Studies on Melt Spinning. VII. Elongational Viscosity and Fiber Morphology of Multiphase Polymer Systems

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Synopsis

Melt spinning experiments were carried out to investigate the elongational behavior and fiber morphology of multiphase polymer systems. Materials chosen for study were blends of calcium carbonate-filled polypropylene with general-purpose polystyrene and blends of calcium carbonate-filled polypropylene with high-impact polystyrene. The former is a three-phase system in which the $CaCO_3$ particles are dispersed, and the latter is a four-phase system in which $CaCO_3$ particles are dispersed, together with rubbery butadiene particles. Note that polypropylene is incompatible with the matrix of high-impact polystyrene. The experimental technique described in part I of this series was used to determine the elongational viscosity. With the four-phase system, the apparent elongational viscosity tends to increase as the stretch ratio is increased above a certain critical value which appears to be ca. 25. This transition does not occur with the three-phase system and is attributable to elongation of the suspended rubber particles. The addition of small amounts of HIPS to PP-$CaCO_3$ increases spinnability in general, whereas larger amounts decrease spinnability.

INTRODUCTION

In some commercial melt spinning operations, fiber-forming materials consist of two or three components and/or contain an additive (or additives) in order to meet a specific desired property. For instance, in order to increase the elastic modulus of a fiber, one sometimes uses copolymers containing a rubbery component. Another example is the addition of titanium oxide pigment to impart luster to a nylon. At other times, one adds a plasticizer, an antioxidant, an antistatic agent, or a flame-retardant component. In all these cases, a foreign component added to a fiber-forming material may affect the spinning characteristics of the material as well as the physical/mechanical properties of the fiber formed. Therefore, it is of fundamental importance to investigate the elongational behavior and spinnability of fiber-forming materials which contain additives.

In a previous study,[1] we found some interesting rheological behavior in *two-phase* polymer systems in the process of fiber formation. We therefore undertook an investigation of the fiber formation process of *multiphase* polymer systems, namely, calcium carbonate-filled polypropylene blended with general-purpose polystyrene and calcium carbonate-filled polypropylene blended with high-impact polystyrene. Note that the former blend yields a three-phase system in which solid particles of $CaCO_3$ are dispersed in the polypropylene/polystyrene phase, and the latter blend yields a four-phase system in which both
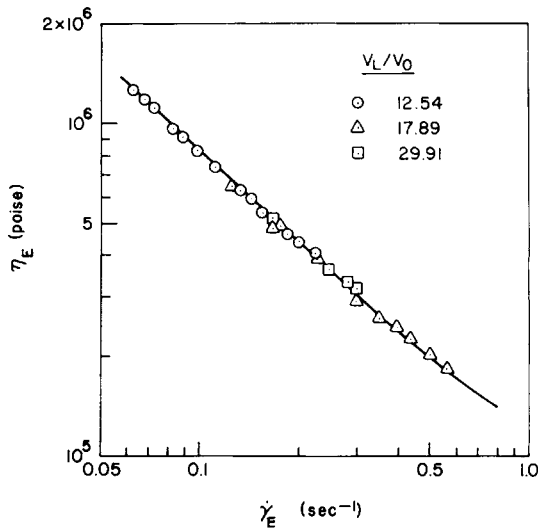
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Fig. 1. Apparent elongational viscosity vs. elongation rate for $CaCO_3$-filled polypropylene at 200°C.

$CaCO_3$ particles and deformable butadiene particles are dispersed in the polypropylene/polystyrene phase.

It should be mentioned that the choice of these materials for investigation was to better understand the role the suspended particles play in the elongational flow field from the rheological point of view. Whether or not fibers made of such polymeric materials are of practical use was not our primary concern. We hope, however, that any fundamental information obtained from this study will be useful for other materials of similar nature, which might be of some commercial importance.

