluid elasticity destabilizes the flow (i.e., increases the severity of draw resonance). Also, whereas the theoretical study of Fisher and Denn<sup>20</sup> claims that cooling should suppress the severity of draw resonance of viscoelastic fluids, the experimental studies of Han and co-workers,<sup>4,5</sup> Vassilatos,<sup>7</sup> Blyler and Gieniewski,<sup>11</sup> and Matsumoto and Bogue<sup>12</sup> show that, under certain spinning conditions, cooling can indeed increase the severity of draw resonance of viscoelastic fluids. There is no dispute, theoretical or experimental, over the fact that cooling should suppress the severity of draw resonance of Newtonian fluids. To summarize, the predictions of the Fisher and Denn analyses<sup>19,20</sup> are not supported by the independent experimental results of several researchers.<sup>4-9,11,12</sup>

As part of our continuing effort to improve our understanding of the phenomenon of draw resonance, we have very recently carried out a further experimental study, with emphasis on identifying the effects of molecular structure and cooling conditions. For the study, we have performed melt spinning experiments by employing several rheologically well-characterized polymeric materials of different molecular structures, different molecular weights, and different molecular weight distributions. Furthermore, different methods of cooling a melt threadline were employed, methods which permitted us to monitor its temperature profile. In this paper, we shall first report the results of our experimental study, and then present our view of the reasons why the Fisher and Denn analyses<sup>19,20</sup> fail to predict the experimental results reported in this paper and those reported by several investigators.<sup>4-9,11,12</sup>

## EXPERIMENTAL

A melt spinning apparatus was constructed, consisting of an extruder, a gear pump, a spinnerette, a variable takeup device, and an isothermal (or heated) chamber. Figure 1 gives a photograph of the apparatus. The spinnerette has three holes, each 1 mm in diameter and 1 mm in length (i.e.,  $L/D = 1$ ).

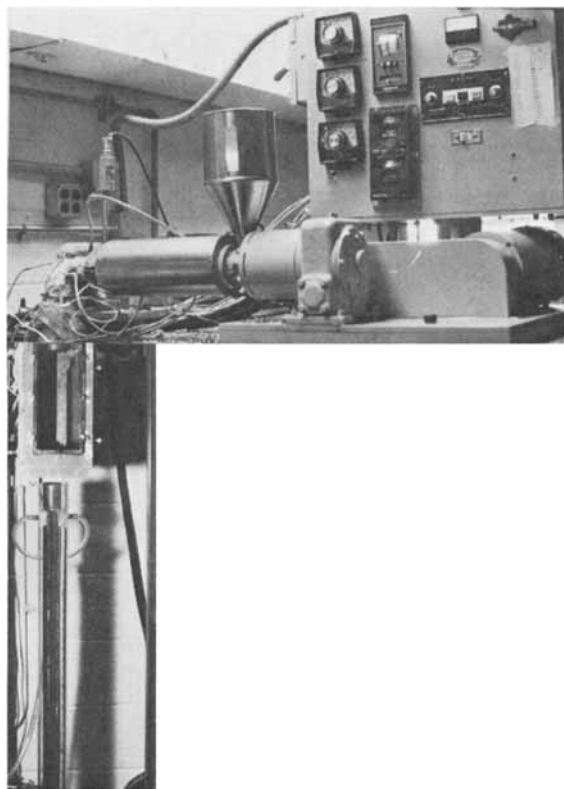


Fig. 1. Photograph of the melt spinning apparatus employed.

In order to have flexibility in cooling the molten threadline upon exiting from the spinnerette, we can install aluminum chambers of various lengths (3, 6, and 12 in.) beneath the spinnerette face. The chamber has a glass window on the front wall, which permits us to take photographs of the molten threadline passing through it. The chamber was heated electrically and the air temperature inside the chamber was controlled with the aid of a Thermistor-regulated controller. By keeping the air temperature inside the chamber the same as the melt extrusion temperature, we were able to isolate rheological effects from those of threadline cooling. At other times, we kept the air temperature inside the chamber below the melt extrusion temperature but above the ambient temperature, so that cooling of the molten threadlines occurred gradually. We also performed spinning experiments with the heated chamber removed, so that the molten threadlines, upon exiting from the spinnerette, are exposed immediately to the ambient air temperature.

Beneath the heated chamber, we installed a plexiglas column about 1.8 m long, with the front side cut open (see Fig. 1). The purpose of this column was to avoid a draft of air on the moving threadlines while the experiment was performed. At times, we forced air across the moving threadlines, so that we were able to observe the effect of a crossflow of air on the severity of resonant behavior.

The materials used were four high-density polyethylenes (HDPEs), two polystyrenes (PS), two polypropylenes (PP), a nylon-6, and a poly(ethylene terephthalate) (PET). Table I gives a list of materials used, the resin manu-

TABLE I  
Summary of the Polymers Investigated and Their Rheological Constants

| Sample code | Resin manufacturer    | Trade name | Extrusion temperature, °C | $\eta_0^a$ , poise | $K^b$ , g sec $^{n-2}$ /cm $^2$ | $n^b$ (dimensionless) | $q^c$ (dimensionless) |
|-------------|-----------------------|------------|---------------------------|--------------------|---------------------------------|-----------------------|-----------------------|
| HDPE-A      | Union Carbide         | DMDJ 5140  | 240                       | $1.05 \times 10^5$ | $3.78 \times 10^4$              | 0.52                  | 0.20                  |
| HDPE-B      | Union Carbide         | DMDJ 4306  | 240                       | $1.15 \times 10^6$ | $5.72 \times 10^4$              | 0.33                  | 0.11                  |
| HDPE-C      | Mitsui Petrochemicals | HIZEX 5000 | 240                       | $0.80 \times 10^6$ | $8.32 \times 10^4$              | 0.49                  | 0.17                  |
| HDPE-D      | Mitsui Petrochemicals | HIZEX 5200 | 240                       | $0.54 \times 10^6$ | $1.13 \times 10^5$              | 0.46                  | 0.12                  |
| PP-A        | Exxon Chemicals       | E 115      | 200                       | $0.60 \times 10^5$ | $4.09 \times 10^4$              | 0.56                  | 0.22                  |
| PP-B        | Amoco Chemicals       | 6014       | 200                       | $0.68 \times 10^5$ | $3.63 \times 10^4$              | 0.45                  | 0.29                  |
| PS-A        | Dow Chemicals         | STYRON 678 | 200                       | $0.39 \times 10^5$ | $1.78 \times 10^4$              | 0.52                  | 0.53                  |
| PS-B        | Dow Chemicals         | STYRON 686 | 220                       | $0.50 \times 10^5$ | $3.95 \times 10^4$              | 0.44                  | 0.36                  |
| Nylon-6     | American Enka         | —          | 280                       | $0.34 \times 10^3$ | —                               | 1.00                  | —                     |
| PET         | American Enka         | —          | 300                       | $0.13 \times 10^3$ | —                               | 0.98                  | —                     |

<sup>a</sup> Zero-shear viscosity.

<sup>b</sup> Power-law constants in steady shear viscosity,  $\eta = K_\gamma n^{-1}$ .

<sup>c</sup> Power-law index in apparent elongational viscosity,  $\eta_E = K_E (db_z/dz)^{q-1}$ .

facturer, the melt extrusion temperature, and the viscometric and elongational flow properties. The viscometric flow properties were determined using the Weissenberg rheogoniometer, and they are given in Figures 2 to 5. The elongational flow property (the power-law index  $q$  in Table I) was determined from measurements of the melt threadline diameter profile in the isothermal chamber and thread tension, fitting the observed kinematic data to a simple power law. Table II gives a list of molecular weights (number average  $\bar{M}_n$  and weight average  $\bar{M}_w$ ) of the four high-density polyethylenes, determined by use of the gel permeation chromatography (GPC) apparatus.

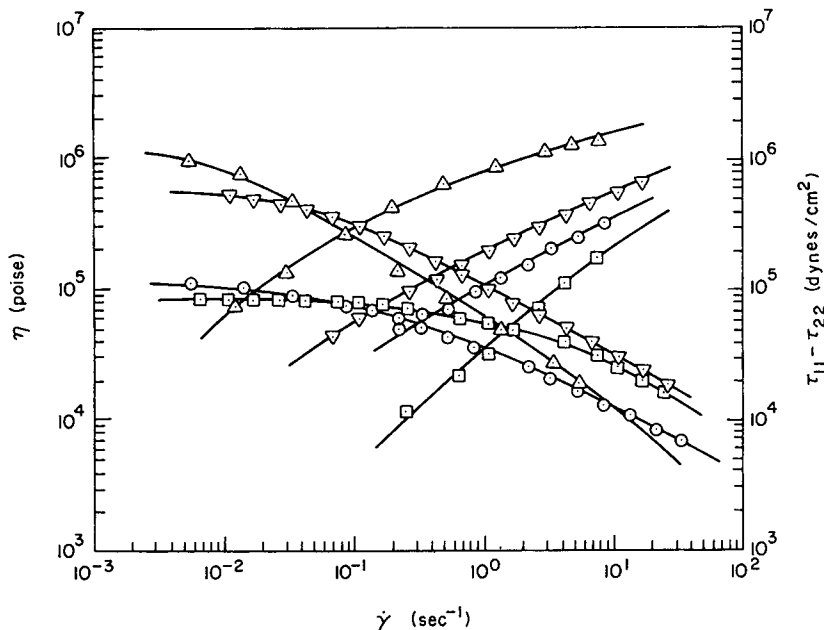


Fig. 2. Rheological properties of the four high-density polyethylenes at 240°C: (○) HDPE-A; (Δ) HDPE-B; (□) HDPE-C; (▽) HDPE-D.

