

Studies on Melt Spinning. V. Elongational Viscosity and Spinnability of Two-Phase Systems

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Synopsis

Isothermal melt spinning experiments were carried out to investigate the elongational flow behavior and spinnability of polymer blends and a calcium carbonate-filled polypropylene. Blends chosen for study were mixtures of polystyrene (Dow Chemical, Styron 678) with high-density polyethylene (Union Carbide, DMDJ 4309), and mixtures of polystyrene (Dow Chemical, Styron 686) with high-density polyethylene (Union Carbide, DMDJ 4309). For the study, measurements were taken of the thread diameter by photographic techniques and of the thread tension by means of a Saxl tensiometer. These measurements were later used to determine the elongational viscosity of the material investigated. It was found that, in all the blends and filled systems investigated, the elongational viscosity decreases with elongation rate and that the relationship between the elongational viscosity and blending ratio is very complex. An attempt is made to offer explanations of the observed complicated relationship with the aid of microphotographs of fiber samples, which display the complexity of fiber morphology in two-phase systems. It was also found that there exists some correlation between the elongational viscosity and the maximum stretch ratio which may be considered as representing fiber spinnability.

INTRODUCTION

In the commercial melt spinning operation, one rarely uses a single fiber-forming material. More often than not, one uses mixtures of two or more fiber-forming materials, together with some kinds of additive. In other words, as in the plastics industry, the fiber industry makes use of blends of two or more polymers in order to obtain certain desired mechanical and/or physical properties of the finished fiber. The composite fiber of nylon and polyester may serve as a good example for this. For the purpose of reinforcement, one uses also reinforcing materials, for instance, fiber glass.

When two fiber-forming materials are spun together, a fundamental question may be raised as to the role that each material plays in the process of fiber formation. Undoubtedly, there must be some interaction between the components in the process of fiber formation. The problem becomes even more complicated when the two materials form separate phases. Despite the fact that these questions are highly important, there is very little information published in the literature dealing directly with the matter.

In view of the importance of the problem as briefly stated above, the authors, using polymer blends and filled polymers, have recently made an experimental study of melt spinning. The primary objective of the study was to investigate the question of spinnability and fiber morphology when two incompatible polymers were spun together and also when a fiber-forming polymer contains an appreciable amount of fillers for reinforcement.

EXPERIMENTAL

Isothermal melt spinning experiments were carried out, using the bench-scale spinning apparatus recently constructed in connection with the earlier research program of Han and Lamonte.¹

The materials used for spinning were blends of high-density polyethylene with two varieties of polystyrene. The high-density polyethylene used was a commercial product of Union Carbide Corp. (DMDJ 4309), and the two polystyrenes were Dow Chemical Co. Styron 678 and Styron 686. These two polystyrenes were chosen in order to see the phase inversion and its effect on the melt spinning of the blends of DMDJ 4309/Styron 678 and DMDJ 4309/Styron 686. Phase inversion is expected to occur because, over the range of shear rates tested, Styron 678 is less viscous than DMDJ 4309, whereas Styron 686 is more viscous. Figure 1 shows plots of shear viscosity versus shear rate, and Figure 2 plots of first normal stress difference versus shear rate for the three homopolymers used for the preparation of blends. According to the previous study by Han and Yu,² these blend systems form two phases in the molten state, in which one component

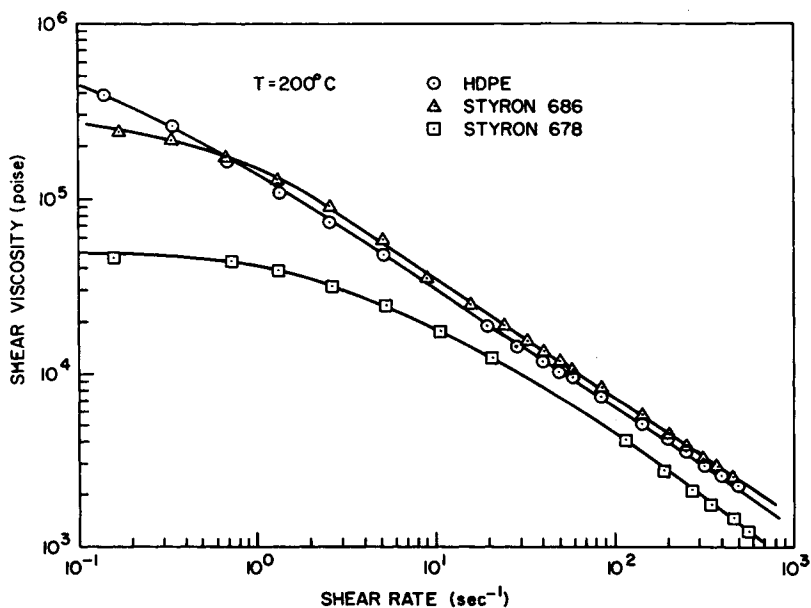


Fig. 1. Plots of shear viscosity vs. shear rate for homopolymers at 200°C.