Our primary interest in the present study, therefore, was to experimentally determine the apparent elongational viscosity of the multiphase polymer systems investigated. Photomicrographs of fiber samples helped us to interpret their rather complicated elongational flow behavior.
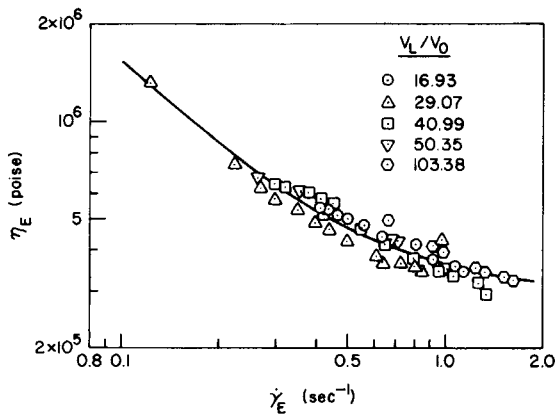

Fig. 2. Apparent elongational viscosity vs. elongation rate for polystyrene at 200°C.
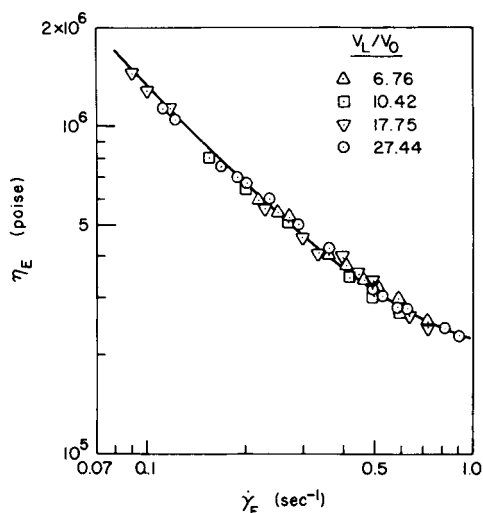
Fig. 3. Apparent elongational viscosity vs. elongation rate for the blend of PS/PP-CaCO$_3$ = 25/75 at 200°C.

EXPERIMENTAL

The spinning apparatus and experimental procedure used were as described in our earlier paper.[2] In the spinning experiment, measurements were taken of the fiber diameter by photographic techniques and of the fiber tension by use of Saxl tensiometer. Photographs of the fiber diameter were taken in an *iso-thermal* chamber through glass windows and, therefore, no cooling took place of the molten fibers inside the chamber. Spinning experiments were carried out at a melt temperature of 200°C.

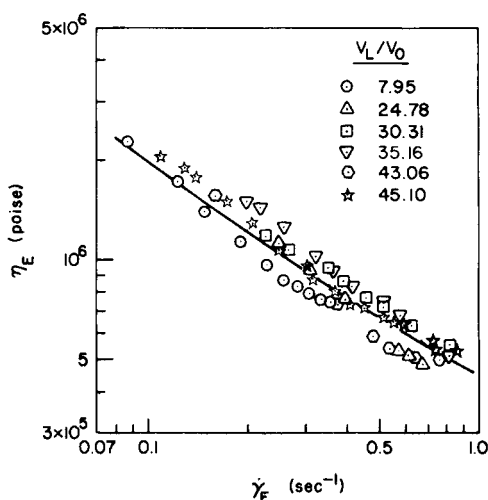The dimensions of the spinnerette hole used were: capillary length-to-di-

Fig. 4. Apparent elongational viscosity vs. elongation rate for the blend of PS/PP-CaCO$_3$ = 50/50 at 200°C.
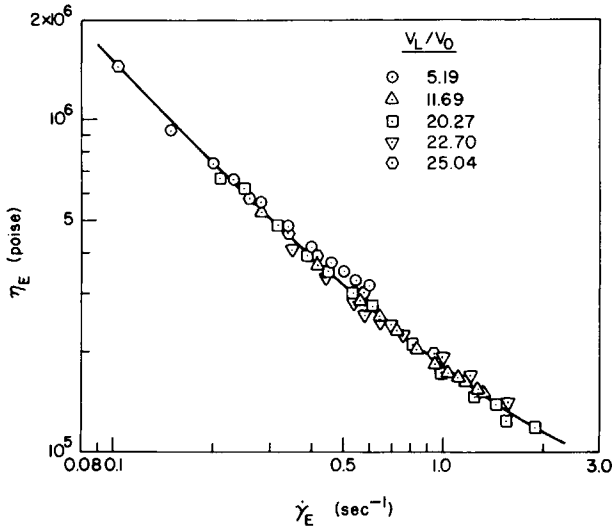
Fig. 5. Apparent elongational viscosity vs. elongation rate for the blend of PS/PP-CaCO$_3$ = 75/25 at 200°C.