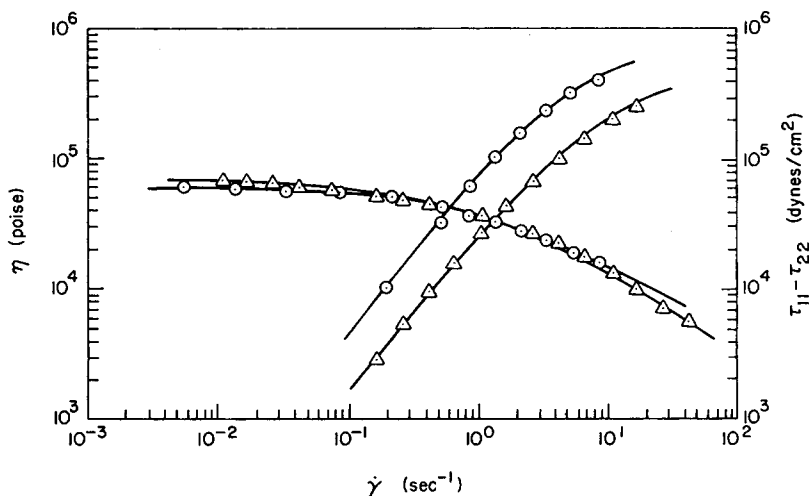


Fig. 3. Rheological properties of the two polypropylenes at 200°C: (○) PP-A; (Δ) PP-B.

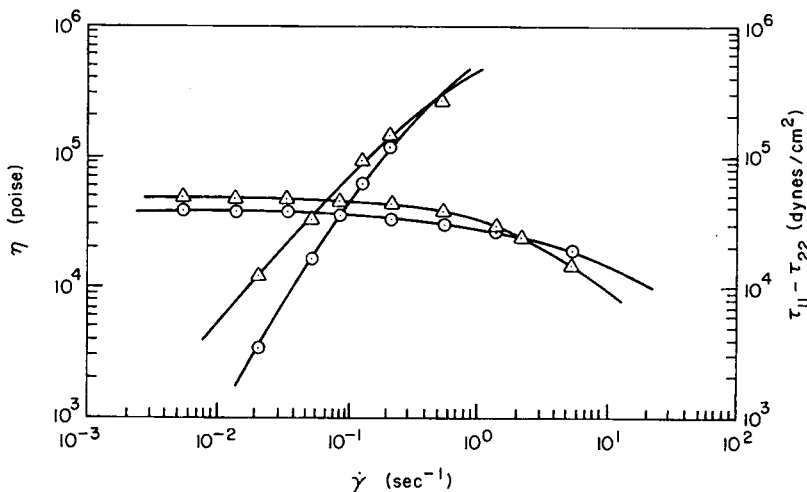


Fig. 4. Rheological properties of the two polystyrenes: (○) PS-A at 200°C; (△) PS-B at 220°C.

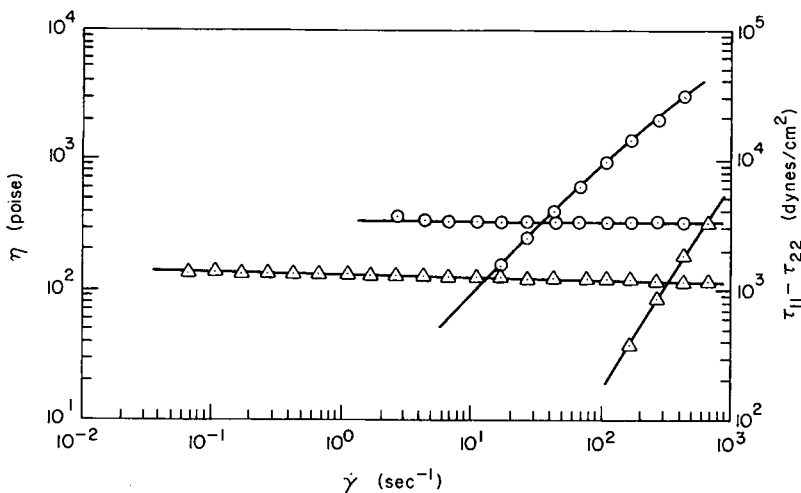


Fig. 5. Rheological properties of nylon-6 and PET: (○) nylon-6 at 280°C; (△) PET at 300°C.

In the melt spinning experiment, the mass flow rate of each material was adjusted so that the average velocity of the melt in the spinnerette hole would be the same in all runs. The spinning variables investigated were (i) melt extrusion temperature; (ii) air temperature inside the heated chamber (either at or below the melt extrusion temperature); (iii) the length of the heated chamber; (iv) takeup speed; and (v) melt flow rate (i.e., the shear rate in the spinnerette). The fibers were wound on a variable speed takeup device, whose speed was gradually increased until a steady pulsation of the threadline could be observed.

Fiber tension was measured with a low-force load cell transducer having a range of 0–50 g. When variation in tension was observed, it was recorded with a Sanborn recorder. The temperature of the molten threadlines was measured by use of a fiber optical probe attached to a Vanzetti Infrared Thermal Monitor (Model TM-1). Variation in temperature was recorded on a Sanborn recorder.

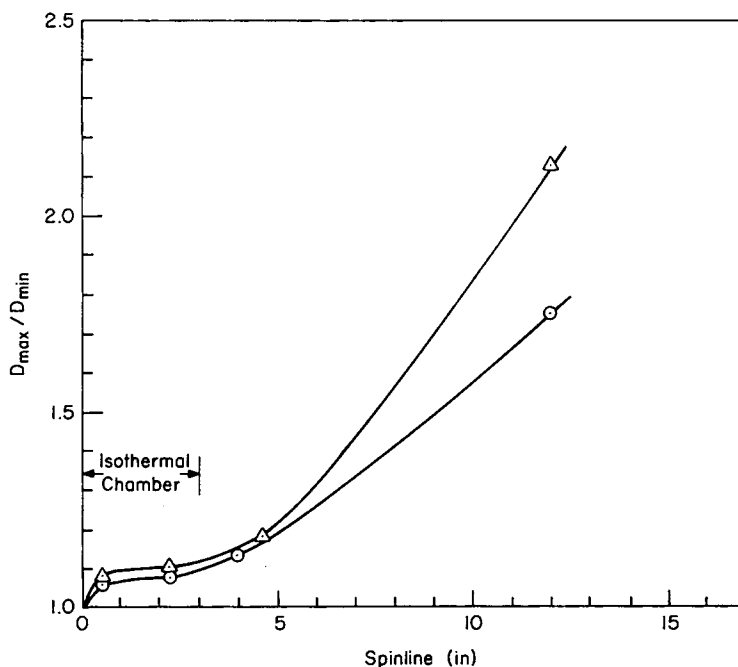


Fig. 6.  $D_{max}/D_{min}$  vs distance along the spinning way for the PP-A being melt-spun at 200°C at various stretch ratios: (○)  $V_L/V_0 = 13.8$ ; (△)  $V_L/V_0 = 103.4$ .

TABLE II  
Molecular Weights of the Four High-Density Polyethylenes Investigated

| Sample code | Resin supplier                      | $\bar{M}_n$        | $\bar{M}_w$        | $\bar{M}_w/\bar{M}_n$ |
|-------------|-------------------------------------|--------------------|--------------------|-----------------------|
| HDPE-A      | Union Carbide<br>DMDJ 5140          | $1.33 \times 10^4$ | $1.74 \times 10^5$ | 13.1                  |
| HDPE-B      | Union Carbide<br>DMDJ 4306          | $0.98 \times 10^4$ | $2.12 \times 10^5$ | 21.7                  |
| HDPE-C      | Mitsui Petrochemicals<br>HIZEX 5000 | $1.51 \times 10^4$ | $1.51 \times 10^5$ | 10.0                  |
| HDPE-D      | Mitsui Petrochemicals<br>HIZEX 5200 | $1.25 \times 10^4$ | $2.43 \times 10^5$ | 19.5                  |

A movie camera (Super 8) was used to record the resonant behavior of the melt threadlines inside and outside the isothermal chamber. The films were later projected on a screen, and the threadline diameters were determined at various positions along the spin direction under different spinning conditions.

## RESULTS AND DISCUSSION

### Effects of Molecular Structure and Cooling Conditions on the Severity of Draw Resonance

Often in the past, the severity of draw resonance was determined by the ratio of maximum-to-minimum diameter ( $D_{max}/D_{min}$ ) of the as-spun filament. This ratio deviates systematically from unity with increasing stretch ratio beyond a

critical value. It should be mentioned, however, that the diameter variation of the as-spun filament cannot describe how the severity of draw resonance may vary along the spinline. For this reason, in the present study the ratio  $D_{\max}/D_{\min}$  was determined by projecting the movie film on a screen. Hereafter we shall refer to  $D_{\max}/D_{\min}$  as a measure of the severity of draw resonance.

Figure 6 gives plots of  $D_{\max}/D_{\min}$  of PP-A at different positions along the spinline, both inside and outside of the isothermal chamber. Similar plots were given for the PP-B in Figure 7, for the PS-B in Figure 8, and for the three HDPEs in Figure 9. Space limitation here does not permit us to present many other experimental results. Note that, in all these plots, the length of the isothermal chamber is 3 in.

Several interesting observations may be made in Figures 6 to 9. First, the severity of draw resonance does not appear to vary much inside the isothermal chamber along the spinline, but, for PP and PS, it increases considerably while the molten threadlines travel through quiescent air at about 20°C, during which time cooling of the molten threadlines occurs. On the other hand, the increase in the severity of draw resonance for the HDPEs (Fig. 9) is very mild, even outside the isothermal chamber. This observation then leads us to conclude that the severity of draw resonance due to cooling depends on the molecular structure of the polymer.

Second, the severity of draw resonance increases as the stretch ratio  $V_L/V_0$  increases above a critical value. It was observed in the spinning of the four

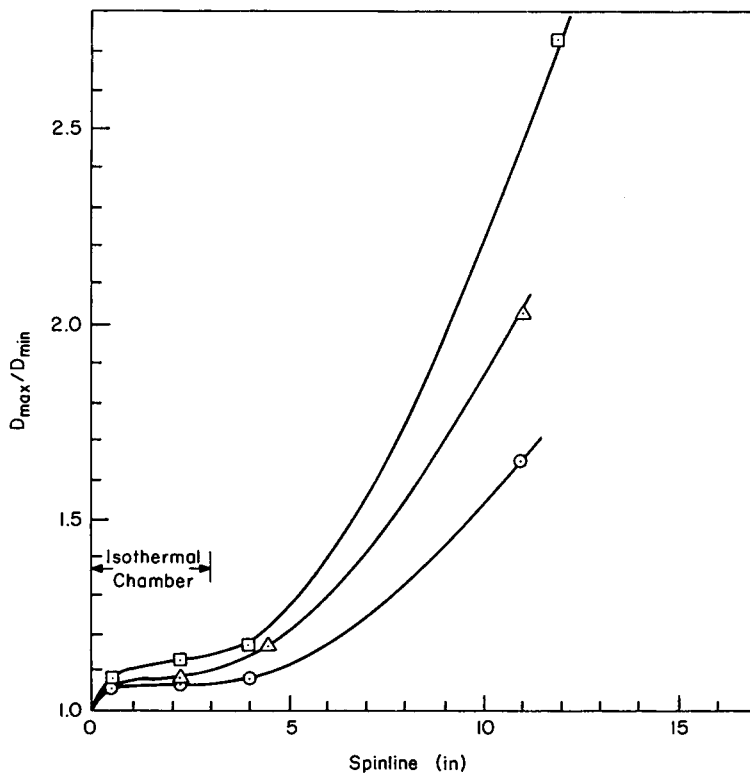


Fig. 7.  $D_{\max}/D_{\min}$  vs distance along the spinning way for the PP-B being melt-spun at 200°C at various stretch ratios: (○)  $V_L/V_0 = 13.8$ ; (△)  $V_L/V_0 = 41.4$ ; (□)  $V_L/V_0 = 68.9$ .



