

Liquid Crystalline Polymer Blends With Stabilized Viscosity

K. H. WEI

*Institute of Materials and Engineering
National Chiao Tung University
Hsinchu, Taiwan 30049, ROC*

and

G. KISS

*Bell Communication Research
Morristown, New Jersey 07962*

The rheology of blends of thermotropic liquid crystalline copolyester co(hydroxybenzoate-isophthalate-hydroquinone) (HIQ) and polyetherimide were studied at different temperatures. As a result of the anisotropic-to-isotropic transition, the viscosity of the biphasic HIQ was found to be able to compensate that of the host polyetherimide at proper composition when the temperature increased or decreased in the capillary rheometer study. The 33% HIQ blend had almost stabilized viscosity between 350 and 370°C, whereas the 15% HIQ blend did not have stabilized viscosity. For the nonisothermal spiral molding trial, the 33% HIQ blend stabilized at a mean length of 21 inches (53 cm) with a standard deviation of 2.1 inch (5.3 cm) when the melt temperature increased by 30 Celsius degrees from 340 to 370°C.

INTRODUCTION

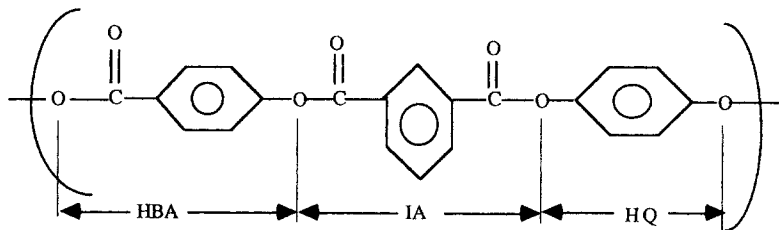
Liquid crystalline polymers (LCPs) have higher stiffness, higher use temperature, better chemical resistance, and lower melt viscosity than those of engineering plastics. From the materials' performance, as well as the processing point of view, the LCPs have high commercial application potential. Owing to the high monomer cost, LCPs have had limited success in the marketplace. In recent application research, blending LCPs with conventional plastics became the major focus. The motivation was to utilize their characteristics without incurring the high cost. Kiss (1) provided an overview of the blending of many commercial engineering plastics with liquid crystalline polymers. There are two major advantages of blending LCPs with engineering thermoplastics. First, the blend melt viscosity is reduced by the presence of an LCP dispersed phase. Second, in extension or shear flows, the LCP can be dispersed and oriented in the thermoplastics matrix to form a microfibrillar structure in solid state. These microfibers serve as reinforcement and increase the modulus of parts made of the LCP blends. A number of studies (2-4) have concentrated on elucidating the rheological, mechanical, and morphological properties of different liquid crystalline polymer blends.

Another unique property of LCPs was that some of the liquid crystalline polyesters could form biphasic melts, coexisting isotropic and anisotropic phases in melts. This is caused by their kink molecular structure such as non-para linkages introduced in para aromatic copolyesters along with their molecular weight. For example, Suto, White, and Fellers (5) studied thermotropic melts of hydroxypropyl cellulose. Simoff and Porter (6) worked on copolyester of bisphenol-E isophthalate. More completely, a series of aliphatic/aromatic polyesters was studied by Wissbrun and Griffin (7). Kiss (8) worked on the copolymer of hydroxybenzoic acid (HBA), isophthalic acid (IA), and hydroquinone (HQ). Their conclusion was that the fraction of isotropic vs. anisotropic would depend on the temperature of the melts, and they all have higher isotropic melt viscosity than the anisotropic melts. This paper is concerned with whether the viscosity increase caused by the anisotropic-to-isotropic phase change of the liquid crystalline polyester can be used to compensate for the viscosity decrease of the matrix polymer melts in LCP blends when the melt temperature increases.

MATERIALS

The material of interest here is HIQ copolyester. The chemical structure of the HIQ polymer is shown in Fig.

Fig. 1. The chemical structure of HIQ copolyester.



1. This copolymer has been found to be thermotropic when its composition contains more than 25% HBA. The minimum melting point for HIQ polymer, 305°C, is reached at 35% HBA. In order to overlap the processing temperature ranges between the HIQ polymer with engineering polymers, the HIQ polymer containing 35% HBA was chosen for this study. The other two copolyesters, used for comparative purposes, were Vectra A950 and B950. Vectra A950 is based on 73% HBA and 27% hydroxynaphthoic acid (HNA), which is shown in Fig. 2. Vectra B950 is a liquid crystalline poly(ester-co-amide), and its composition is unknown. All three LCPs were obtained from the Hoechst Celanese Corporation. Polyetherimide (trade name: Ultem 1000, General Electric) was used as a matrix material because of its high melting point, comparable to that of the HIQ35 copolyester.