TABLE I
Blend Ratio of the Materials Used and Stretch Ratio Chosen

Blend system	Stretch ratio
Styron 686/HDPE	
wt. ratio 25/75	10.5, 11.4, 28.7
50/50	8.3, 20.9
75/25	2.4, 6.7, 18.1
HDPE/Styron 678	
wt. ratio 25/75	39.9, 109.2, 120.9
50/50	6.8, 12.0, 20.1, 66.1
75/25	2.5, 4.5, 6.4

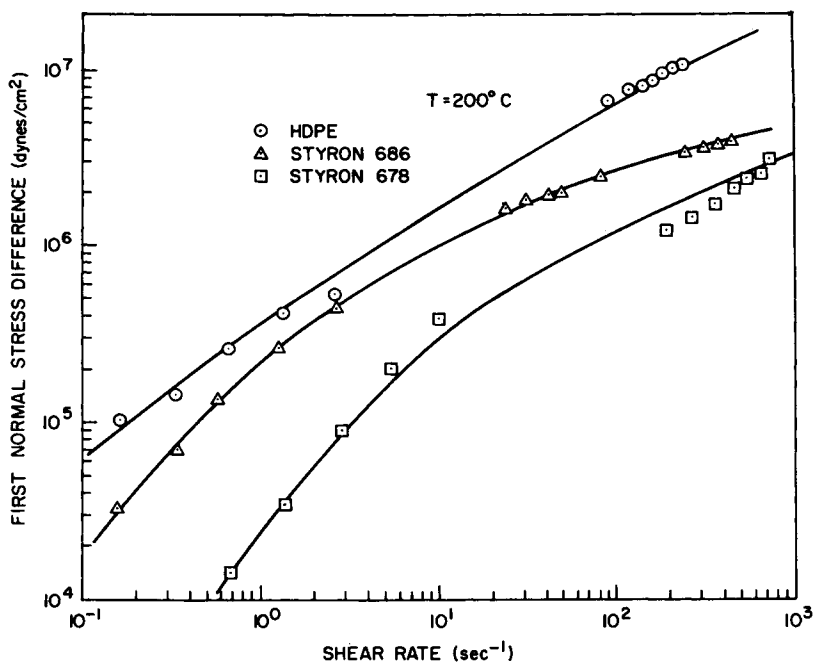


Fig. 2. Plots of normal stress difference vs. shear rate for homopolymers at 200°C.

gets dispersed into the other to an extent depending on the extrusion conditions, as they affect the viscosity ratio of the individual components.

Blends were prepared by mixing together pellets of the two polymers in a tumbling device. For each blend system, three blending ratios were chosen: 25-75 wt-%, 50-50 wt-%, and 75-25 wt-% (see Table I).

Also used for the melt spinning experiment was a calcium carbonate-filled polypropylene, which was prepared in a twin-screw compounding machine (ZSK 53/L, Werner & Pfleiderer Corp.). The filler concentrations employed in the melt spinning experiment were 10, 20, and 40 wt-% calcium carbonates (Camel-Wite from H. T. Campbell & Sons) in the

polypropylene (Enjay Chemicals, Resin E 115). The rheological properties of the filled polypropylene used have been reported in a paper by Han.³

In the spinning experiment, measurements were taken of the thread diameter by photographic techniques and of the thread tension by use of a Saxl tensiometer. These measurements were later analyzed to determine the elongational viscosity. Details of fiber morphology were also investigated by taking microphotographs of the fiber samples collected at various spinning conditions.

RESULTS AND DISCUSSION

Determination of Elongation Rate

Elongation rate can be determined once one has information of the axial profiles of thread diameter. Namely, at any given position x , the thread velocity can be determined with the aid of the continuity equation

$$V(x) = 4W/\pi\rho D(x)^2 \quad (1)$$

where ρ is the fluid density, W is the mass flow rate, and $D(x)$ is the thread diameter at position x . It should be noted that eq. (1) is valid only for *isothermal* melt spinning where mass transfer is absent.

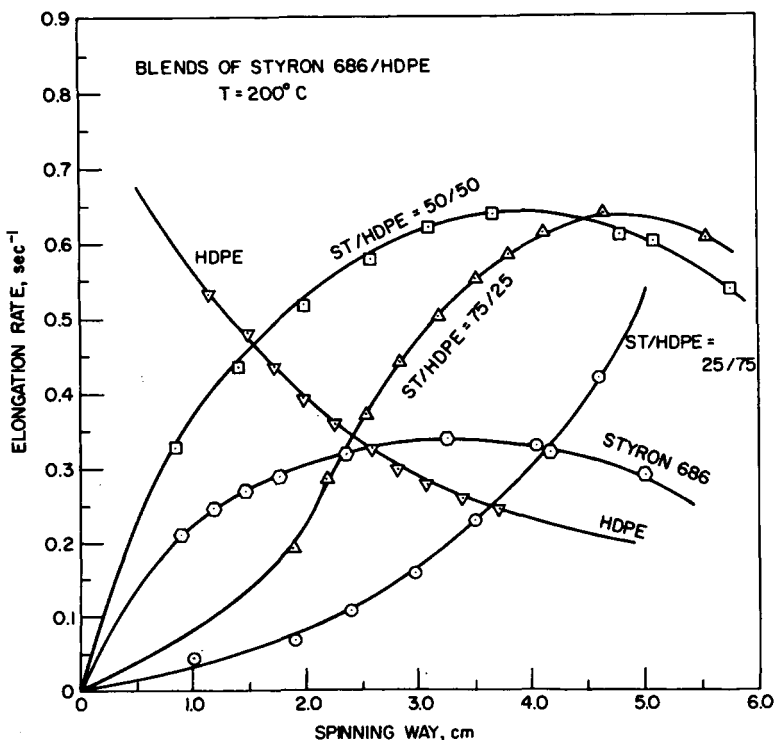


Fig. 3. Representative profiles of elongation rate along the spinning way for Styron 686/HDPE blends.