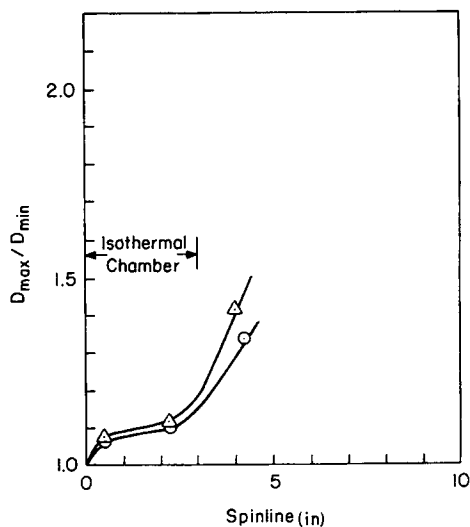


Fig. 8  $D_{\max}/D_{\min}$  vs distance along the spinning way for the PS-B being melt spun at 200°C at various stretch ratios: (○)  $V_L/V_0 = 95$ ; (△)  $V_L/V_0 = 237$ .

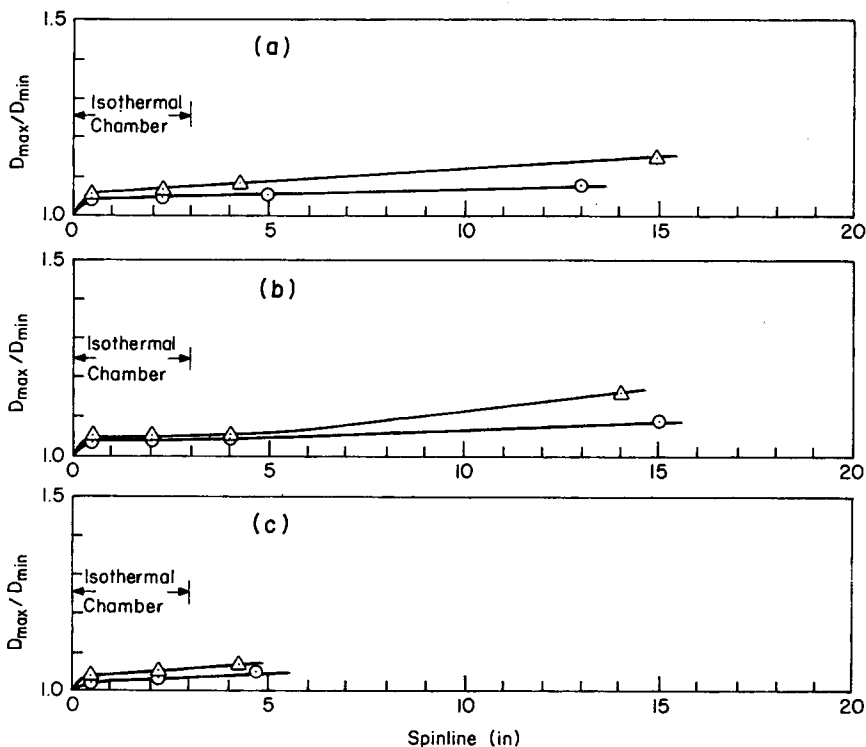


Fig. 9.  $D_{\max}/D_{\min}$  vs distance along the spinning way for the three high-density polyethylenes being melt spun at 240°C: (a) HDPE-A: (○)  $V_L/V_0 = 13.6$ ; (△)  $V_L/V_0 = 27.3$ ; (b) HDPE-C: (○)  $V_L/V_0 = 14.3$ ; (△)  $V_L/V_0 = 48.2$ ; (c) HDPE-D: (○)  $V_L/V_0 = 14.1$ ; (△)  $V_L/V_0 = 35.3$ .

HDPEs (Table II) that, under the identical spinning conditions, the polymer with broad molecular weight distribution (BMWD) gave rise to lower melt strength than the polymer with narrow molecular weight distribution (NMWD),

and the the BMWD polymer gave rise to a lower critical stretch ratio for the onset of draw resonance than the NMWD polymer.

Third, as may be seen in Figure 10, under the identical spinning conditions, an increase in the length of the isothermal chamber tends to suppress the severity of draw resonance outside the isothermal chamber (compare Figs. 7 and 10). The use of a 12-in.-long isothermal chamber considerably suppressed the severity of draw resonance outside the isothermal chamber.

Fourth, in reference to Figures 6 to 9, air cooling of molten threadlines outside the isothermal chamber clearly increases the severity of draw resonance. However, if the melt has been attenuated to very nearly its final diameter in an isothermal chamber below the spinnerette, a rapid quench beyond that point to a temperature below the melting point or glass-transition temperature ( $T_g$ ) should suppress the severity of draw resonance. A model situation might be one having a liquid quench immediately following a relatively long isothermal zone.

Figure 11 gives plots of  $D_{\max}/D_{\min}$  versus spin distance for the PS-B being spun first into the 3-in.-long chamber heated at 45°C and then into quiescent air at 20°C. Figure 12 gives plots of  $D_{\max}/D_{\min}$  versus spin distance for the HDPE-A being spun first into the 9-in.-long chamber heated at 65°C and then into quiescent air at 20°C. It is seen that the direct exposure of the molten threadline upon exiting the spinnerette into quiescent air at low temperature increases the severity of draw resonance considerably, as long as the threadline stays above the melting point or glass transition temperature.

It can, therefore, be concluded from the above observations that a careful

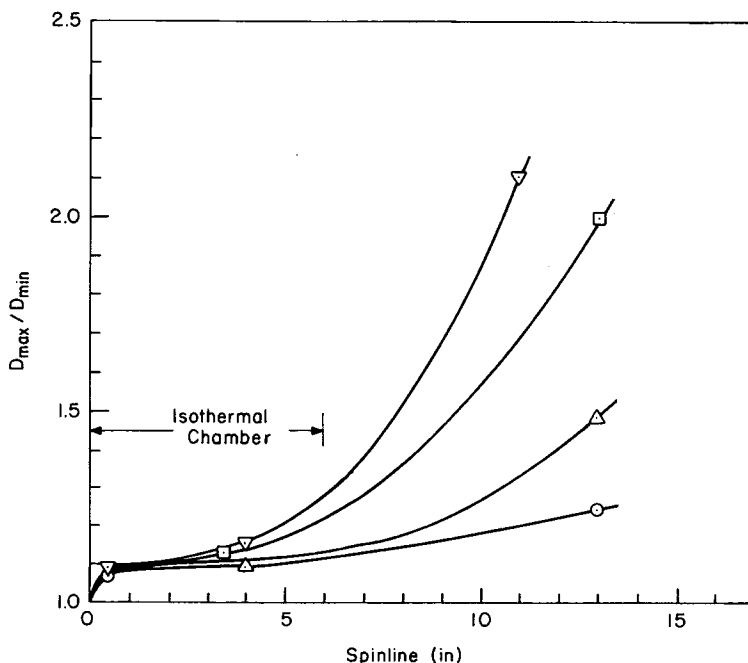


Fig. 10.  $D_{\max}/D_{\min}$  vs distance along the spinning way for the PP-B being melt spun at 200°C at various stretch ratios: (○)  $V_L/V_0 = 14.1$ ; (△)  $V_L/V_0 = 35.3$ ; (□)  $V_L/V_0 = 105.8$ ; (▽)  $V_L/V_0 = 176.3$ .

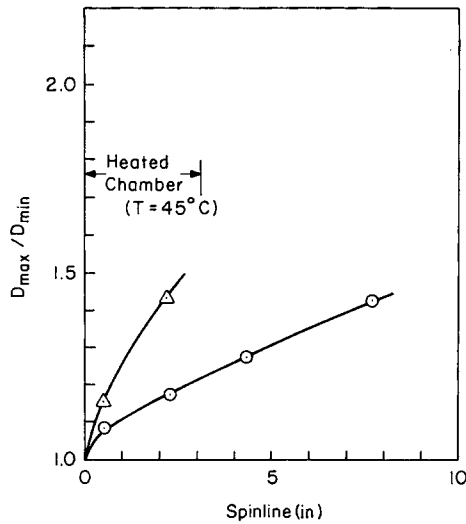


Fig. 11.  $D_{\max}/D_{\min}$  vs distance along the spinning way for the PS-B being melt spun at 220°C into a heated chamber at 45°C: (○)  $V_L/V_0 = 57.0$ ; (△)  $V_L/V_0 = 95.0$ .

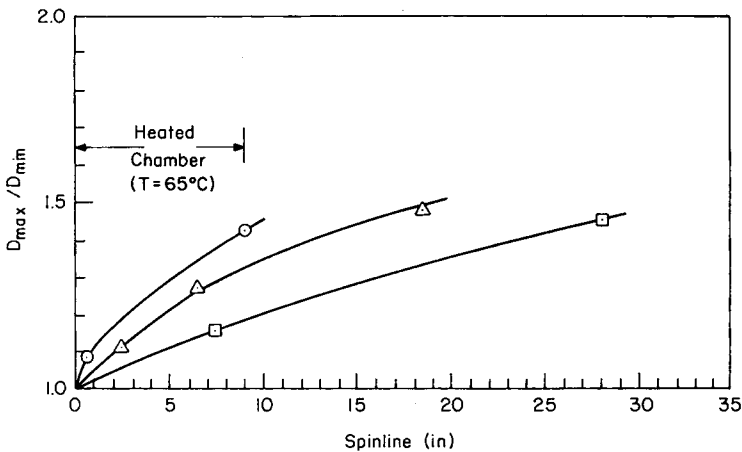


Fig. 12.  $D_{\max}/D_{\min}$  vs distance along the spinning way for the HDPE-A being melt spun at 240°C into a heated chamber at 65°C: (○)  $V_L/V_0 = 82.6$ ; (△)  $V_L/V_0 = 62.1$ ; (□)  $V_L/V_0 = 19.9$ .

control of the temperature profile of a molten threadline is an effective means of suppressing the severity of draw resonance.