EXPERIMENTAL

Capillary Viscosity Measurement

The melt viscosities of all polymers were measured with a capillary die 20 mm long and 1 mm in diameter in a Goettfert rheometer. The three LCPs, HIQ35, Vectra A950 and Vectra B950, and the Ultem 1000, were vacuum-dried at 120°C for 12 h before the measurement. Also, the blends containing 15% and 33%

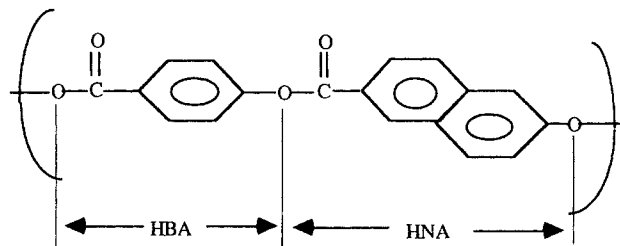


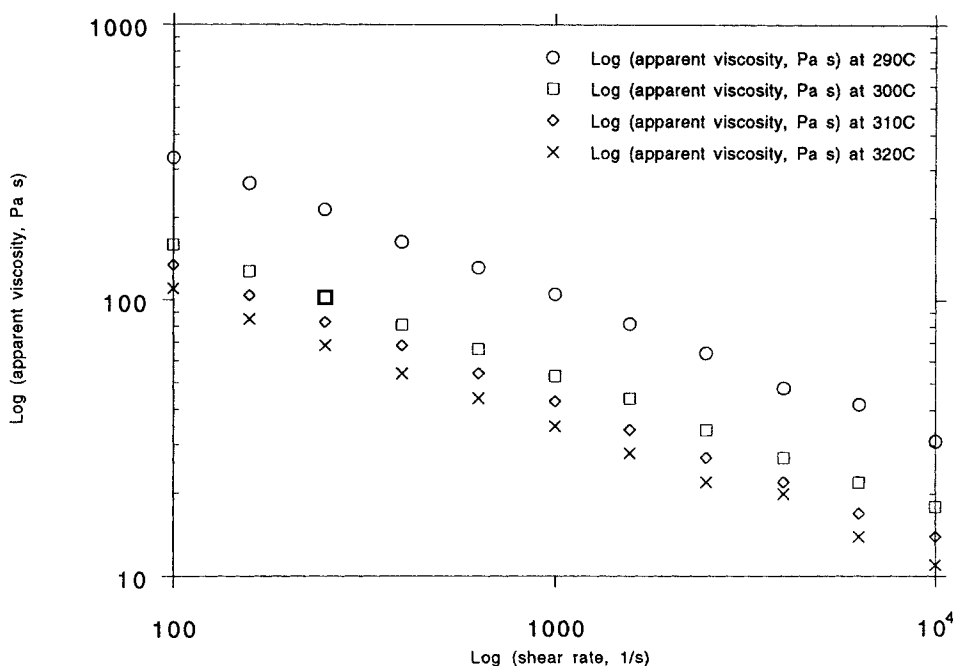
Fig. 2. The chemical structure of Vectra A950.

HIQ35 and the Ultem were prepared through melt mixing in a 60-mm Werner & Pfleiderer twin-screw extruder at a rate of 18 kg/h and 80 rpm.

Spiral Flow Molding

Spiral flow molding experiments were carried out with a spiral mold 66 inches (168 cm) long and a cross section of half circular shape $\frac{5}{16}$ inches (0.8 cm) in diameter. Two sets of spiral molding experiments were carried out. During the first spiral flow experiment, the mold temperature was kept at 140°C and the injection pressure was kept at 19,000 psi (1300 atm). The hold pressure was zero. Three melt temperatures, 340, 350, and 360°C, were chosen for the molding

Fig. 3. The apparent viscosity of Vectra A950 at different temperatures measured with capillary rheometry.