In the present study, measurements were taken photographically of the thread diameter $D(x)$ in an isothermal chamber about 6 in. long, attached to the spinnerette face and maintained at the same temperature as that of the molten threadlines moving downward. Once the axial profiles of the thread diameter were determined by curve fitting, the elongation rate $dV(x)/dx$ was determined by taking the derivative of $V(x)$ with respect to x , with the aid of eq. (1).

Figure 3 shows representative profiles of elongation rate along the spinning way for Styron 686/HDPE blends. The purpose of the plots given in Figure 3 is to display the variability of the shape of the axial profiles of elongation rate for different materials. It is quite clear in Figure 3 that elongation rate is not constant along the spinning way.

Elongational Viscosity of Two-Phase System

Figure 4 gives plots of elongational viscosity versus elongation rate for the three homopolymers investigated. Some observations on these plots are worth noting. First, elongational viscosity decreases as the elongation rate is increased, over the range of elongation rates tested. Elongational

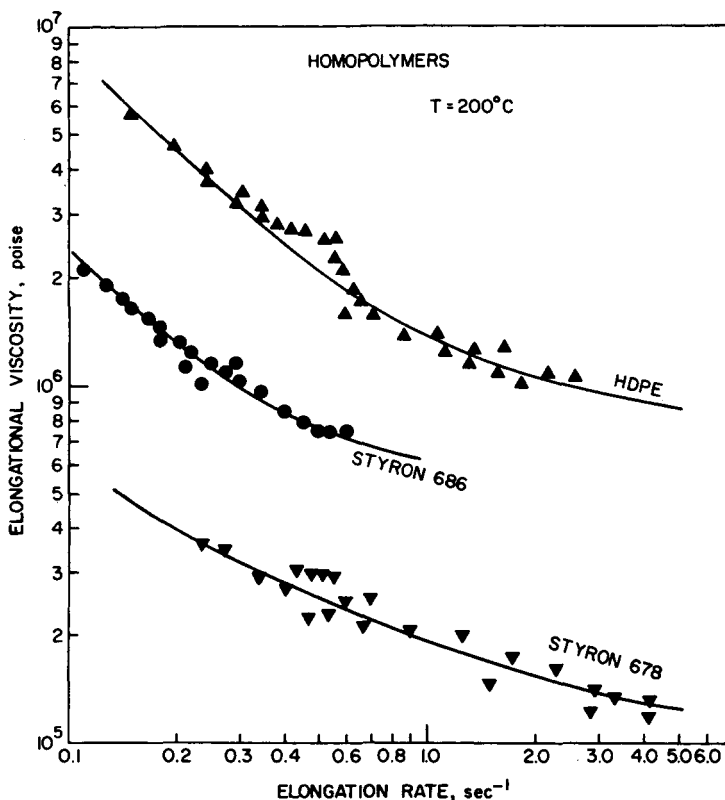


Fig. 4. Elongational viscosity vs. elongation rate for homopolymers at 200°C.

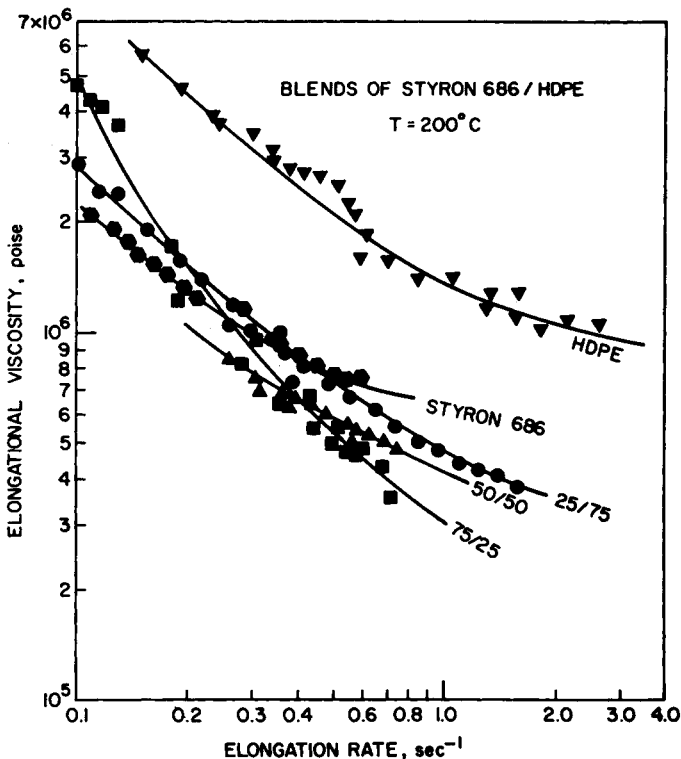


Fig. 5. Elongational viscosity vs. elongation rate for Styron 686/HDPE blends at 200°C.

viscosities for each material were obtained at various stretch ratios, as given in Table I. It should be noted that two (DMDJ 4309 and Styron 686) of the three polymers listed in Figure 4 had been tested in a previous study by Han and Lamonte.¹ Considering that this type of experiment is very difficult to control, it can be said that the reproducibility of the experimental results is reasonably good.