ameter (L/D) ratio of 1 $(D = 1.0$ mm), reservoir-to-capillary diameter (D_R/D) ratio of 4, and entrance angle of 60 degrees.

The materials used for spinning were blends of calcium carbonate (CaCO$_3$)-filled polypropylene and a general-purpose polystyrene (PS) (Dow Chemical Co. Styron 686), and blends of calcium carbonate-filled polypropylene and a high-impact polystyrene (HIPS) (Union Carbide Corp. TGDB 2100). The high-impact polystyrene used in this study has about 24.5 wt % of rubbery component, and the viscometric rheological properties of this material in the molten state are reported in an earlier paper by Han.[3] The CaCO$_3$-filled poly-
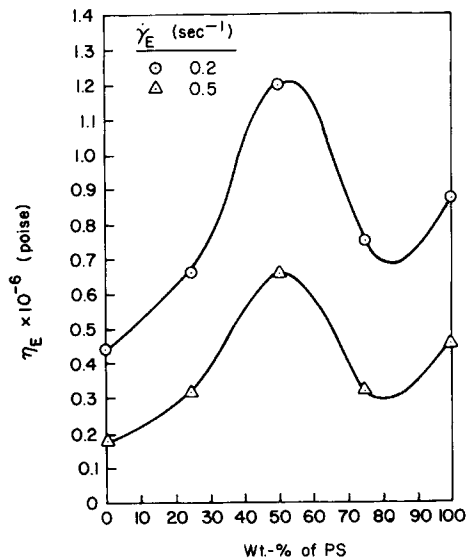

Fig. 6. Apparent elongational viscosity vs. blending ratio for PS/PP-CaCO$_3$ blends at 200°C.
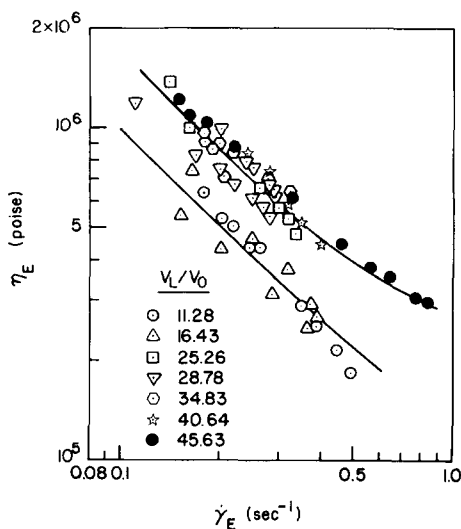
Fig. 7. Apparent elongational viscosity vs. elongation rate for the blend of HIPS/PP-CaCO$_3$ = 5/95 at 200°C.

propylene used has 10 wt % CaCO$_3$, and this material was prepared by the use of a twin-screw compounding machine. The viscometric rheological properties of this material are reported in an earlier paper by Han (4).

Blends were prepared by mixing together pellets of the two polymers in a tumbling device. Additional mixing took place when the blends in the molten state were forced to flow through a commercially available Static Mixer (Kenics Corp., Thermogenizer),[5] which was installed between the outlet of the extruder and the spinnerette. Table I gives blends of various blending ratios used in the experiment.
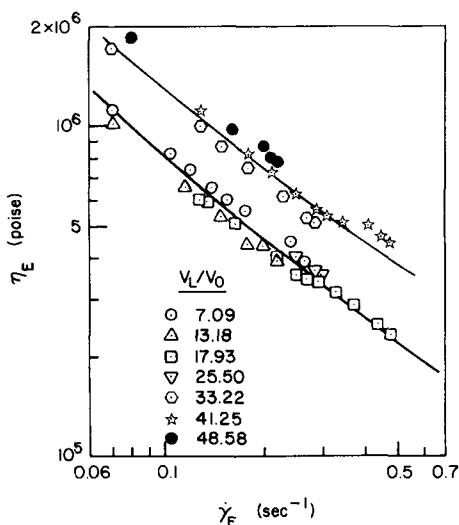

Fig. 8. Apparent elongational viscosity vs. elongation rate for the blend of HIPS/PP-CaCO$_3$ = 10/90 at 200°C.