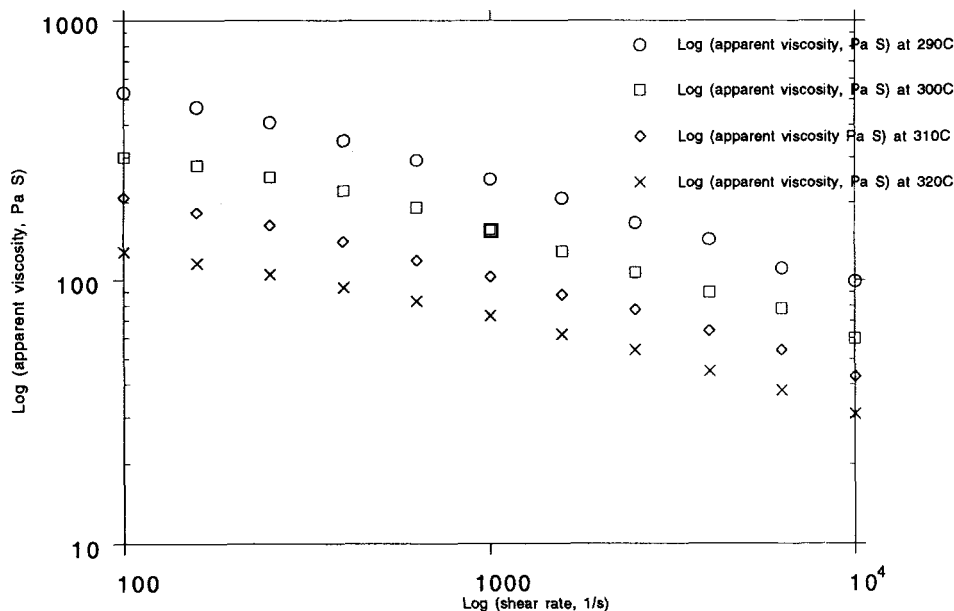


Fig. 4. The apparent viscosity of Vectra B950 at different temperatures.

experiment. The cycle time for the molding was 20 s. The other spiral molding experiment was done by fixing the mold temperature and the injection pressure at 149°C and at 12,000 psi (816 atm), respectively. In the beginning, the melt temperature was kept at 340°C. The cycle time was 17 s. After the molding reached a steady state, a step change of the melt temperature, from 340 to 370°C, was introduced to see the fluctuation of the spiral length that resulted from this temperature variation. The mold was heated with a Mokon oil heater, and the injection molding machine was a 60-ton Van Dorn press.

Scanning Electron Microscopy (SEM)

The SEM study was carried out with a Hitachi model S-2500 microscope. The spirals made of the LCP blends were fractured under liquid nitrogen and at room temperature and sputter coated with a 10-nm-thick layer of gold for the conducting path. Both the center and the edge of the spirals were observed at different magnifications.

RESULTS AND DISCUSSION

The apparent viscosities of Vectra A950, Vectra B950, and HIQ35 are shown in Figs. 3, 4, and 5.

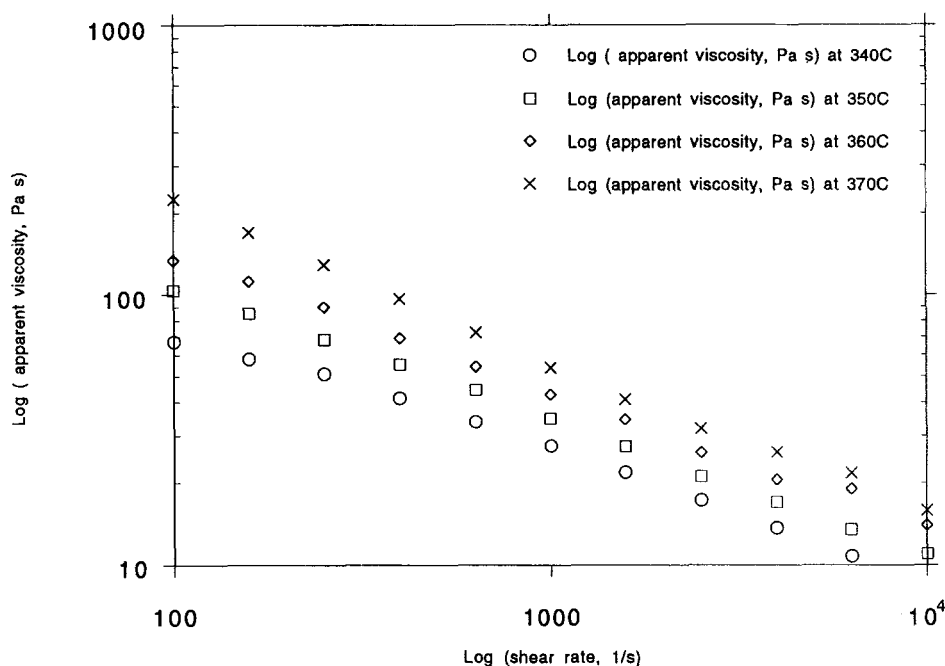
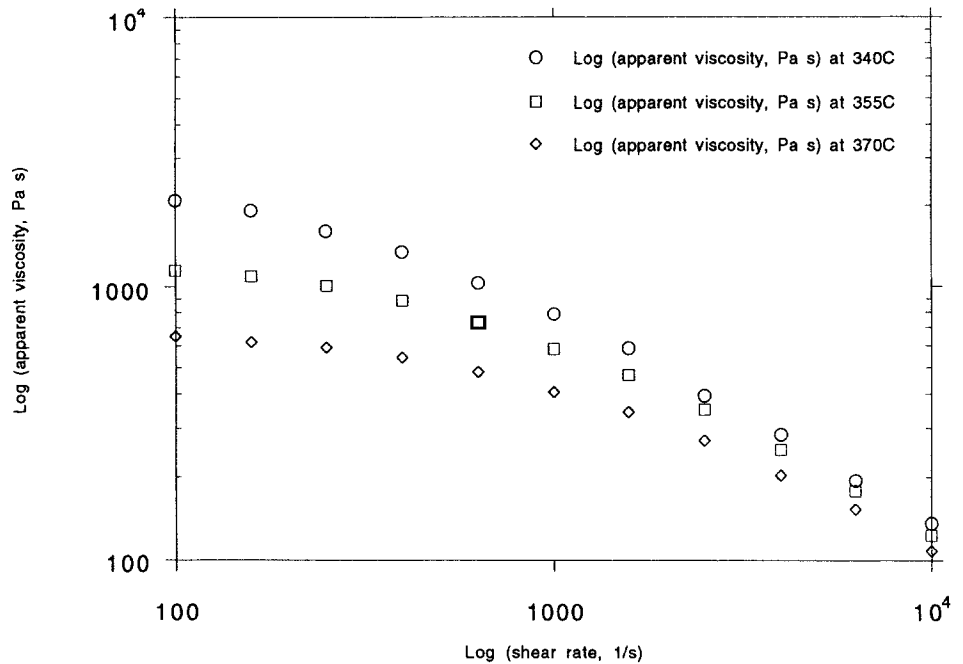