Note that the elongational viscosity was determined by following the procedure described in an earlier paper by Han and Lamonte.¹ Briefly stated, the tensile stress was determined from the tension measurement with the aid of the overall force balance. This permitted us to calculate the so-called rheological force F_{rheo} , which is the force required only for the deformation of the thread. In other words, proper steps were taken to take into account other forces (e.g., the gravitational force, the drag force, and the inertial force) in calculating the rheological force F_{rheo} . Having determined the elongation rate, as discussed above, and the tensile stress T_{xx} , the elongational viscosity η_E was calculated from

$$\eta_E = T_{xx} \left/ \frac{dV(x)}{dx} \right. \quad (2)$$

in which T_{xx} is defined as $F_{\text{rheo}}/A(x)$, with $A(x)$ being the cross-sectional area of a thread at the position x , i.e., $\pi D(x)^2/4$.

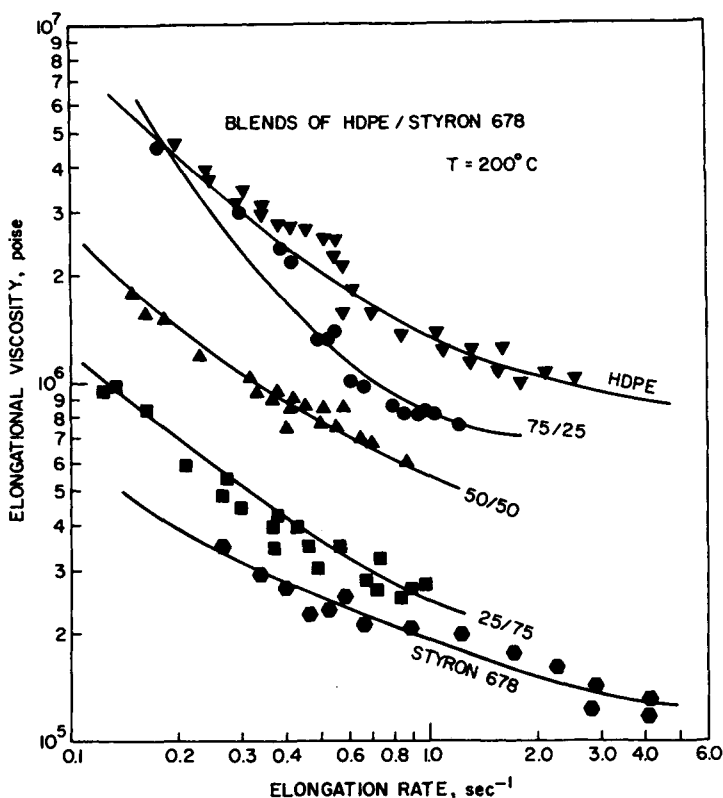


Fig. 6. Elongational viscosity vs. elongation rate for Styron 678/HDPE blends at 200°C.

The elongational viscosities of the polymer blends tested are given in Figure 5 for Styron 686/HDPE blends and in Figure 6 for Styron 678/HDPE blends. It is seen that in all cases elongational viscosity decreases with elongation rate. It is interesting to note in Figure 5 that blends of Styron 686/HDPE give rise to elongational viscosities even lower than those of the pure components, whereas elongational viscosities of the blends of Styron 678/HDPE lie somewhere between those of the pure components. In order to observe the effect of blending ratio on elongational viscosity more clearly, cross plots of Figure 5 are given in Figure 7, and cross plots of Figure 6 are given in Figure 8.

It is seen in Figure 7 that elongational viscosity goes through a minimum at a blending ratio of 75 wt-% of Styron 686 to 25 wt-% of HDPE. On the other hand, Figure 8 shows that, as the weight percentage of HDPE is increased in the blends of Styron 678/HDPE, the elongational viscosity also increases correspondingly, but without going through a minimum. In other words, the two blend systems respond quite differently in the fiber-forming operation. An explanation for the observed elongational flow behavior of the two-phase polymer systems investigated needs some information of the possible interaction between the components in the molten

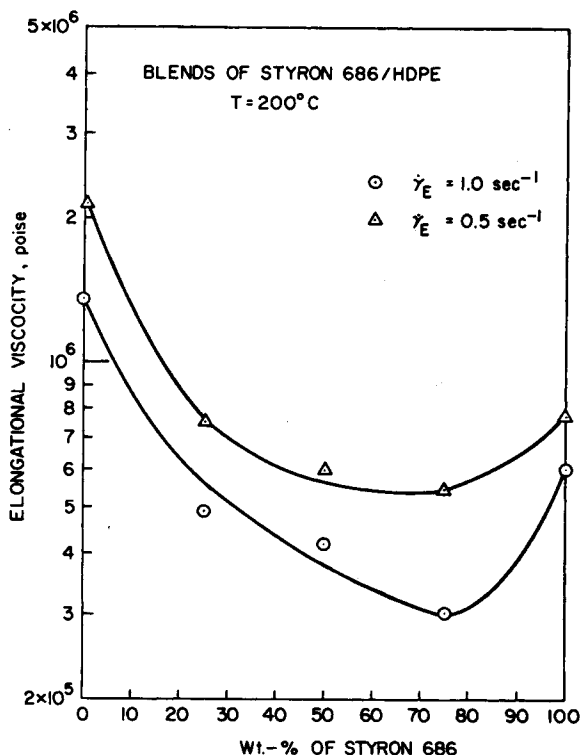


Fig. 7. Elongational viscosity vs. blending ratio for Styron 686/HDPE blends.

state. Such information may be obtained only when one examines the microstructure of the fiber spun, which we shall discuss below.