TABLE I
Polymer Systems Investigated

Sample code	Material
a. 3-Phase-System	
PS	general purpose polystyrene
PP-$CaCO_3$	$CaCO_3$-filled polypropylene (10 wt % of $CaCO_3$)
PS/PP-$CaCO_3$ = 25/75	blend of 25 wt % of polystyrene with 75 wt % of $CaCO_3$-filled polypropylene
PS/PP-$CaCO_3$ = 50/50	blend of 50 wt % of polystyrene with 50 wt % of $CaCO_3$-filled polypropylene
PS/PP-$CaCO_3$ = 75/25	blend of 75 wt % of polystyrene with 25 wt % of $CaCO_3$-filled polypropylene
b. 4-Phase System	
HIPS	high-impact polystyrene (24.5 wt % of rubber)
PP-$CaCO_3$	$CaCO_3$-filled polypropylene (10 wt % $CaCO_3$)
HIPS/PP-$CaCO_3$ = 5/95	blend of 5 wt % of high-impact polystyrene with 95 wt % of $CaCO_3$-filled polypropylene
HIPS/PP-$CaCO_3$ = 10/90	blend of 10 wt % of high-impact polystyrene with 90 wt % of $CaCO_3$-filled polypropylene
HIPS/PP-$CaCO_3$ = 20/80	blend of 20 wt % of high-impact polystyrene with 80 wt % of $CaCO_3$-filled polypropylene

RESULTS AND DISCUSSION

Figures 1–5 give plots of apparent elongational viscosity versus elongation rate for the blends of PS/PP-$CaCO_3$. It is seen that, in all blends and homopolymers, apparent elongational viscosity decreases as the elongation rate is increased over the range of elongation rates tested. Note that the apparent elongational viscosity was determined by following the procedure described in an earlier paper by Han and Lamonte.[2] Of particular interest in Figures 1–5 is that, for a given
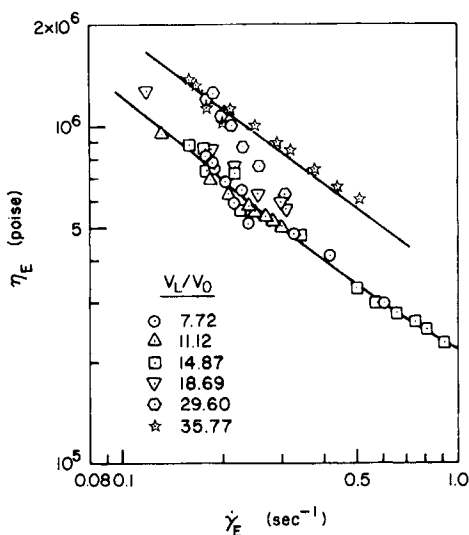

Fig. 9. Apparent elongational viscosity vs. elongation rate for the blend of HIPS/PP-$CaCO_3$ = 20/80 at 200°C.

material, different values of stretch ratio still give a uniform elongational curve.

In order to observe the effect of blending ratio on the elongational viscosity of the blend system, cross plots of Figures 1–5 are given in Figure 6. It is seen that *apparent* elongational viscosity goes through a maximum at a blending ratio of about 50 wt % of polystyrene (PS) and also goes through a minimum at a blending ratio of about 80 wt % of PS. An explanation for the observed elongational flow behavior of this blend system should seek for information of the microstructure of the melt-spun fibers.