Fig. 5. The apparent viscosity of HIQ35 at different temperatures.

Fig. 6. The apparent viscosity of Ultem 1000 at different temperatures.



respectively. The viscosity of Vectra A950 decreases with increasing temperature from 290 to 320°C, and is dependent on the apparent shear rate to the power of -0.48 , as shown in Fig. 4. This is quite consistent with the behavior of thermotropic polymers. One noticeable point was that the Vectra A950 viscosity changed much less between 310 and 320°C than that between 290 and 300°C. For Vectra B950, the viscosity is less dependent on the shear rate at the low shear rate, similar to that of the Ultem shown in Fig. 6. As in Fig. 5, the viscosity of HIQ35 increased with temperature from 340 to 370°C, showing a positive viscosity-temperature coefficient, as described in Kiss's work (7).

The HIQ35 viscosity is dependent on the apparent shear rate to the power of -0.47 , similar to that of the Vectra A950. The viscosity of Ultem 1000 is about one order of magnitude higher than that of the three LCPs discussed above. The viscosities of the 15% and 33% HIQ35/Ultem blends are shown in Figs. 7 and 8. Adding 15% or 33% HIQ35 to Ultem reduced the viscosity of the blend to one-half that of the neat Ultem. The maximum viscosity for the 15% HIQ/Ultem blend was at the lowest temperature, 350°C. This trend is in line with the behavior of the thermoplastic materials. For the 33% HIQ/Ultem, the maximum viscosity was at 360°C. The viscosity of 33% HIQ35/Ultem was af-

Fig. 7. The apparent viscosity of (15/85) HIQ/Ultem 1000 polymer blend.

