

# Effect of Interfacial Interaction on Rheological Behavior of Blends of a Semiflexible Liquid-Crystalline Polyester and Polycarbonate

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**ABSTRACT:** A liquid-crystalline polyester based on hydroxybenzoic acid, hydroquinone, sebacic acid, and suberic acid (named as BQSESU) was melt blended with polycarbonate (PC) at the BQSESU concentration of 2 wt %. It was found that the extent of viscosity reduction induced by the addition of BQSESU depends on the compounding temperature and the relation between them is not monotonic. The lowest viscosity was achieved by blending at 280°C. GPC measurements indicate that molecular weight reduction induced by the compounding is not a major contributor to the viscosity reduction. SEM study shows that when compounded at 280°C the blend is partially miscible with particle size at the submicron level. At the same time a large  $T_g$

depression was observed, which indicates strong interactions between the flexible segments of BQSESU and PC in the interfacial regions. The lowest viscosity achieved by blending at 280°C is thus proposed as an interfacial phenomenon. When compounded at 265°C, BQSESU particle size is larger, which gives a small interfacial area and hence less viscosity reduction. When compounded at 300°C a nearly miscible morphology was achieved, which also leads to less viscosity reduction. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3051–3058, 2003

**Key words:** liquid-crystalline polymers (LCP); blends; viscosity; miscibility; interfaces

## INTRODUCTION

Blends of thermotropic liquid-crystalline polymers (TLCPs) and conventional thermoplastics have been intensively studied in the past two decades. It was found that an addition of a TLCP into an isotropic polymer at a very low TLCP concentration may lead to a drastic reduction in viscosity under some circumstances.<sup>1–3</sup> For most immiscible TLCP-containing blends, the large viscosity reduction was attributed to the deformation of TLCP domains under extensional flow<sup>4</sup> or to the interlayer slipping effect,<sup>5</sup> whereas Whitehouse et al.<sup>6</sup> proposed that flow-induced TLCP chain alignment may cause alignment and disentanglement of the matrix molecules and hence the viscosity reduction. Hsieh<sup>7</sup> suggested that the enhanced alignment and lubrication of TLCPs at the molecular level are responsible for the synergistic flow behavior and low viscosity of a miscible TLCP/polycarbonate blend. In all cases, the miscibility between the TLCP (i.e., a rodlike polymer) and the conventional thermoplastic (i.e., a coil-like polymer) was considered as an important factor affecting rheological behavior of the

blends, whereas the miscibility is determined by not only chemical functionality but also rigidity of the two polymers. It is thus interesting to see when a TLCP with a rod–coil type of chain structure is mixed with a flexible chain polymer how rheological behaviors of the blends would be affected by the miscibility of the blends.

Recently we designed and synthesized a series of polyesters based on 4-hydroxybenzoic acid (HBA), hydroquinone (HQ), sebacic acid (SEA), and suberic acid (SUA).<sup>8</sup> In this system SEA and SUA units are long flexible spacers, whereas HBA and HQ form rigid mesogens. The polyesters can thus be classified as rod–coil type of polymers with rods and coils of different lengths statistically distributed along the chains. Our early study has demonstrated that all the HBA/HQ/SEA/SUA polyesters in this series can exhibit nematic phase despite their containing a relatively high concentration of the flexible spacers.<sup>8</sup> A polyester in this series has fairly low melting temperature and very broad nematic phase range, which fits well to the processing temperature window of polycarbonate (PC). It was therefore used to blend with PC to act as a processing aid. This study describes the effect of miscibility between this rod–coil polymer and PC on rheological properties of the blends. Our study shows that the extent of the viscosity reduction induced by the addition of the HBA/HQ/SEA/SUA polyester is closely related to the miscibility of the system, al-

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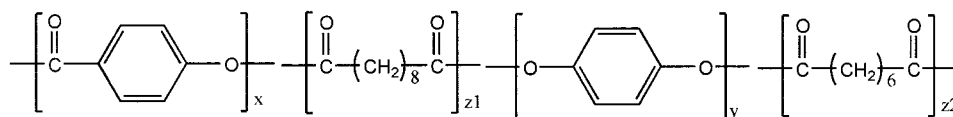


Figure 1 Chemical structures of the repeat units of BQSESU.

though the relation between them is not monotonic. The largest viscosity reduction is achieved when the blend is partially miscible with a large interfacial area.