At this point it is worth mentioning that the authors have earlier reported[1] shear viscosity behavior of polymer blends that exhibited both a maximum and a minimum in shear viscosity at certain blending ratios, quite similar to the elongational behavior shown in Figure 6. Such behavior was attributed to the quite different morphological states of the blends at different blending ratios.[1]

Figures 7–9 give plots of apparent elongational viscosity versus elongation rate for the blends of PP-CaCO₃/HIPS. It is seen that apparent elongational viscosity tends to increase as the stretch ratio is increased above a certain critical value. Although it is very difficult to experimentally determine such a critical stretch ratio, it appears to lie somewhere about 25.

The apparent existence of a transition from one set of elongational viscosities to another set may be attributable to a possible change in the structural formation of the fiber as the stretch ratio is increased from low to high values. This indeed appears to be the case, as we shall discuss below with the aid of photomicrographs of fiber samples.

Figure 10 shows that, at low elongation rates, the apparent elongational viscosity tends to go through a maximum and also a minimum as the weight percentage of HIPS is increased in the CaCO₃-filled PP/HIPS blend. However,

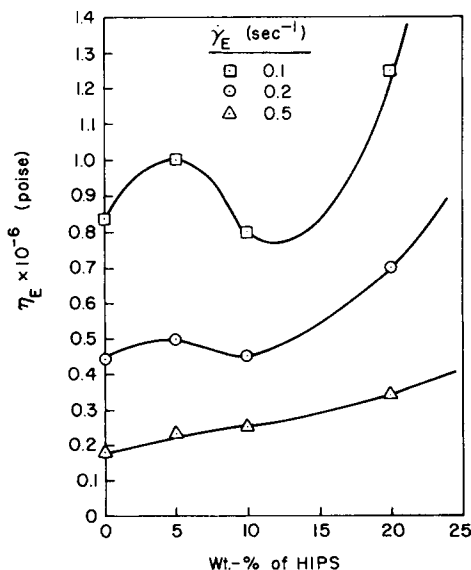

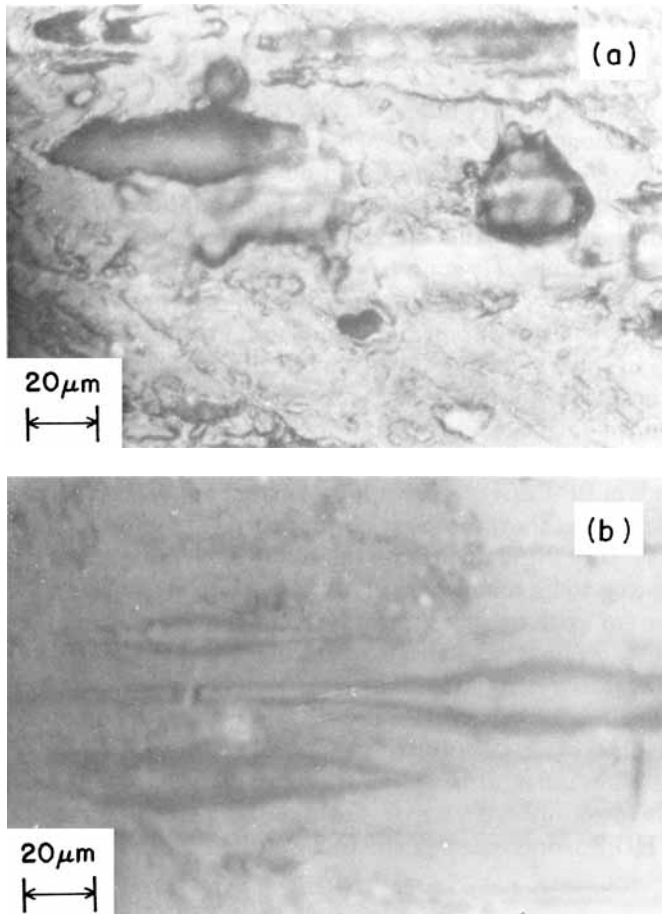Fig. 10. Apparent elongational viscosity vs. blending ratio for HIPS/PP/CaCO₃ blends at 200°C.