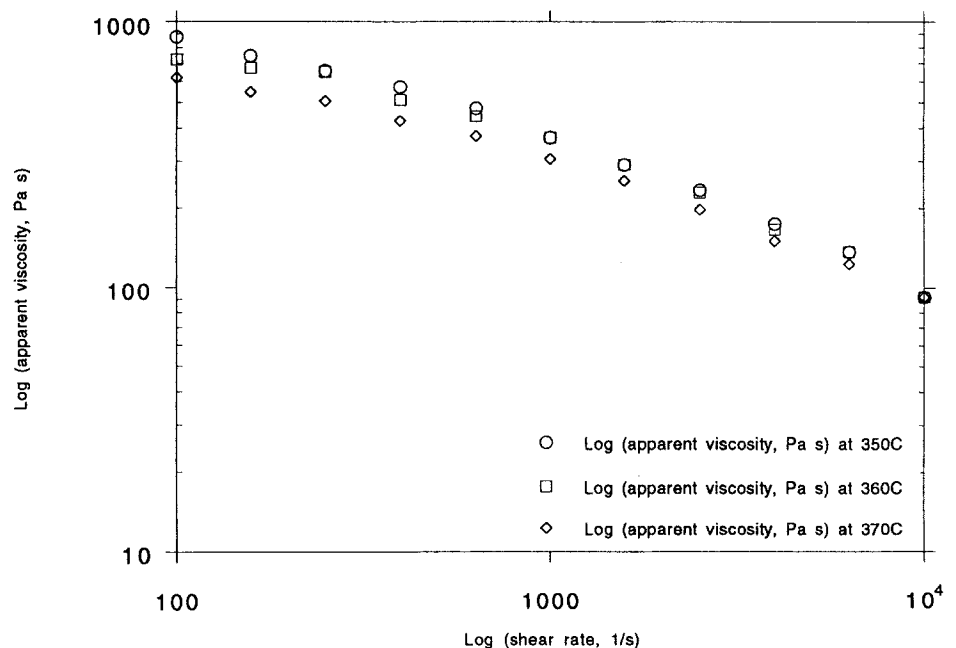
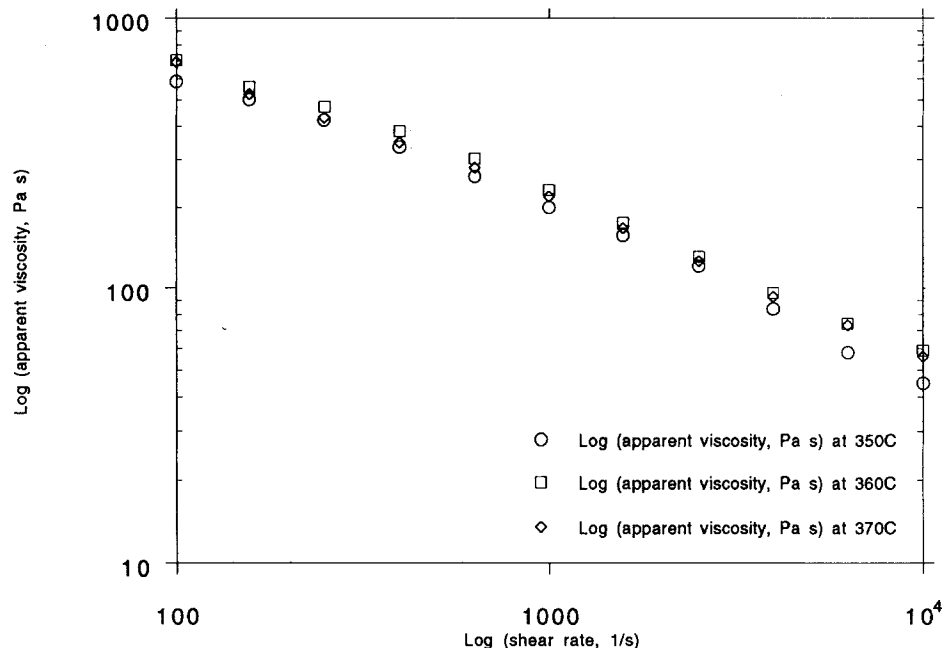


Fig. 8. The apparent viscosity of (33/67) HIQ/Utem 1000 polymer blend.



affected much less by the temperature than the 15% HIQ35 between 350 and 370°C. An apparent viscosity-temperature plot is presented in Fig. 9. The absolute values of the slopes for various blends indicate the extent of the temperature dependence. The 33% HIQ/Utem has an absolute slope of 5.2, compared with 12.95 for 15% HIQ/Utem and 48.133 for neat Utem. Therefore, this strongly suggests that the viscosity compensation effect resulting from adding the biphasic HIQ to the Utem has been obtained in the thermally steady-state experiment for the 33% HIQ/Utem blend.

Further study on the HIQ's viscosity compensation effect was carried out in the spiral molding experi-

ments, which were designed to mimic the flow length in the injection molding. The spiral lengths made of the three LCP blends at different temperatures are listed in Table 1. The spiral length data indicate that 15% HIQ35/Utem blend has some effect in stabilizing the spiral length between 340 and 350°C, but not at higher temperatures. That the spiral lengths of the 10% Vectra A950/Utem and 10% Vectra B950/Utem are larger than that of the 15% HIQ/Utem can be explained by the effect of the viscosity difference of the three LCPs at 340, 350, and 360°C.

The result of the second spiral experiment is presented in Table 2. In Table 2, the shot number 0

Fig. 9. The effect of the temperature on the viscosity of blends measured in capillary rheometry.