Typical tension measurements are given for the PP-A in Figure 13, and similar plots for the HDPE-A in Figure 14. Note that no variation in the thread tension was observed when the stretch ratio was below a critical value (i.e., when no visible resonant behavior of molten threadlines was detected). It is of interest to note, in Figures 13 and 14, that the variation of threadline tension is not describable by a well-defined periodic function. This is understandable in view of our experimental observation that both the amplitude and frequency of the resonant behavior of a threadline vary along the spinline, and therefore the variation of threadline tension would be different from point to point along the spinline.

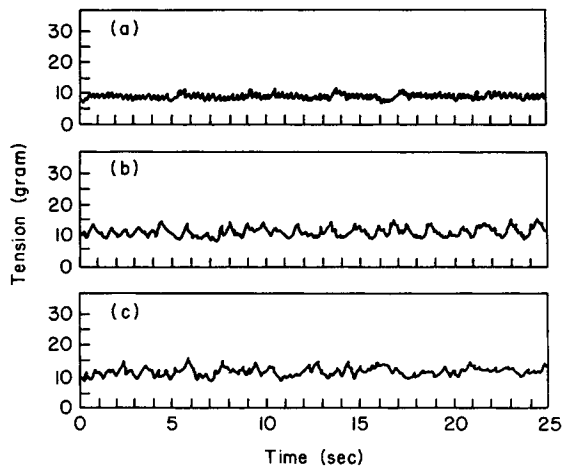


Fig. 13. Tension vs time for the polypropylene PP-A at 200°C at various stretch ratios: (a)  $V_L/V_0 = 13.8$ ; (b)  $V_L/V_0 = 68.9$ ; (c)  $V_L/V_0 = 103.4$ .

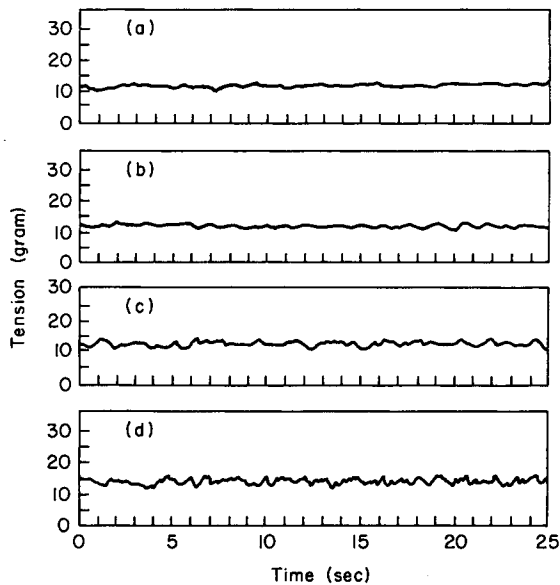


Fig. 14. Tension vs time for the high-density polyethylene HDPE-A at 240°C at various stretch ratios: (a)  $V_L/V_0 = 13.6$ ; (b)  $V_L/V_0 = 40.9$ ; (c)  $V_L/V_0 = 68.2$ ; (d)  $V_L/V_0 = 95.5$ .

### Rheological Interpretation of Draw Resonance

A convenient rheological parameter for describing the importance of fluid elasticity in an unsteady flow situation is the Deborah number  $N_{De}$  defined as<sup>22</sup>

$$N_{De} = \lambda/\theta \quad (1)$$

where  $\lambda$  is a characteristic time, often referred to as the "relaxation time," of a fluid, and  $\theta$  is the residence time. When  $\lambda > \theta$ , the fluid will not have time to approach its steady response, and therefore the relaxation phenomenon may dominate the process.

There are different ways of determining the values of  $\lambda$ . For instance, using a constitutive equation of state, one can determine values of  $\lambda$  by curve fitting the experimentally determined viscosity or normal stress data to the theoretical expressions for viscosity function or normal stress function. Table III gives values of  $\lambda$  determined with the Spriggs four-constant model, using the steady shear flow data given in Figures 2 to 4.

In the present study,  $\theta$  in eq. (1) represents the flight time for a filament to travel through the isothermal chamber. Since the axial velocity  $v_z$  of a filament changes along the spin direction, the flight time  $\theta$  may be evaluated from

$$\theta = \int_0^l \frac{dz}{v_z} \quad (2)$$

in which  $l$  denotes the length of the isothermal chamber.

Table III gives representative values of  $\theta$  and  $N_{De}$  determined from our experimental data, using the 3-in.-long isothermal chamber. Note that, for the calculation of  $\theta$  from eq. (2), we first determined the axial velocity  $v_z$  of a filament inside the isothermal chamber, by reading off the filament diameter from the movie film projected on a screen and by using the mass balance equation

$$W = \rho \pi R(z)^2 v_z(z) \quad (3)$$

in which  $W$  is the melt flow rate,  $\rho$  is the melt density,  $R$  is the filament radius, and  $v_z$  is the axial velocity.

It is seen in Table III that the values of  $\lambda$  (and hence  $N_{De}$ ) for the polypropylenes and polystyrenes are smaller than those for the high-density polyethylenes. On the other hand, the severity of draw resonance, in terms of the variation of  $D_{max}/D_{min}$ , is greater with the polypropylenes and polystyrenes than with the high-density polyethylenes.

It is of interest to note that Weinberger et al.<sup>8</sup> report that a fluid having a large value of  $\lambda$  gives rise to a lower critical stretch ratio (at which draw resonance starts) than a fluid having a small value of  $\lambda$ , and they conclude that the fluid elasticity destabilizes the elongational flow. It should be pointed out that Weinberger et al.<sup>8</sup> determined the values of  $\lambda$  by taking the limiting values of viscometric oscillatory data, i.e.,

$$\lambda_0 = \lim_{\omega \rightarrow 0} \frac{G'(\omega)}{\eta'(\omega)\omega^2} \quad (4)$$

TABLE III  
Summary of the Values of  $\lambda$ ,  $\theta$ , and  $N_{De}$  Determined for the Viscoelastic Fluids Investigated

| Material | $V_L/V_0^a$ | $\lambda,^b$ sec | $\theta,^c$ sec | $N_{De} = \frac{\lambda}{\theta}$ |
|----------|-------------|------------------|-----------------|-----------------------------------|
| HDPE-A   | 27.3        | 7.6              | 3.2             | 2.4                               |
| HDPE-B   | 4.0         | 65.2             | 1.9             | 34.3                              |
| HDPE-C   | 42.8        | 2.9              | 2.9             | 1.0                               |
| HDPE-D   | 35.3        | 15.3             | 3.0             | 5.1                               |
| PP-A     | 41.4        | 1.6              | 2.8             | 0.6                               |
| PP-B     | 41.4        | 2.2              | 2.6             | 0.9                               |
| PS-A     | 95.0        | 1.1              | 2.5             | 0.4                               |
| PS-B     | 95.8        | 1.3              | 2.5             | 0.5                               |

<sup>a</sup> Apparent stretch ratio.

<sup>b</sup>  $\lambda$  is determined with the Spriggs four-constant model using the steady shear flow data.

<sup>c</sup>  $\theta$  is the flight time defined by  $\int_0^l dz/v_z$ , where  $v_z$  is the axial velocity profile in the threadline.

where  $G'(\omega)$  and  $\eta'(\omega)$  are the in-phase components of the complex storage modulus and viscosity, respectively, and  $\omega$  is the frequency of oscillation.

One difficulty in determining  $N_{De}$  is a proper choice of relaxation time. For instance, if one chooses a convected Maxwell model

$$\tau + \lambda(\Pi) \frac{d\tau}{dt} = \eta(\Pi) \mathbf{d} \quad (5)$$

the relaxation time  $\lambda$  is defined by

$$\lambda(\Pi) = \eta(\Pi)/G \quad (6)$$

in which  $\Pi$  is the second invariant of the rate-of-deformation tensor,  $G$  is a shear modulus, and  $\eta(\Pi)$  is a shear viscosity.

Figures 15 to 18 give plots of relaxation times  $\lambda$  versus shear rate  $\dot{\gamma}$ , for the high-density polyethylenes, polypropylenes, polystyrenes, nylon-6, and PET used in our melt spinning experiments. These plots were prepared using the steady shear flow data given in Figures 2 to 5 and the definition given by eq. (6). It is seen that the relaxation time decreases with shear rate  $\dot{\gamma}$ .

Earlier, some researchers<sup>23,24</sup> proposed use of the "deformation-dependent" maximum relaxation time  $\lambda_{\text{eff}}$  (often referred to as the effective relaxation time), defined as

$$\lambda_{\text{eff}} = \lambda_0 / (1 + a \lambda_0 \langle \Pi_d^{1/2} \rangle_{\text{av}}) \quad (7)$$

in which  $a$  is a constant characteristic of the fluid and  $\langle \Pi_d^{1/2} \rangle_{\text{av}}$  is the average value

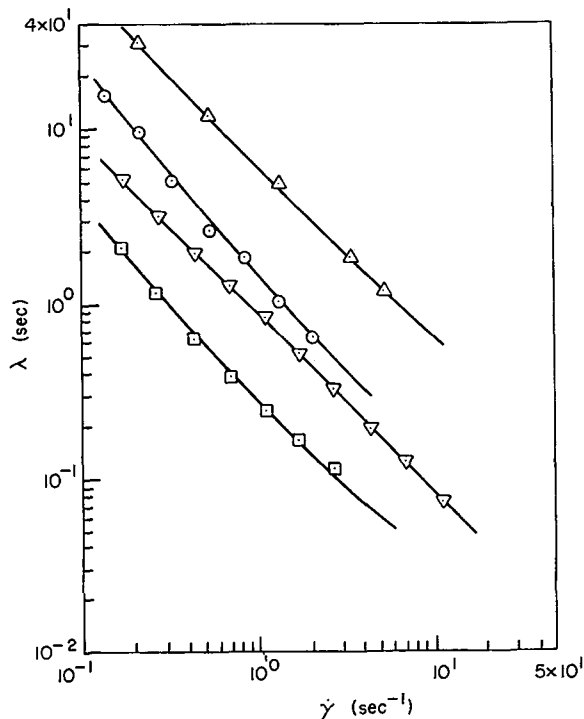


Fig. 15. Relaxation time vs shear rate for the four high-density polyethylenes at 240°C: (○) HDPE-A; (△) HDPE-B; (◻) HDPE-C; (▽) HDPE-D.