It seems appropriate at this point to comment that the value of the experimentally determined elongational viscosity (see Figs. 4, 5, and 6) is not as predicted by many theoretical studies reported in the literature.⁴⁻⁶ Today, when looking at the literature, one can easily be confused with many "apparently" contradictory experimental results reported by different groups of researchers. Some researchers^{7,8} report that elongational viscosity is constant, independent of elongation rate; and others^{9,10} report that it increases with elongation rate; and still others^{1,11} report that it decreases with elongation rate. Unfortunately, however, the experimental techniques employed by different research groups often do not provide us with a common ground on which to compare one set of experimental data with another. For example, some researchers^{7,8} attempted to maintain the elongation rate constant along the direction of stretching, whereas others^{1,11} maintained the velocity of the elongating fluid constant at a fixed position. In the latter case, maintaining the elongation rate constant is very difficult, if not impossible. Moreover, for practical reasons in melt spinning, the control of the velocity at the take-up device is far more important than the control of elongation rate along the threadline.

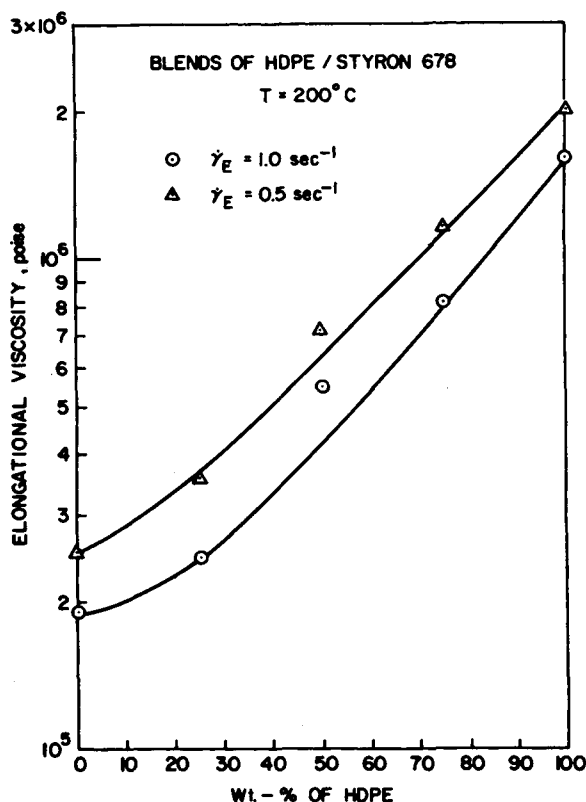


Fig. 8. Elongational viscosity vs. blending ratio for Styron 678/HDPE blends.

On the other hand, almost all theoretical studies reported in the literature^{4,5,6,12,13} assume a constant elongation rate in the analysis of steady, elongational flow; and yet some predict elongational viscosity increasing with elongation rate,^{4,5,6} whereas others predict that elongational viscosity may increase or decrease with elongation rate.^{12,13} However, as may be seen in Figure 1, the basic assumption made in those theoretical studies, namely, that the elongation rate is constant, does not hold in the melt spinning experiments reported here. Therefore, any theoretical prediction based on the assumption of constant elongation rate is not applicable. This is not to say that the theoretical approach is wrong, but that certain experimental techniques such as fiber spinning do not provide us with a constant elongation rate.

Figure 9 shows plots of elongational viscosity versus elongation rate for calcium carbonate-filled polypropylene at 200°C. It is seen that, as in blend systems, the elongational viscosity decreases with elongation rate, and the elongational viscosity increases as the filler concentration is increased. This behavior is expected because the solid particles of CaCO_3 do not deform under stretching and hence they will exert more resistance

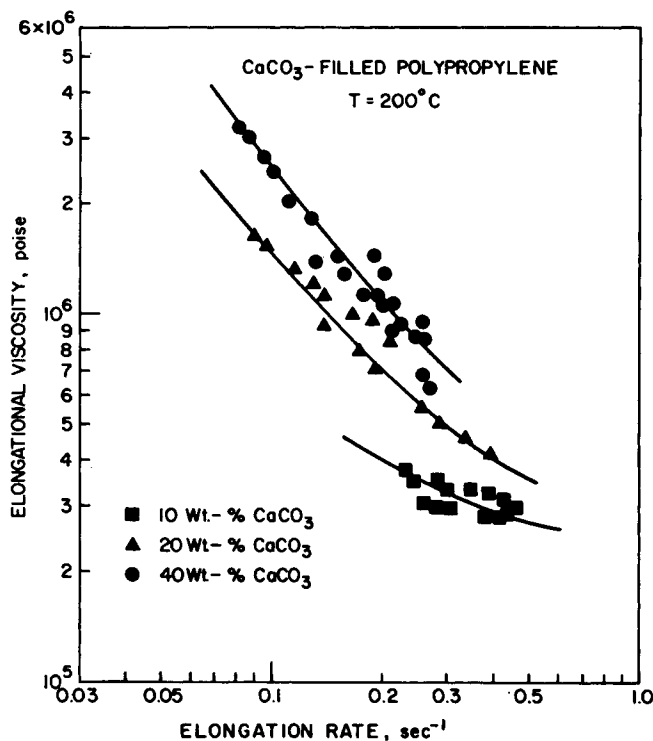


Fig. 9. Elongational viscosity vs. elongation rate for calcium carbonate-filled polypropylene at 200°C.

to the flow of molten threadline as the concentration of CaCO₃ is increased. We shall discuss below the fiber morphology as seen from microphotographs.