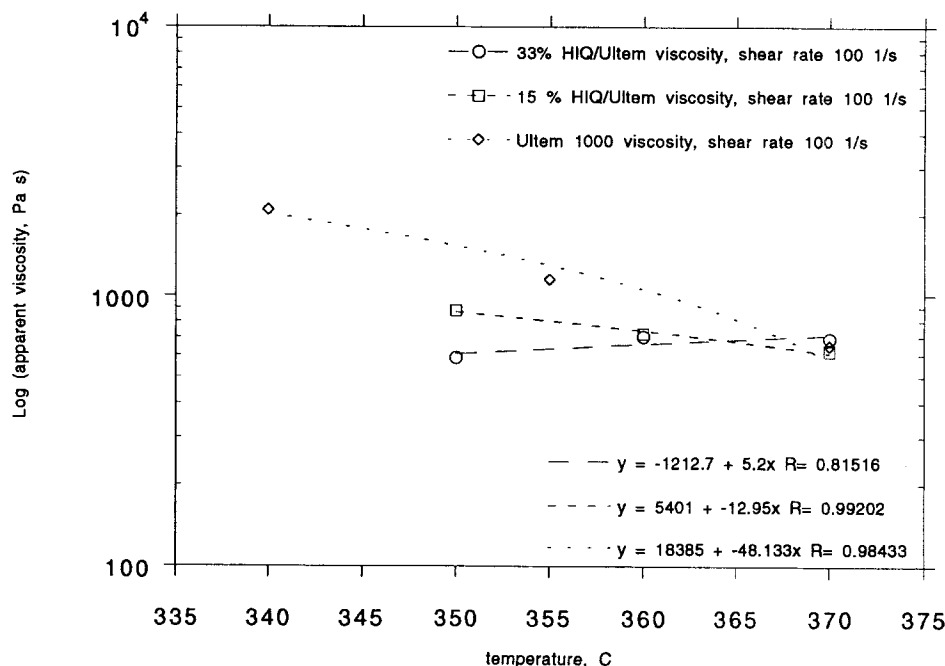


Table 1. The Spiral Length Made of the Vectra and the HIQ35 LCP Blends.

	Spiral Length in Inches		
	340°C	350°C	363°C
Uitem 1000	9.5	10.5	13.0
Vectra A950/Uitem 1000 (10/90)	14.5	15.5	18.5
Vectra B950/Uitem 1000 (10/90)	22.0	23.5	25
HIQ 35/Uitem 1000 (15/85)	11.3	11.5	14

indicates that the setting for the melt temperature was changed to 370°C after this particular shot. Negative shot numbers represent the stabilized spiral length maintained prior to the temperature change. On the twentieth shot, the temperature controller on the injection molding machine indicated that the melt-temperature set-point had been reached. The change in the spiral length for Uitem and 33% HIQ/Uitem blends are 4.7 and 3.6 inches (12 and 9 cm), respectively. The percentage change differed greatly for these two cases. In *Fig. 10*, the percentage change was plotted against the shot number. The increase in the spiral length for the 33% HIQ/Uitem case was about 20%, whereas the increase in the spiral length for the neat Uitem was about 75% when the melt temperature increased by 30°C. The increase in the spiral length for the 15% HIQ/Uitem case was about 70%. The mean spiral lengths for Uitem, 15% HIQ/Uitem and 33% HIQ/Uitem were 8.7, 13, and 20.1 inches (22, 33, and 51 cm), respectively, whereas the standard deviations for the three cases were 2.9, 7.6, and 2.1, respectively. Therefore, the 15% HIQ in the blend was not effective in stabilizing the spiral lengths when the temperature increased by 30°C, and the viscosity compensation effect was verified in the spiral experiment for the 33% HIQ/Uitem case.

The spirals made of the HIQ35/Uitem blend were fractured in liquid nitrogen. The fracture surfaces near the center of the cross section area of the spirals showed that they were porous, and two distinctive phases existed, as shown in *Fig. 11*. Near the edge of the cross section area of the spiral, there were fibrillar structures appearing, as shown in *Fig. 12*. Therefore, these two polymers, HIQ35 and Uitem 1000, were not miscible, and inhomogeneous morphology such as skin and core structure appeared in the spirals.

The difference between the slight viscosity increase with the temperature during the capillary measurement as in *Fig. 9* and the increase in the spiral length of the 33% HIQ blend with temperature as in *Table 2* can be explained by the fact that these are two different types of flows. The spiral molding took place in a nonisothermal environment. The molten melts encountered a mold temperature of 140°C. The fountain flow effect in spiral flow also resulted in a skin of liquid crystalline polymers, as evidenced by the fractured surface of the spiral in *Fig. 12*. The shear rate in the spiral molding was about $10,000 \text{ s}^{-1}$, whereas the shear rate in the capillary flow was about 1000 s^{-1} . At high shear rates, the difference in viscosity caused by

Table 2. The Spiral Lengths of the Neat Uitem 1000 and HIQ35 Blends at Mold Temperature 300°F and injection pressure 12,000 psi, melt temperature 340°C and Cycle Time 17 s.