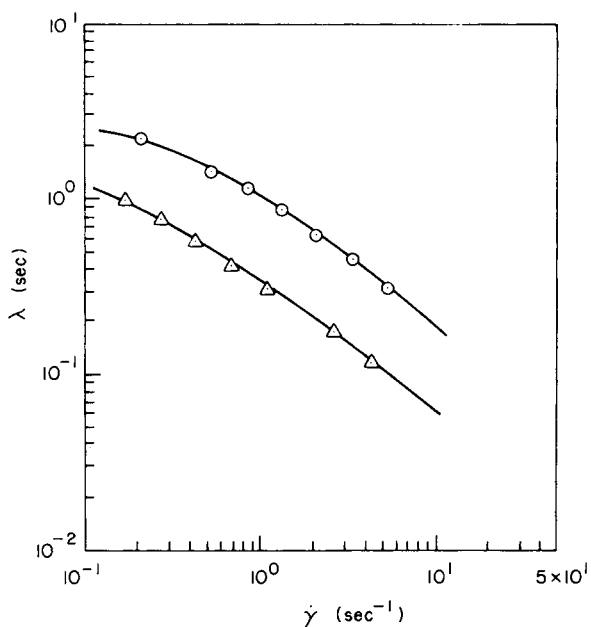


Fig. 16. Relaxation time vs shear rate for the two polypropylenes at 200°C: (○) PP-A; (Δ) PP-B.

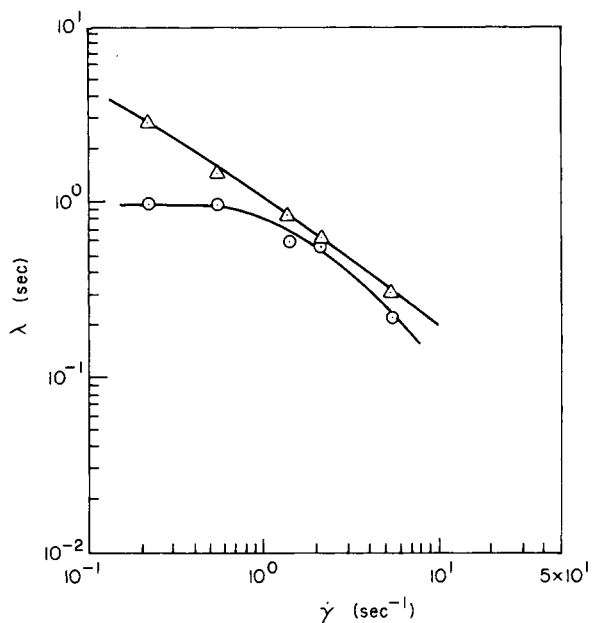


Fig. 17. Relaxation time vs shear rate for the two polystyrenes: (○) PS-A at 200°C; (Δ) PS-B at 220°C.

of the square root of the second invariant of the rate-of-deformation tensor. Note in eq. (7) that

$$\lambda_0 = \lim_{\dot{\gamma} \rightarrow 0} \lambda_{\text{eff}} \quad (8)$$

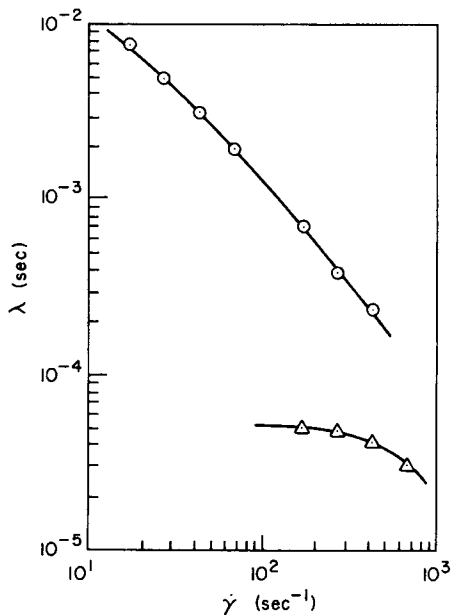


Fig. 18. Relaxation time vs shear rate for nylon-6 and PET: (○) nylon-6 at 280°C; (△) PET at 300°C.

In view of the facts that the “effective” relaxation time of the polymers used in our melt spinning experiment decreases with shear rate (see Figs. 15 to 18) and that the shear rate in the spinnerette hole is very high in general (say, 1000  $\text{sec}^{-1}$ ), the use of  $\lambda_0$  (the limiting value of  $\lambda_{\text{eff}}$  as  $\dot{\gamma}$  approaches zero) in determining  $N_{\text{De}}$  is subject to serious question.

A parameter of considerable rheological significance in melt spinning is the extent of extrudate swell. Much has been discussed in the literature<sup>25</sup> about the use of extrudate swell (i.e., die swell ratio) as a measure of fluid elasticity. Furthermore, there is abundance of experimental evidence<sup>25</sup> that the die swell ratio depends on die geometry. Figure 19 gives representative plots of die swell ratio  $d_j/D$  versus length-to-diameter ( $L/D$ ) ratio, and Figure 20 gives representative plots of  $d_j/D$  versus reservoir-to-capillary diameter ( $D_R/D$ ) ratio. It is then not difficult to imagine that the time required for attaining an equilibrium die swell ratio would also depend on the geometry of the spinnerette hole, as well as on the molecular structure of the polymer and the cooling conditions. If we now define  $\lambda_e$  as the time required for complete recovery of strains outside the spinnerette hole in the absence of stretching (i.e., recovery of unconstrained strain), we may write

$$\lambda_e = (L/D, D_R/D, \alpha, \text{flow rate, melt temperature,} \\ \text{molecular weight and its distribution, molecular structure}) \quad (9)$$

in which  $\alpha$  denotes die entry angle.

Figure 21 gives plots of  $d_j/D$  versus time for HDPE-C and HDPE-D at 240°C. The die swell ratio  $d_j/D$  was determined by first stopping the extruder (and pump), cutting the polymer melt stream (still flowing) at the die exit, and then by recording the extrudate diameter on a movie film for 3 min. It should be noted that the polymer melt stream flowed through an isothermal chamber (see



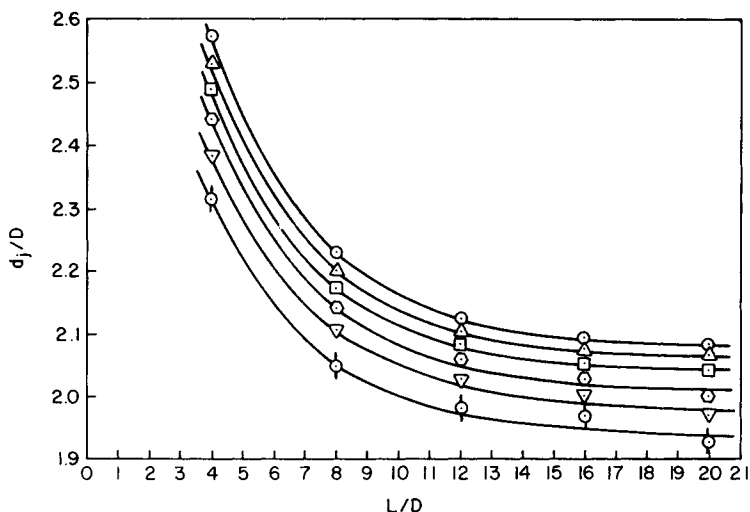


Fig. 19. Die swell ratio vs  $L/D$  for high-density polyethylene (HDPE-B) at  $180^\circ\text{C}$  at various shear rates (ref. 24): ( $\odot$ )  $700 \text{ sec}^{-1}$ ; ( $\Delta$ )  $600 \text{ sec}^{-1}$ ; ( $\square$ )  $500 \text{ sec}^{-1}$ ; ( $\diamond$ )  $400 \text{ sec}^{-1}$ ; ( $\nabla$ )  $300 \text{ sec}^{-1}$ ; ( $\circ$ )  $200 \text{ sec}^{-1}$ .

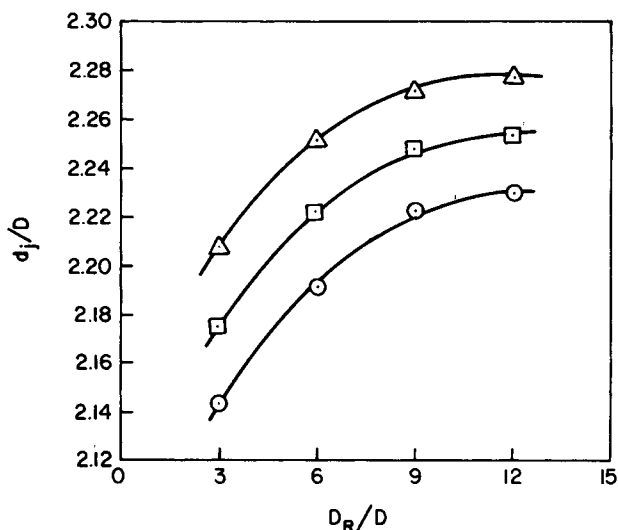


Fig. 20. Die swell ratio vs  $D_R/D$  for the high-density polyethylene (HDPE-B) at  $180^\circ\text{C}$  at various shear rates (ref. 24): ( $\Delta$ )  $400 \text{ sec}^{-1}$ ; ( $\square$ )  $350 \text{ sec}^{-1}$ ; ( $\circ$ )  $300 \text{ sec}^{-1}$ .