## EXPERIMENTAL

The chemical structures of the repeat units of the HBA/HQ/SEA/SUA polyester, designated as BQSESU in this study, are shown in Figure 1. The nematic phase range and other important thermal properties of BQSESU are listed in Table I. The detailed synthesis and characterization methods were reported earlier.<sup>8</sup> Lexan 141R-111, an injection-molding grade polycarbonate, was supplied by GE Plastics (USA).

Before blending, BQSESU and PC were dry-mixed at the TLCP concentration of 2 wt % and vacuum dried at 80°C for 24 h. The mixture was then extruded using a Leistritz twin-screw extruder (L/D = 30) at the screw speed of 40 rpm. The temperature of the last metering zone was set at 265, 280, and 300°C, respectively, and the corresponding products were designated Blend-265, Blend-280, and Blend-300, respectively. Pure PC was also extruded at 300°C as a reference.

The melt viscosity of BQSESU was measured using a ThermoHaake (Bersdorff, Germany) parallel-plate rheometer with 2-cm-diameter plates. Steady-state tests were performed at 280°C and the shear rate was from 10 to 140 s<sup>-1</sup>. Rheological measurements of the blends were performed using a Gottfert Rheograph 6000 capillary rheometer with a round-hole die of aspect ratio of 10/1 and run angle of 180° in the shear rate range of 100 to 2500 s<sup>-1</sup>. The testing temperature was set at 260, 280, and 300°C, respectively, for all three blends and the pure PC. All tests were repeated twice and an average was taken. The apparent shear rate and shear viscosity were used in the plots without any corrections.

The molecular weight of the PC matrix of the blends was determined using an Agilent Series 1100 gel per-

meation chromatography (GPC) with tetrahydrofuran (THF) and dichloromethane (DCM) as eluant and polystyrene as standard at 35°C. The samples were all dissolved in a mixture of THF and DCM (THF/DCM = 80/20 vol %) and filtrated through a filter of 0.2 μm pore diameter before being injected into the GPC column.

The morphology of the extrudates collected during the compounding and the capillary rheometer tests was examined using a JEOL JSM-5310 (Peabody, MA) scanning electron microscope. The extrudates were manually fractured in liquid nitrogen. A thin layer of gold was sputtered on the fractured surface before the examination.

Blend samples collected from the capillary rheometer tests at the shear rate of 1000 s<sup>-1</sup> were cut into circular thin sections of about 10 μm, from which infra spectra were recorded using a Perkin-Elmer 2000 FTIR microscope (reflection mode; Perkin Elmer Cetus Instruments, Norwalk, CT) at both the center and the edge of the extrudates. The scanning range was 750–4000 cm<sup>-1</sup>, with resolution set at 2 cm<sup>-1</sup>.

A TA Instruments DSC 2920 (New Castle, DE) modulated differential scanning calorimeter (MDSC) was used to measure glass-transition temperatures ( $T_g$ 's) of the blends and the pure PC. All the samples were quickly heated to 300°C before being ramped to 80°C at a cooling rate of 5°C/min. The samples were then heated to 200°C again at a heating rate of 5°C/min. Blend-280 was also quickly heated to 310°C and kept at 310°C for 5 min. It was then ramped to 80°C and heated to 200°C at the rate of 5°C/min. The  $T_g$  values were determined from the reversible heat flow curves of the second heating runs. For all the samples,  $T_g$  measurements were repeated five times and an average was taken.