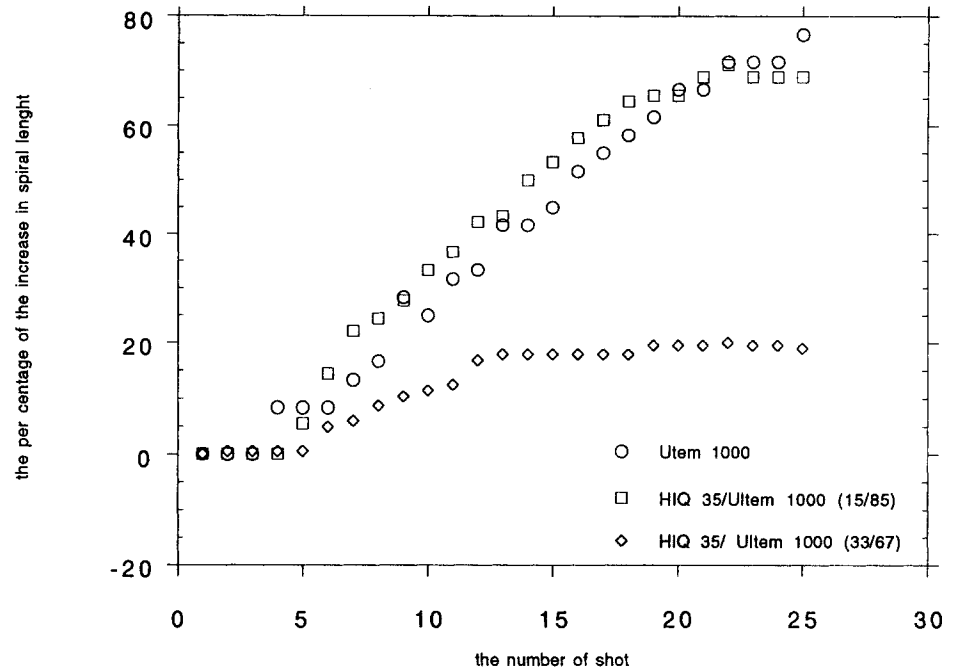
Spiral Length (Inches)			
Shot Number	Uitem 1000	15% HIQ	33% HIQ
-6	6.0	9.0	18.3
-5	6.0	9.0	18.3
-4	6.0	9.0	18.3
-3	6.0	9.0	18.3
-2	6.0	9.0	18.3
-1	6.0	9.0	18.3
0	6.0	9.0	18.3
melt temperature changed to 370°C			
1	6.0	9.0	18.4
2	6.0	9.0	18.5
3	6.0	9.0	18.5
4	6.5	9.0	18.5
5	6.5	9.5	18.5
6	6.5	11.0	19.5
7	6.8	11	19.5
8	7.0	11.2	20.0
9	7.7	11.5	20.3
10	7.5	12.0	20.5
11	7.9	12.3	20.7
12	8.0	12.8	21.5
13	8.5	12.9	21.7
14	8.5	13.5	21.7
15	8.7	13.8	21.7
16	9.1	14.2	21.7
17	9.3	14.5	21.7
18	9.5	14.8	21.7
19	9.7	14.0	22.0
20	10.0	14.9	22.0
21	10.0	15.2	22.0
22	10.3	15.4	22.1
23	10.3	15.2	22.0
24	10.3	15.2	22.0
25	10.6	15.2	21.9
26	10.6	15.4	22.0
27	10.6	15.2	22.0
28	10.6	15.2	22.0
29	10.6	15.4	21.9
30	10.7	15.2	21.9

the temperature difference became smaller, as shown in *Fig. 5*. A combination of the above three possible causes resulted in the slight difference in the data in *Fig. 9* and *Table 2*.

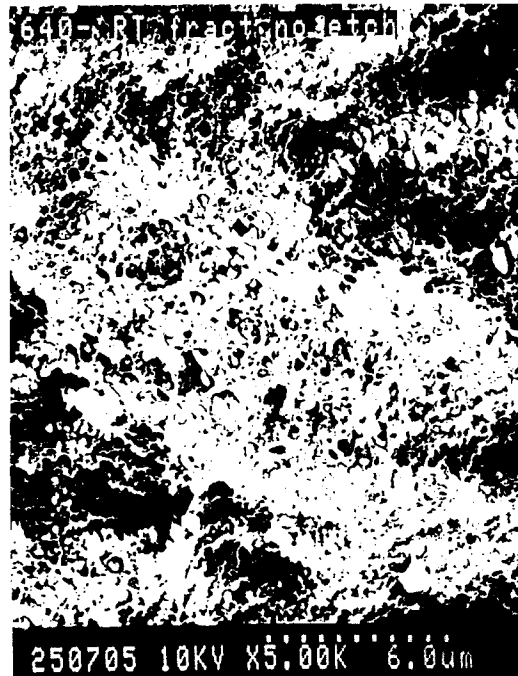
CONCLUSION

Adding the LCPs Vectra A950, Vectra B950, and HIQ35 to the thermoplastic Uitem reduced the viscosity of the host thermoplastic to different extents. Additionally, the unique anisotropic-to-isotropic phase transition of the biphasic HIQ resulting in an increase of the viscosity when the temperature increases can effectively stabilize the viscosity of the blends. The adding of the proper weight fraction of the HIQ LCP compensates for the change of the viscosity of the host thermoplastic when the temperature changes in the proper range. In this study, adding 33% HIQ to Uitem provided a blend that was within 15% of stabilized viscosity at low shear rates in the capillary die exper-

Fig. 10. The percentage increase of the spiral length when the melt temperature changed from 340°C to 370°C.