Fig. 1) equipped with a Pyrex window, and therefore there was no cooling of the approximately 2 in. of extrudate that was still hanging from the spinnerette face. This experimental technique did not work for the polymer melt whose melt strength (or melt viscosity) was not high enough to support the weight of the extrudate against gravity. It is seen in Figure 21 that it took about 20 sec for the extrudate to attain its equilibrium diameter. Note, however, that the melt temperature and the flow geometry of the spinnerette hole profoundly influences the value of  $\lambda_e$ , the time required for achieving an equilibrium die swell.

Figure 22 gives plots of  $d_j/D$  versus apparent stretch ratio  $V_L/V_0$  for the PP-A

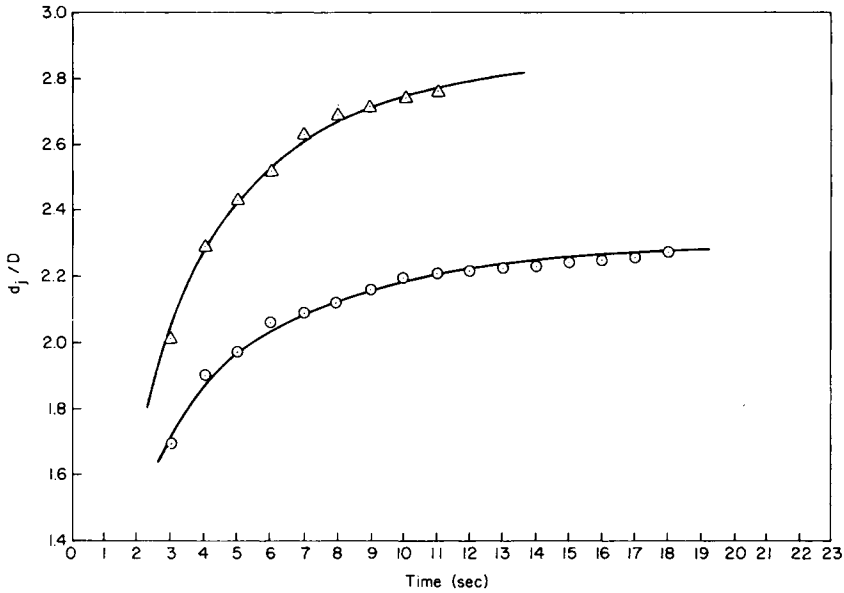


Fig. 21. Die swell ratio vs time for the high-density polyethylenes being melt spun at 240°C: (○) HDPE-C at  $\dot{\gamma} = 609 \text{ sec}^{-1}$ ; (△) HDPE-D at  $\dot{\gamma} = 625 \text{ sec}^{-1}$ .

at 200°C, for different values of spinnerette  $L/D$  ratio. It is clearly seen that the  $L/D$  ratio greatly influences the extent of extrudate swell, and that, as might be expected, stretching decreases  $d_j/D$ . Note that the values of  $d_j/D$  in Figure 22 were determined by taking photographs of the polymer melt stream flowing through the isothermal chamber.

On the basis of the experimental results presented above, and the earlier experimental evidence that the severity of draw resonance is strongly influenced by die geometry,<sup>6,7,12</sup> shear rate in the spinnerette hole,<sup>6,7</sup> melt temperature,<sup>6,7</sup> and cooling conditions,<sup>6,7,12</sup> we propose the use of  $\lambda_e$  in determining the value of  $N_{De}$ , i.e.,

$$N_{De} = \lambda_e/\theta \quad (10)$$

Table IV qualitatively summarizes the experimental results for the severity of draw resonance in terms of  $N_{De}$  defined by eq. (10). It may be concluded, therefore, that any change (in processing variables, die geometry, or molecular structure) that increases the value of  $\lambda_e$ , and hence of  $N_{De}$ , is expected to increase the severity of draw resonance. This conclusion leads us to speculate that fluid elasticity causes an increase in the severity of draw resonance. We shall discuss more about it later, when we review some past theoretical attempts made to explain the phenomenon of draw resonance.

It is expected from the theoretical point of view that cooling will stabilize the disturbed flow of Newtonian liquids. In melt spinning, for instance, the elongational viscosity,  $\eta_E$  is three times the Newtonian shear viscosity  $\eta_0$  (i.e.,  $\eta_E = 3\eta_0$ ). Therefore, cooling should increase the elongational viscosity, following

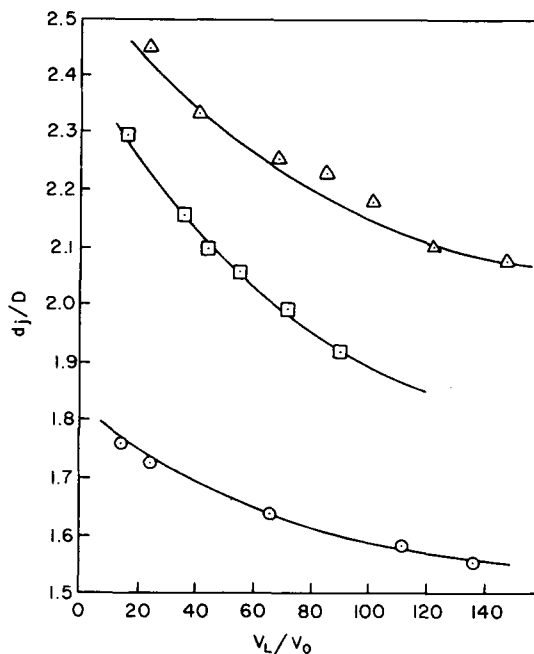


Fig. 22. Die swell ratio vs stretch ratio for the polypropylene PP-A at 200°C under isothermal spinning conditions: ( $\Delta$ )  $L/D = 0$ ,  $\dot{\gamma} = 718 \text{ sec}^{-1}$ ; ( $\square$ )  $L/D = 1.0$ ,  $\dot{\gamma} = 843 \text{ sec}^{-1}$ ; ( $\circ$ )  $L/D = 4.0$ ,  $\dot{\gamma} = 707 \text{ sec}^{-1}$ .

TABLE IV  
Summary Describing the Effects of Spinning Variables on the Severity of Draw Resonance in Isothermal Melt Spinning

| Variables<br>(isothermal<br>spinning)                 | $\lambda_e$ | $\theta$ | $N_{De}$ | Severity of<br>draw resonance<br>(experimental<br>observation) |
|---|-------------|----------|----------|--|
| Increase in<br>$L/D$ ratio                            | Decrease    | —        | Decrease | Decrease   |
| Increase in<br>melt temperature                       | Decrease    | —        | Decrease | Decrease   |
| Increase in<br>draw-down<br>zone ( $l$ ) <sup>a</sup> | —           | Increase | Decrease | Decrease   |
| Increase in<br>takeup<br>speed ( $V_L$ )              | —           | Decrease | Increase | Increase   |
| Increase in<br>shear rate in<br>the spinnerette       | Increase    | —        | Increase | Increase   |

<sup>a</sup>  $l$  is the length of the isothermal chamber.

the Arrhenius relationship. Since, for Newtonian fluids, there is no other rheological property to speak of than the viscosity, the cooling of a Newtonian threadline would be expected to decrease the severity of draw resonance. As a matter of fact, Ishihara and Kase<sup>18</sup> noted that blowing air across a PET

threadline enhances its stability. We have observed in the present study that cooling tends to decrease the severity of draw resonance when molten threadlines of nylon-6 (and PET) were spun directly into quiescent air at 20°C. Note that both the PET and the nylon-6 used are essentially Newtonian fluids. Vassilatos<sup>7</sup> also reports that, in the nonisothermal spinning of a PET, the critical stretch ratio increased as the air-gap distance increased. This observation indicates that cooling tends to decrease the severity of draw resonance of PET melt threadlines.

In the air-gap spinning of a PET, Ishihara and Kase<sup>18</sup> report, however, that the severity of draw resonance first increased as the air-gap distance was increased from 0.5 to 3.0 cm, and it then stayed constant as the air-gap distance was increased from 3.0 to 7.0 cm. Finally, it decreased as the air-gap distance was increased beyond 7.0 cm. They, however, offered no plausible explanation for their experimental observation. On the other hand, they assert that draw resonance can occur only when the spinning is carried out under approximately isothermal conditions, by stating that "conventional industrial melt spinning is always stable," because the threads solidify in air prior to takeup. Such an assertion may be true only for Newtonian fluids (e.g., nylon-6, PET), but is certainly not true for viscoelastic fluids, as clearly demonstrated in Figures 6 to 12.

Matsumoto and Bogue<sup>12</sup> observed that, in the spinning of an amorphous polymer, polystyrene, the spinline is stable if its entire length is kept above the glass-transition temperature  $T_g$ . If the temperature drops below  $T_g$ , it is unstable. They therefore associated the resonant behavior of the polystyrene filament with  $T_g$ , and suggested that the rheological behavior of polystyrene in the neighborhood of  $T_g$  be considered for a better understanding of the effect of cooling on the onset of draw resonance. They also noted that cooling increases the elastic and viscous properties in the die swell region, and they speculated that factors tending to increase the elasticity in the die swell region will tend to make the resonance more severe.