## RESULTS AND DISCUSSION

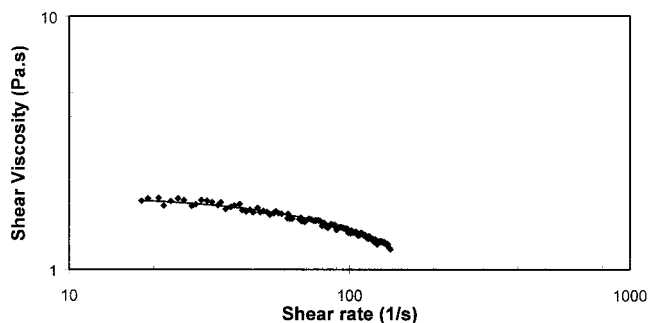
### Rheological behaviors of the TLCP and the blends

Shear viscosity of BQSESU as a function of shear rate at 280°C is shown in Figure 2. In the tested shear rate range the viscosity of BQSESU is very low, less than 2 Pa·s. This is an extremely low value even among TLCPs, which may be attributed to its semiflexible structure that leads to shear aligning and limits tumbling.<sup>9,10</sup>

Figure 3 shows the apparent viscosity of Blend-265 as a function of apparent shear rate in comparison

TABLE I  
Important Thermal Properties of BQSESU

Glass-transition temperature	55.5°C
Melting temperature	185°C
Temperature range for nematic dominant structure	220–310°C
Clearing temperature	>340°C
Degradation temperature (at 5% weight loss)	378°C



**Figure 2** Melt viscosity of BQSESU measured using a parallel-plate rheometer at 280°C.

with that of the pure PC at different testing temperatures. The curves show obvious viscosity reduction induced by the addition of the TLCP. At the low shear rate end, the viscosity ratio of Blend-265 to the pure PC ranges from 0.17 to 0.29 depending on the testing temperature, which means that viscosity reduction of 71 to 83% was achieved. At the high shear rate end, the viscosity reduction is about 36 to 63%. The larger viscosity reduction at lower shear rates can be partially attributed to the reduction of zero-shear viscosity of the blends caused by molecular weight reduction, which is discussed further in the next section.

At the same testing temperature and shear rate, there are significant differences in viscosity among the blends compounded at different temperatures. At high shear rates, the viscosity of Blend-280 is significantly lower than that of either Blend-265 or Blend-300. The trend is very pronounced at the testing temperature of 280°C, as shown in Figure 4. This indicates that the compounding temperature has a substantial

impact on the viscosity of the blends, although the relation between them is not monotonic.

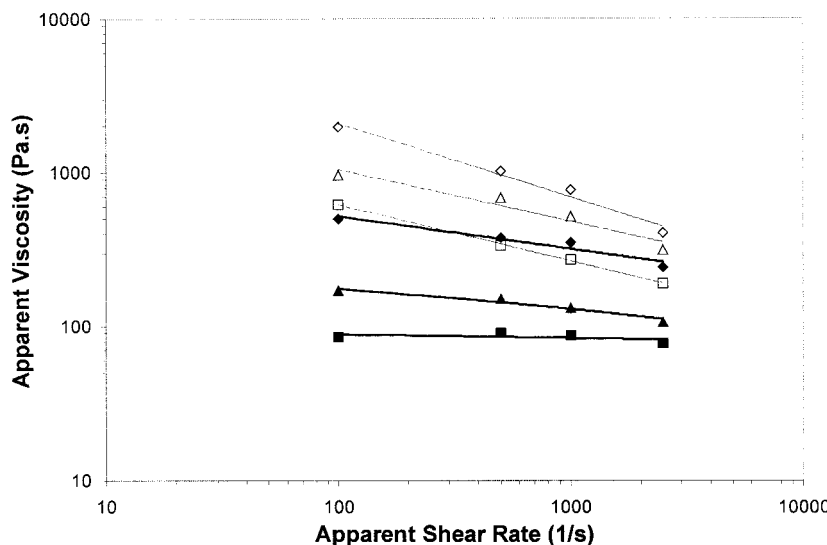
### Effect of molecular weight reduction on the viscosity reduction

The molecular weight measurement results are summarized in Table II. For all three blends, as well as the pure PC, there is a decrease in the molecular weight of PC after the compounding. The higher the compounding temperature, the lower the molecular weight. This phenomenon was also reported for other TLCP/PC blend systems.<sup>11</sup> The molecular weight reduction is attributed to thermal degradation of PC and the transesterification reaction between PC and BQSESU. Both reactions are more active at a higher temperature.