(a)



(b)

Fig. 11. The SEM micrographs of the fractured surface near the center of the spiral a) at 500 magnification; b) at 5000 magnification.

iment (similar to industrial extrusion) when the processing temperature is between 350 and 370°C. For the nonisothermal spiral molding experiment, the spiral length made of the same 33% HIQ blend increased only 20% when the melt temperature increased by 30°C from 340 to 370°C. The mean spiral length for the 33% HIQ blend in the above temperature range was 21 inches (53 cm), with a standard deviation of 2.1 inches (5.3 cm).

Therefore, the viscosity compensation effect of HIQ also worked in the nonisothermal case. The HIQ and the Ultem appeared to be immiscible in the spirals.

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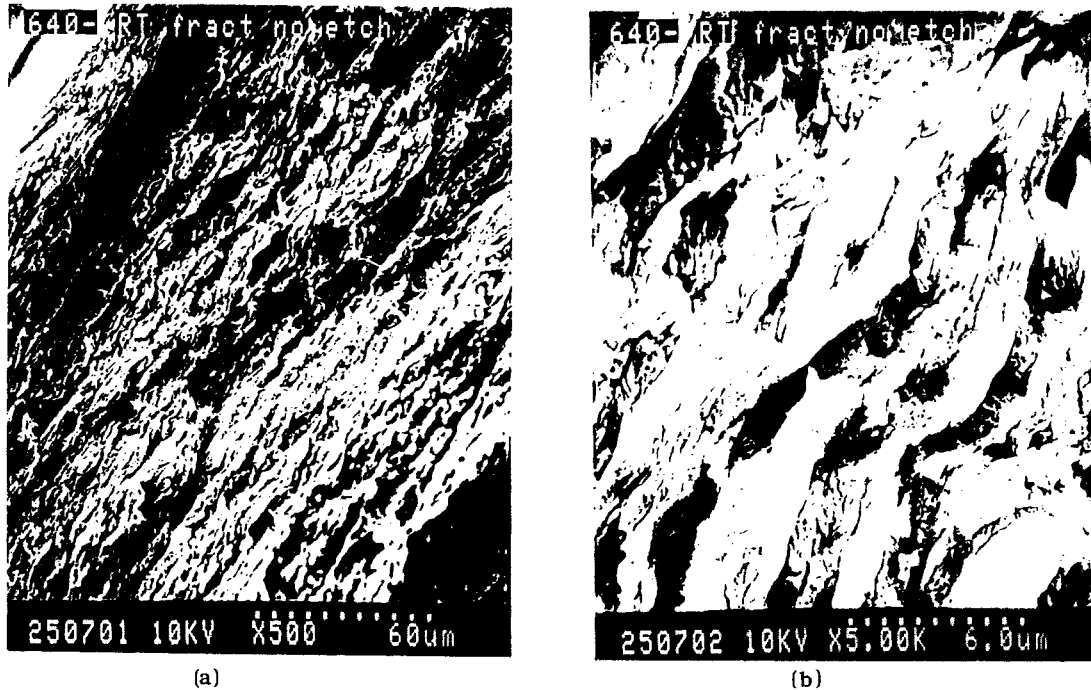


Fig. 12. The SEM micrographs of the fractured surface near the edge of the spiral a) at 500 magnification; b) at 5000 magnification.

REFERENCES

1. G. Kiss, *Polym. Eng. Sci.* **27**, 410 (1987).
2. K. G. Blizard and D. G. Baird, *Polym. Eng. Sci.*, **27**, 653 (1987).
3. A. Kohli, N. Chung, and R. A. Weiss, *Polym. Eng. Sci.*, **29**, 573 (1989).
4. A. Mehta and A. I. Isayev, *Polym. Eng. Sci.*, **31**, 963 (1991).
5. S. Suto, J. L. White, and J. F. Fellers, *Rheol. Acta*, **21**, 62 (1982).
6. D. A. Simoff and R. S. Porter, *Mol. Cry. Liq. Crys.*, **110**, 1 (1984).
7. K. F. Wissbrun and A. C. Griffin, *J. Polym. Sci. Phys.*, **20**, 1835 (1982).
8. G. Kiss, *J. Rheol.*, **30**, 585 (1986).