Vassilatos<sup>7</sup> noted that blowing air across a threadline of polypropylene decreased the critical stretch ratio. His observation is in agreement with that of Han et al.<sup>4</sup> It appears then that cooling may or may not increase the severity of draw resonance, depending on whether the fluid under consideration is viscoelastic or not. It should be noted that, for viscoelastic fluids, the rate of cooling, and the temperature of a melt threadline, play important roles in either suppressing or enhancing the severity of draw resonance. This has been clearly demonstrated by the recent experimental results of Blyler and Gieniewski<sup>11</sup> and Matsumoto and Bogue.<sup>12</sup>

A decrease in melt temperature increases the extent of extrudate swell, and hence increases the time  $\lambda_e$  required for achieving equilibrium die swell. For instance, the lower the melt temperature, the larger the relaxation time constant  $\lambda$ , as shown in Figure 23.  $\lambda$  was evaluated using a convected Maxwell model and steady shear flow data. Blowing air across the molten threadline as it exits the spinnerette, effectively decreases  $l$  (the distance from the spinnerette face required for reaching the solidification temperature). This decreases  $\theta$  (the flight time or residence time), which then increases  $N_{De}$ , assuming that  $\lambda_e$  remains constant [see eq. (10)]. However, cooling will also affect  $\lambda_e$ . For instance, slower cooling may effectively increase  $\lambda_e$ , and hence increase  $N_{De}$ , but fast cooling will

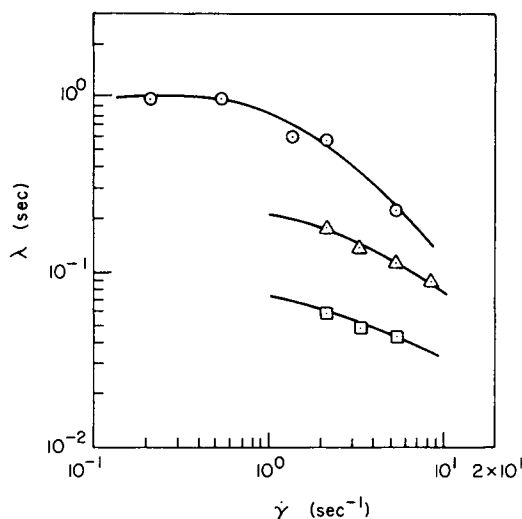


Fig. 23. Relaxation time vs shear rate for the PS-A at various melt temperatures: (○)  $T = 200^{\circ}\text{C}$ ; (Δ)  $T = 220^{\circ}\text{C}$ ; (◻)  $T = 240^{\circ}\text{C}$ .

decrease  $\lambda_e$  and hence will decrease  $N_{\text{De}}$  if  $\Delta\lambda_e < \Delta\theta$ , i.e., if the change in  $\lambda_e$  is less than the change in  $\theta$ . Therefore, cooling may increase or decrease the severity of draw resonance of viscoelastic fluids, depending on whether  $\Delta\lambda_e > \Delta\theta$  or  $\Delta\lambda_e < \Delta\theta$ .

### CRITIQUE OF THEORETICAL ANALYSES OF DRAW RESONANCE

There appears little disagreement among researchers over the roles that the rheological and processing variables play in controlling the severity of draw resonance of Newtonian fluids. Thus, for such fluids, an increase in viscosity, due to either molecular structure or cooling, tends to suppress the severity of draw resonance. However, in dealing with viscoelastic fluids, the theoretical analyses by Fisher and Denn<sup>19,20</sup> predict roles for fluid elasticity and cooling that are not supported by the experimental results of several researchers.<sup>4-9,11,12</sup> We shall now critically examine some possible reasons for the discrepancies between the theoretical predictions and the experimental observations.

Using a convected Maxwell model defined by eq. (5), Fisher and Denn<sup>19</sup> carried out a stability analysis of isothermal melt spinning, and constructed a plot of critical stretch ratio  $(V_L/V_0)_{\text{crit}}$  versus dimensionless variable  $\alpha$  (called the elasticity number) defined as

$$\alpha = (3^{(n-1)/2}K/G) (V_0/L)^n \quad (11)$$

in which  $V_0$  is the average velocity of the fluid in the spinnerette,  $L$  is the draw-down distance,  $G$  is the shear modulus, and  $K$  and  $n$  are constants appearing in the power-law relationship defined by

$$\eta(\Pi) = K(\Pi/2)^{(n-1)/2} \quad (12)$$

$\eta(\Pi)$  is the viscosity function in steady shearing flow and  $\Pi$  is the second invariant of the rate-of-deformation tensor. Fisher and Denn<sup>19</sup> assumed  $G$  to be a constant, but it may be evaluated from steady viscometric flow data by

$$G = \lim_{\dot{\gamma} \rightarrow 0} \left( \frac{2\tau_{12}^2}{\tau_{11} - \tau_{22}} \right) \quad (13)$$

in which  $\tau_{12}$  is the shear stress and  $\tau_{11} - \tau_{22}$  is the first normal stress difference.

Our rheological measurements on the eight viscoelastic polymers employed for the melt spinning experiment (see Table I) show that  $G$  increases with shear rate  $\dot{\gamma}$ , as shown in Figures 24 to 26. Therefore, the assumption that  $G$  is constant

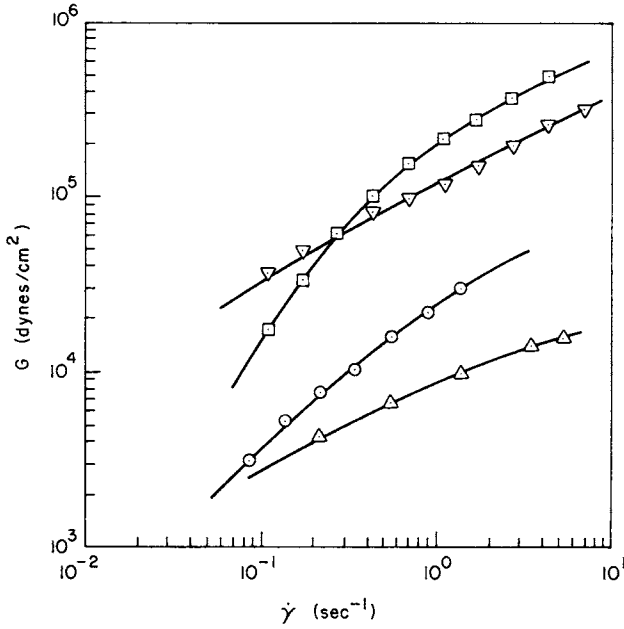


Fig. 24. Shear modulus vs shear rate for four high-density polyethylenes at 240°C: (○) HDPE-A; (Δ) HDPE-B; (□) HDPE-C; (▽) HDPE-D.

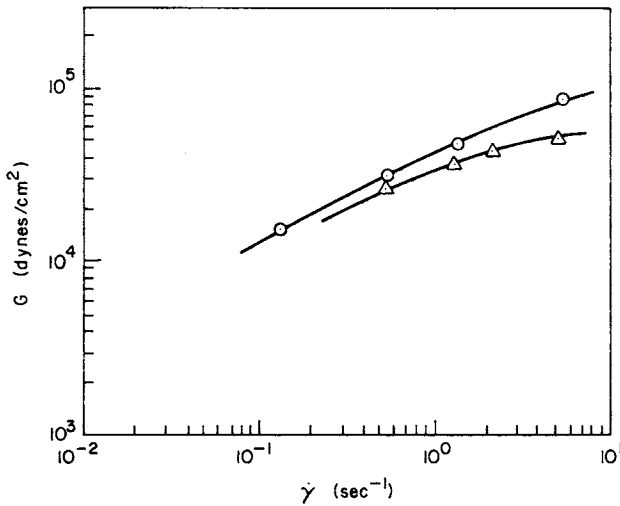


Fig. 25. Shear modulus vs shear rate for two polystyrenes: (○) PS-A at 200°C; (Δ) PS-B at 220°C.

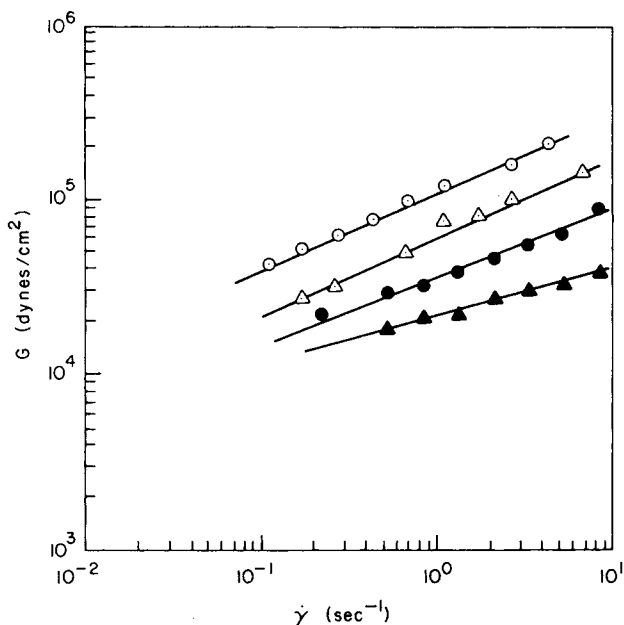


Fig. 26. Shear modulus vs shear rate for two polypropylenes. Open symbols for PP-A: (○)  $T = 200^{\circ}\text{C}$ ; (△)  $T = 220^{\circ}\text{C}$ . Closed symbols for PP-B: (●)  $T = 200^{\circ}\text{C}$ ; (▲)  $T = 220^{\circ}\text{C}$ .

is not supported by our experimental data. This now raises a serious question concerning the validity of the Fisher and Denn analysis, which makes use of the so-called elasticity number  $\alpha$  defined by eq. (11), in which  $G$  is assumed to be constant.

In isothermal melt spinning experiments with low- and high-density polyethylenes, a polypropylene, and a polystyrene, Weinberger et al.<sup>8</sup> found that fluids having large values of  $\alpha$  give rise to lower critical stretch ratios than fluids having small values of  $\alpha$ , indicating that the fluid elasticity increases the severity of draw resonance. Having seen that their finding contradicted the result of the Fisher and Denn analysis, Weinberger et al.<sup>8</sup> criticized the latter on two counts: (i) the rheological parameters used by Fisher and Denn are to be determined in shear flow whereas the kinematics involved in the phenomenon of draw resonance are to be described in extensional flow; (ii) there is *no a priori* reason to expect that the convected Maxwell model [see eq. (5)] used by Fisher and Denn should correctly predict the phenomenon of draw resonance, in view of the fact that their analysis does not include the dependence of elongational viscosity upon the third invariant of the rate-of-deformation tensor.

There are some polymeric materials which behave in an almost Newtonian manner [e.g., nylon-6, and poly(ethylene terephthalate)]. But many polymeric materials exhibit viscoelastic behavior. A unique feature of viscoelastic fluids is the dependence of their rheological behavior on the history of deformation (or strain). There is an abundance of published literature describing this dependence, particularly when the flow is very rapid (i.e., for large  $N_{De}$ ).

One important problem in analyzing draw resonance is initial conditions. One needs to know the proper extrudate swell. Fisher and Denn<sup>19</sup> state that their analysis yields a result which is not sensitive to a choice of initial conditions. They assume that the stress distribution for fully developed laminar flow prevails

in the spinnerette. This essentially is equivalent to saying that their analysis is insensitive to the use of spinnerettes of different  $L/D$  ratios.