Fiber Morphology in Two-Phase System

Fiber samples collected were mounted in epoxy (room temperature cure) and subsequently ground and polished. The polystyrene phase was then dissolved with toluene in order to provide positive identification of the two phases. Samples were then photographed in reflection in order to obtain the in situ distribution of the components, with the aid of an optical microscope.

Figure 10 shows pictures of the microstructure of fiber samples of 50 wt-% Styron 678 to 50 wt-% HDPE at three different stretch ratios. Note in Figure 10 that the dark area represents Styron 678 dissolved by toluene, and the white area represents high-density polyethylene (HDPE). It is seen that the HDPE is the discrete phase, dispersed in the Styron 678, which is the continuous phase. It is seen, also, that the dispersed polyethylene forms longer fibriles as the stretch ratio is increased. This is attributable to the fact that both phases are deformable in the molten state.

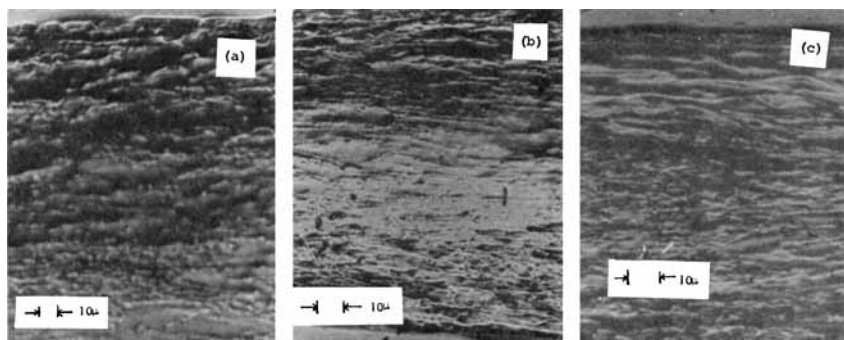


Fig. 10. Pictures of fiber samples of the blend of 50 wt-% Styron 678 to 50 wt-% HDPE: (a) stretch ratio 80; (b) stretch ratio 162; (c) stretch ratio 240.

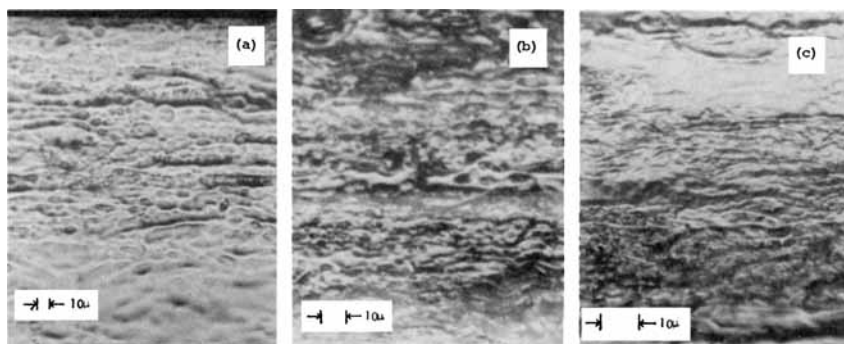


Fig. 11. Pictures of fiber samples of the blend of 75 wt-% of Styron 686/25 wt-% HDPE: (a) stretch ratio 75; (b) stretch ratio 162; (c) stretch ratio 308.

Figure 11 shows pictures of the microstructure of fiber samples of 75 wt-% Styron 686 to 25 wt-% HDPE at three different stretch ratios. Here, the Styron 686 (dark area) forms the discrete phase, dispersed in the HDPE. This is quite the opposite of the blends of Styron 678/HDPE. That is to say, there is a phase inversion between the two blends systems, depending upon which of the two polystyrenes is blended with the HDPE.

We can now discuss which of the rheological properties, melt viscosity or melt elasticity, would determine the mode of dispersion. The answer may come directly from the rheological data of the three homopolymers given in Figures 1 and 2. In other words, Styron 686 is more viscous than HDPE at the shear rate which the melts experienced in the spinnerette holes (about 1000 sec^{-1}), and HDPE is more viscous than Styron 678. It appears, then, that the more viscous component would form the discrete phase (droplets) and the less viscous component would form the continuous phase. The surface tension force is expected to play virtually no significant role here, especially since the magnitude of the shear stresses in molten polymer is considerably greater than that of the surface tension force. It may therefore be concluded that the criterion we have just dis-

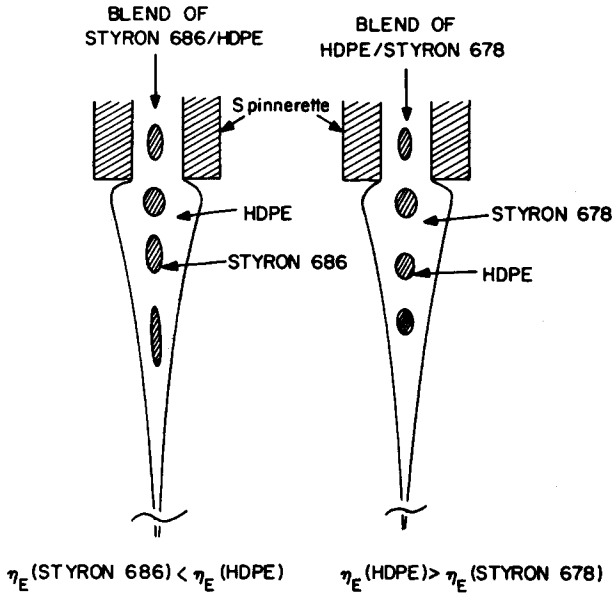


Fig. 12. Sketch illustrating deformation of liquid droplets suspended in another liquid medium.

cussed is consistent with the observations we have made in microphotographs (see Figs. 10 and 11).