Fig. 11. Photomicrographs of fiber samples of the HIPS/PP-CaCO$_3$ = 5/95 blend: (a) V_L/V_0 = 11.3; (b) V_L/V_0 = 58.6.

as the elongation rate is increased, the elongational viscosity tends to increase monotonically with the amount of HIPS in the blend. This behavior is not surprising, since a change in the fiber structure may occur as the elongation rate is increased from low to high values.

Figure 11 gives representative photographs of the microstructure of fiber samples of the 5/95 blend of HIPS/PP-CaCO$_3$, at two different values of stretch ratio. Here, stretch ratio V_L/V_0 is defined by the ratio of the fiber velocity at the take-up device and the average velocity of the melt in the spinnerette hole. It is seen in Figure 11 that, as the stretch ratio is increased from 11.3 to 58.6, the rubber particles suspended in the continuous matrix get elongated along the direction of stretching. In other words, for a given system there ought to be a critical value of stretch ratio beyond which suspended rubber particles may start to elongate. Note that the rubber particles have viscosities much greater than the continuous polystyrene phase. Similar photomicrographs were obtained for other blends containing 10 wt % and 20 wt % of HIPS. Space limitations do not permit us to present many other similar photomicrographs.
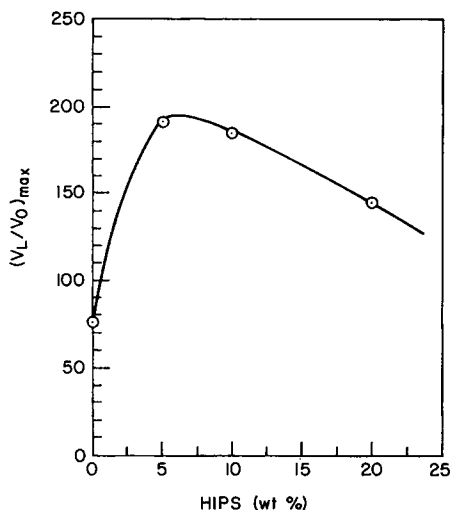
Fig. 12. Maximum stretch ratio vs. blending ratio for HIPS/PP-CaCO$_3$ blends at 200°C.

With the aid of photomicrographs, we are now able to explain the seemingly strange behavior of elongational viscosities given in Figures 7–9. The increase in elongational viscosity above a certain value of stretch ratio must be related to the stretchability of the suspended rubber particles. When rubber particles were barely elongated at low stretch ratios, the total tensile force exerted on the fiber might have been carried primarily by the continuous phase. However, when the rubber particles started to elongate at high stretch ratios, an additional force might have been required to stretch them, giving rise to greater values of elongational viscosity. Interestingly enough, the displacement of the elongational viscosity curve appears to occur at almost the same critical stretch ratio, independent of the amount of the rubbery component present in the blends (see Figs. 7–9).

Figure 12 gives a plot of maximum stretch ratio versus weight per cent of HIPS in the blend. Here, the maximum stretch ratio $(V_L/V_0)_{max}$ is the value of stretch ratio at which fibers start to break under tension. Although $(V_L/V_0)_{max}$ is not a rheological property that may be represented in terms of material functions, it may be considered as a convenient parameter for comparing the spinnability of one material with that of others. It is of interest to note in Figure 12 that the addition of a small amount of HIPS to PP-CaCO$_3$ increases spinnability in general and that, as the weight per cent of HIPS increases, spinnability is seen to decrease. The observed decrease in spinnability with the increase in the amount of HIPS may be attributable to the possible interference of the rubber particles with others stretching. Therefore, it appears that the rubber particles present in the fiber enhance the spinnability of the base polymer as long as they can deform under stretching without much hindrance from the presence of other particles. This observation may be of practical significance in the development of new fibers or in the modification of existing fibers.

References

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4. C. D. Han, *J. Appl. Polym. Sci.,* **18,** 821 (1974).
5. S. J. Chen and W. E. Segl, paper presented at 32nd ANTEC of SPE, San Francisco, May 13–16, 1974.