It should be remembered however that die swell ratio  $d_j/D$  strongly depends on  $L/D$  ratio (see Figs. 19 and 22), and that, in melt spinning operations of practical importance, the spinnerette  $L/D$  ratio lies somewhere between 1 and 5. These are far too small to yield the stress distribution for fully developed laminar flow, when processing viscoelastic fluids. Moreover, the experimental studies of Han and Kim,<sup>6</sup> Vassilatos,<sup>7</sup> and Matsumoto and Bogue<sup>12</sup> show clearly that the  $L/D$  ratio plays a significant role in the onset of draw resonance. More specifically stated, a small value of  $L/D$  ratio (i.e., a short spinnerette) yields a low critical stretch ratio and hence increases the severity of draw resonance. Therefore the Fisher and Denn analysis is inapplicable, if not irrelevant, to describing the phenomenon of draw resonance in the industrial spinning operation of viscoelastic fluids. Therefore, any comparison of the Fisher and Denn analysis with the experimental results of Han and Kim,<sup>6</sup> Vassilatos,<sup>7</sup> and Matsumoto and Bogue<sup>12</sup> will lead to nothing but confusion.

Note that the dependence of draw resonance on the flow geometry of the spinnerette is not to be expected for Newtonian fluids. It is very unfortunate that, when Fisher and Denn<sup>19</sup> carried out an analysis of the draw resonance of viscoelastic fluids using a convected Maxwell model, they compared their theoretical prediction to the experimental data of Ishihara and Kase.<sup>18</sup> The latter used a PET, which is essentially a Newtonian fluid (i.e., it has a power-law index  $n$  of 1.0, and a relaxation time of approximately  $10^{-3}$  sec). Their general statement that "the onset of draw resonance instability, the magnitude of diameter fluctuations in the unstable region, and a second stable region at high draw ratio are predicted accurately" is misleading to say the least, because their theory was not tested against experimental results obtained with viscoelastic fluids.

It should be mentioned further that, in the experimental data of Ishihara and Kase,<sup>18</sup> it is not clear how much of the deformation took place in the air gap and how much of it took place in the water bath. Recently, Vassilatos<sup>26</sup> performed a calculation of the stretch ratio between the spinnerette and the water surface for the Ishihara and Kase conditions,<sup>18</sup> and found that for the air-gap distance shorter than 0.8 cm the stretch ratio in the air gap is about 20 out of the total stretch ratio imposed of 50. This indicates that considerable stretching occurs below the water surface under severe nonisothermal conditions. Vassilatos<sup>26</sup> observed further that as the mass flow rate is increased, the stretching in the air gap is decreased significantly. His observations seems to indicate that, for the experiments reported by Ishihara and Kase,<sup>18</sup> the stretch ratio in the air gap is not 48.6 as reported, but smaller, especially for short air-gap distances. In other words, the stretching in the water bath may be significant. On the basis of this argument, Fisher and Denn's comparison of such experiments with their theory<sup>19</sup> raises a serious question as to its validity because in one of their theoretical computations, Fisher and Denn assumed a constant stretch ratio of 50 in the air gap.

Whereas the Fisher and Denn analysis predicts a stabilizing role for fluid elasticity, experimental results show that it has a destabilizing effect in the occurrence of draw resonance. The Fisher and Denn analysis ignores the deformation history that the viscoelastic fluid experiences before exiting the spinnerette, and also the die swell region where the relaxation process takes place.



A realistic theoretical approach would be, then, to consider both the deformation history up to the die exit and the strain history from the die downward, including the die swell region. Chen et al.<sup>23</sup> suggest that the tensile stress  $S_{zz}(z)$  in a molten threadline be estimated by

$$S_{zz}(z) = \underbrace{S_{zz}(0)e^{-t/\lambda_0}}_{\substack{\text{history up} \\ \text{to the die} \\ \text{exit}}} + \int_0^t \underbrace{m(t-t')(C_{zz}^{-1} - C_{rr}^{-1}) dt'}_{\substack{\text{history from the die} \\ \text{downward}}} \quad (14)$$

in which  $S_{zz}(0)$  denotes the tensile stress at  $z = 0$  (spinnerette face),  $C_{zz}^{-1}$  and  $C_{rr}^{-1}$  are components of the Finger deformation tensor  $\mathbf{C}^{-1}$ , and  $m(t)$  is the memory function defined as

$$m(t) = \int_{-\infty}^{\ln \lambda_{\text{eff}}} \frac{H[\lambda/(1 - a\lambda \langle II_d^{1/2} \rangle_{av})]}{1 - a\lambda \langle II_d^{1/2} \rangle_{av}} \left( \frac{e^{-t/\lambda}}{\lambda} \right) d \ln \lambda \quad (15)$$

where  $\lambda_{\text{eff}}$  is as defined by eq. (7). Note in eq. (14), however, that the die swell region is neglected and that the additive rule is assumed for the deformation history up to the die exit and from the die downward. In real situations, where the die swell region should be included in a mathematical formulation, the additive rule may not hold. What is needed is, first, to predict the tensile stresses in the die swell region with the deformation history known up to the die exit, and, second, to determine the tensile stresses in the molten threadline along the spin direction from the die swell region downward. The mathematical formulation of such a problem requires further research.

It is also important to point out that the analysis of inelastic fluids should not be used to predict the phenomenon of draw resonance for viscoelastic fluids. Pearson and co-workers<sup>16,17,27</sup> used the following empirical power-law model in elongational flow:

$$\eta_E = \eta_0 e^{E/RT} \left| \frac{dv_z}{dz} \right|^{q-1} \quad (16)$$

for the theoretical analysis of the phenomenon of draw resonance. This model included neither the fluid elasticity nor the deformation history. Therefore, the use of this model for describing the phenomenon of draw resonance of viscoelastic fluids is not justifiable. Hence, the direct comparison of their theoretical analyses<sup>27</sup> to experimental results for viscoelastic polymer melts is *not* justifiable.

There is little doubt that cooling stabilizes a Newtonian threadline. Temperature variations may be a dominant factor in determining the stability of nonisothermal elongational flow of inelastic fluids. The fluid cools as it is being stretched. For Newtonian fluids, the thinner portions cool more rapidly and so require a larger viscosity, thus leading to greater stability.<sup>16,17</sup> Considering an exponential dependence of viscosity on temperature, Shah and Pearson<sup>16</sup> concluded from their theoretical analysis that nonisothermal spinning of inelastic fluids is more stable than isothermal spinning, when draw resonance is the cause of threadline instability.

Whereas the theoretical study of Fisher and Denn<sup>20</sup> claims that cooling should stabilize a viscoelastic threadline, the experimental results of Han and co-workers,<sup>4,5</sup> Blyler and Gieniewski,<sup>11</sup> and Matsumoto and Bogue<sup>12</sup> show that

cooling can increase the severity of draw resonance of viscoelastic fluids. It should be kept in mind that the theoretical prediction of the flow of a viscoelastic melt threadline under cooling is not possible unless it correctly includes the effect of temperature on the elastic property.

In their analysis of nonisothermal melt spinning of viscoelastic fluids, Fisher and Denn<sup>20</sup> assumed that the shear modulus  $G$  is independent of temperature, and that the variation of relaxation time  $\lambda$  with temperature is of the Arrhenius type, due to the variation of shear viscosity,

$$\lambda(T) = \eta_0 e^{(E/R)(1/T - 1/T_0)} / G \quad (17)$$

Our rheological measurements show, however, that  $G$  also varies with temperature (for example, see Fig. 26). Their conclusion that cooling suppresses the severity of draw resonance of viscoelastic fluids is not confirmed by experiment. In all our studies with viscoelastic melts, cooling is seen to increase the severity of draw resonance, as may be seen in Figures 6 to 12.

More recently, Pearson et al.<sup>27</sup> carried out a stability analysis of the fiber spinning process, and concluded that the elasticity of a "frozen" fiber appears to destabilize the spinning process. However, it is very doubtful whether, in reality, a "frozen" threadline can ever exhibit draw resonance to any practical extent. Therefore it is fair to say that, at present, there is no dependable theoretical analysis reported in the literature, which properly considers the elasticity of a melt threadline under cooling.

On the other hand, on the basis of their experimental results, Han et al.<sup>4</sup> and Vassilatos<sup>7</sup> have concluded that cooling can destabilize a viscoelastic melt threadline. It appears, then, that one can observe either the stabilizing effect of cooling on threadline when a Newtonian (or near Newtonian) fluid (e.g., nylon-6, PET) is melt spun, or the destabilizing effect of cooling when a viscoelastic polymeric fluid (e.g., polypropylene, polyethylene, polystyrene) is melt spun.

## CONCLUDING REMARKS

The following conclusions may be drawn from the present investigation: (i) The severity of draw resonance depends strongly on the distribution of molecular weight, and molecular structure; (ii) cooling may increase the severity of draw resonance of viscoelastic fluids in general. However, the degree varies from material to material; (iii) cooling decreases the severity of draw resonance of Newtonian fluids (e.g., nylon-6, PET); (iv) a control of the temperature profile in a molten threadline is very important in suppressing the severity of draw resonance and hence in obtaining uniform fiber diameters; and (v) the severity of draw resonance appears to depend on the morphological state of the macromolecules in a threadline being stretched and cooled.

It appears that a complete theoretical understanding of the phenomenon of draw resonance of viscoelastic fluids can be realized only when one incorporates into a mathematical formulation the nature of the nonlinear memory function, as advocated by Ide and White<sup>28,29</sup> and the distribution of molecular weights, as advocated by Takaki and Bogue.<sup>30</sup> In view of the experimental evidence published in the literature, the use of a fluid model with a strong memory function is required, so that we can properly account for the deformation history of the

fluid. Moreover, one should properly consider the relaxation and cooling processes in the die swell region and the region just below it, for the development of a new kind of draw resonance theory. For a general treatment of the non-isothermal draw resonance, the work of Matsui and Bogue<sup>31,32</sup> would seem the best starting point coupled with careful considerations of solidification temperatures. This would involve knowing the interaction of applied stress and cooling rate.<sup>33</sup>

The authors wish to acknowledge that Professor D. C. Bogue and Professor J. L. White at the University of Tennessee and Dr. G. Vassilatos at E. I. DuPont de Nemours and Company kindly read the original manuscript and made a number of constructive comments. Their comments led us to improve the content of our original manuscript.

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Received March 31, 1978

Revised June 7, 1978