Now, in order to explain the "apparently" unusual behavior of two-phase polymers in the elongational flow field, as shown in Figures 7 and 8, let us consider the sketch given in Figure 12, illustrating the process of elongational deformation of liquid droplets suspended in another liquid. At this juncture, refer to Figure 4, which shows the elongational viscosity of individual pure components. In the case of the Styron 686/HDPE blend systems, Styron 686, which forms the discrete phase (i.e., droplets), has an elongational viscosity lower than HDPE. Therefore, as the thread is stretched under tension, the droplets of Styron 686 can be expected to elongate much more easily than the HDPE, which forms the continuous phase. On the other hand, in the case of the HDPE/Styron 678 blend system, the situation is exactly the opposite. That is, since HDPE, which forms the discrete phase, has an elongational viscosity greater than Styron 678, it is to be expected that, under stretching, the HDPE droplets would elongate much less than the continuous phase, Styron 678. Furthermore, it is to be expected that HDPE/Styron 678 blends would give less elongation than pure Styron 678.

The extreme case of an HDPE/Styron 678 blend system would be the filled system, CaCO_3 -filled polypropylene. Figure 13 shows microphotographs of fiber samples of the filled polymer. It is seen that solid particles are suspended in the molten polypropylene. Since CaCO_3 particles can be assumed to possess infinitely large viscosity compared to molten poly-

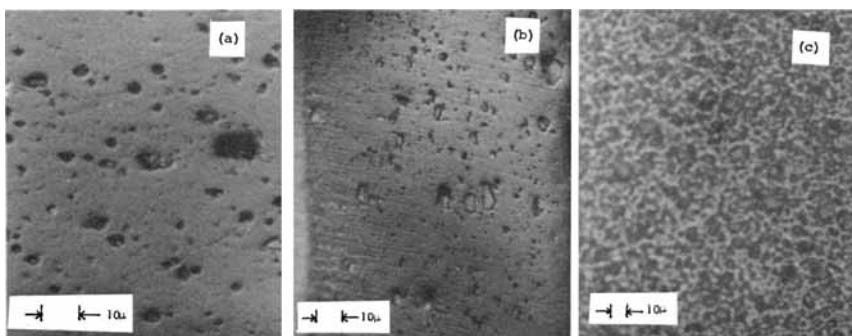


Fig. 13. Pictures of fiber samples of calcium carbonate-filled polypropylene: (a) 10 wt-% CaCO_3 ; (b) 20 wt-% CaCO_3 ; (c) 40 wt-% CaCO_3 .

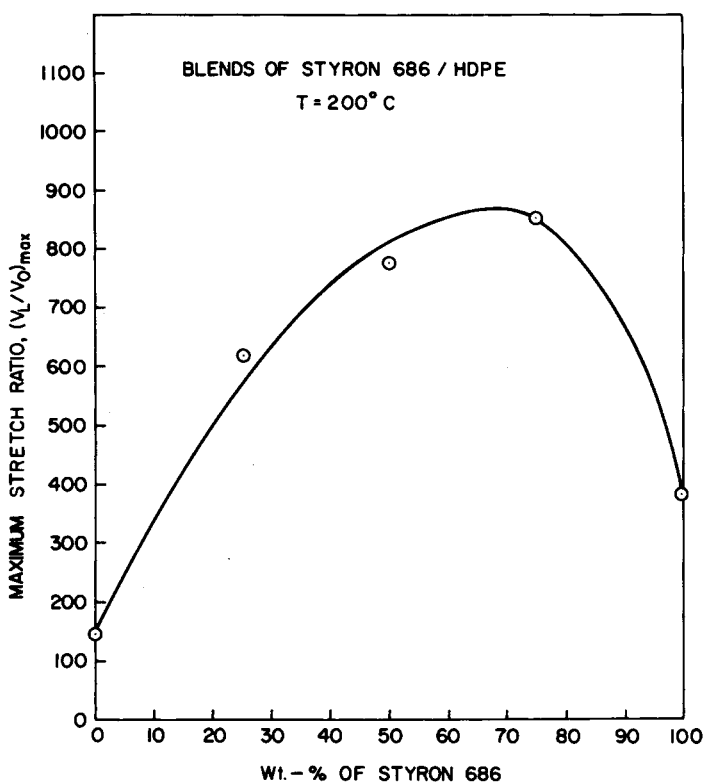


Fig. 14. Maximum stretch ratio vs. blending ratio for Styron 686/HDPE blends.

propylene, the CaCO_3 particles would require much greater forces to move in the molten threadline of polypropylene. This would then give less elongation of the fiber under stretching, borne out in Figure 9.

It may be concluded, therefore, that a study of the fiber morphology helps one to interpret the elongational flow behavior of two-phase polymer systems.

Spinnability of Two-Phase System

At present, there seems to be more than one way of determining the spinnability of a given material. For the purpose of our discussion here, we shall use the maximum stretch ratio $(V_L/V_0)_{\max}$ for comparing the spinnability of different materials. Here, V_L denotes the take-up velocity and V_0 , the linear velocity of the melt in the spinnerette. Based on this criterion for spinnability, it can be said that the larger the value of $(V_L/V_0)_{\max}$, the more spinnable a material is. This is because higher values of $(V_L/V_0)_{\max}$ allow greater elongation of the thread without breaking it. Note that at a given mass flow rate (i.e., constant V_0), $(V_L/V_0)_{\max}$ is determined by the maximum value of take-up velocity, $(V_L)_{\max}$, at which the thread breaks. Figure 14 gives plots of $(V_L/V_0)_{\max}$ versus blending ratio for Styron 686/-HDPE blend systems, and Figure 15, for HDPE/Styron 678 blend systems.

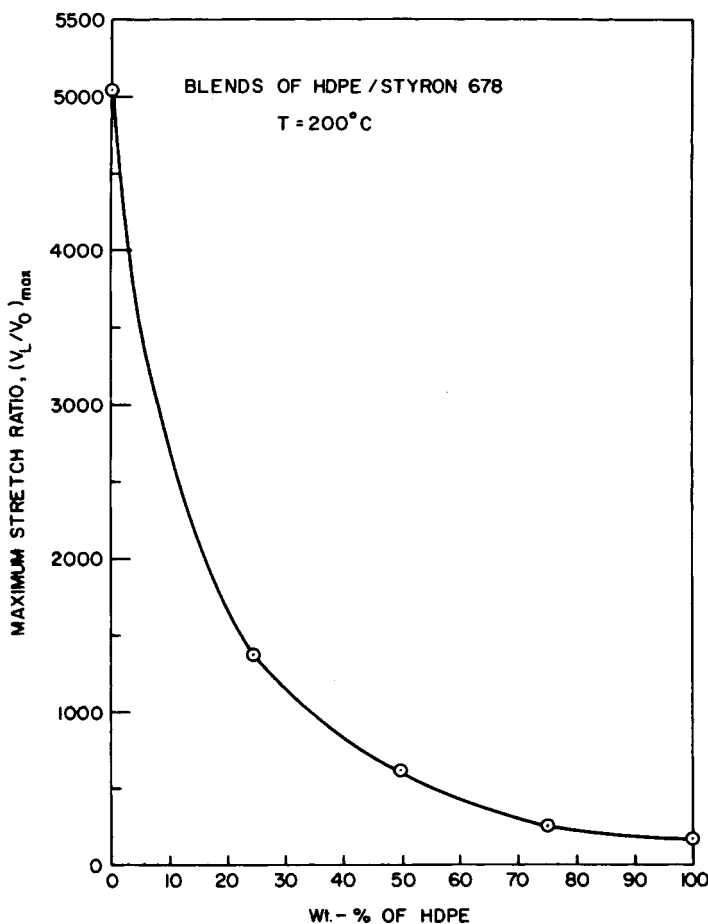


Fig. 15. Maximum stretch ratio vs. blending ratio for Styron 678/HDPE blends.

TABLE II
Maximum Stretch Ratio of Homopolymers Investigated

Material	$(V_L/V_0)_{\max}$
HDPE	155
Styron 686	366
Styron 678	5096

Comparing Figures 7 and 14, and also Figures 8 and 15, it is seen that the material having the lower elongational viscosity gives rise to a higher $(V_L/V_0)_{\max}$ than the material having the higher elongational viscosity. In other words, there is a clear evidence that elongational viscosity is correlatable with spinnability. Based on this observation and Figure 4, it can also be said that, among the three homopolymers used, Styron 678 has better spinnability than HDPE and Styron 686. Table II proves this contention.

The work was supported in part by American Enka Company and by the National Science Foundation under Grant No. GK-38549, for which the authors are very grateful.

References

1. C. D. Han and R. R. Lamonte, *Trans. Soc. Rheol.*, **16**, 447 (1972).
2. C. D. Han and T. C. Yu, *J. Appl. Polym. Sci.*, **15**, 1163 (1971).
3. C. D. Han, *J. Appl. Polym. Sci.*, **18**, 821 (1974).
4. A. S. Lodge, *Elastic Liquids*, Academic Press, New York, 1964.
5. J. L. White, *J. Appl. Polym. Sci.*, **8**, 2339 (1964).
6. M. J. Yamamoto, *J. Phys. Soc. (Japan)*, **12**, 1148 (1957).
7. R. L. Ballman, *Rheol. Acta*, **4**, 1938 (1965).
8. J. Meissner, *Trans. Soc. Rheol.*, **16**, 405 (1972).
9. F. N. Cogswell, *Rheol. Acta*, **8**, 187 (1969).
10. J. A. Spearot and A. B. Metzner, *Trans. Soc. Rheol.*, **16**, 495 (1972).
11. D. Acierno, J. N. Dalton, J. M. Rodriguez, and J. L. White, *J. Appl. Polym. Sci.*, **15**, 2395 (1971).
12. R. I. Tanner, *Trans. Soc. Rheol.*, **12**, 155 (1968).
13. G. Marrucci, G. Titomanlio, and G. C. Sarti, *Rheol. Acta*, **12**, 269 (1973).

Received December 21, 1973

Revised February 14, 1974