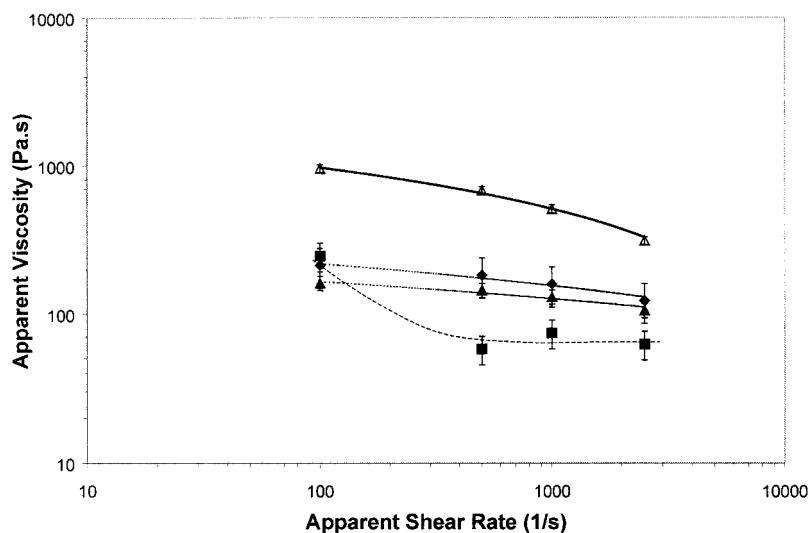
We can use the following equation to estimate the contribution of the molecular weight reduction to the viscosity reduction:

$$\eta_0 = KM_w^{3.4}$$

where  $\eta_0$  is the zero-shear viscosity,  $M_w$  is the weight-average molecular weight, and  $K$  is a constant. From Table II, we can see that the  $M_w$  of Blend-265 is 48,085, whereas the  $M_w$  of the extruded PC is 52,309. Purely because of this molecular weight difference, the reduction of zero-shear viscosity achieved by Blend-265 would be 25%, although from Figure 3 we can see that at the shear rate of 50 s<sup>-1</sup> and testing temperature of 260°C, the real viscosity reduction achieved by Blend-265 is about 71%. Similarly, from Figure 4 we can see that at the shear rate of 1000 s<sup>-1</sup> and testing temperature of 280°C, the viscosity ratio of Blend-280 to



**Figure 3** Apparent viscosity of Blend-265 and pure PC versus apparent shear rate measured using a capillary rheometer.  $\diamond$ ,  $\triangle$ , and  $\square$  represent the viscosity of pure PC measured at 260, 280, and 300°C, respectively;  $\blacklozenge$ ,  $\blacktriangle$ , and  $\blacksquare$  represent the viscosity of Blend-265 measured at 260, 280, and 300°C, respectively.



**Figure 4** Apparent viscosity of the blends and pure PC versus apparent shear rate measured using a capillary rheometer at 280°C.  $\Delta$  represents the viscosity of pure PC;  $\blacktriangle$ ,  $\blacksquare$ , and  $\blacklozenge$  represent the viscosity of Blend-265, Blend-280, and Blend-300, respectively.

Blend-265 is about 0.58. Although purely based on their molecular weight difference, the zero-shear viscosity ratio of Blend-280 to Blend-265 should be 0.70, and the viscosity ratio at 1000  $\text{s}^{-1}$  should certainly be much larger than 0.70. Furthermore, Blend-300 has the lowest molecular weight but the highest viscosity among the three blends. It is thus obvious that the effect of the compounding temperature on the viscosity reduction cannot be attributed to the different molecular weight obtained at different compounding temperatures.

Another argument is that the molecular weight of the PC matrix may decrease further during the capillary rheometer tests. To eliminate any doubt, Blend-300 samples were collected after the rheological tests at different temperatures and the molecular weight of the PC matrix of these samples was also measured. The results are also listed in Table II. The data show that when the capillary rheometer barrel temperatures

were set at 260 and 280°C, the molecular weight of the PC matrix would scarcely decrease during the tests.

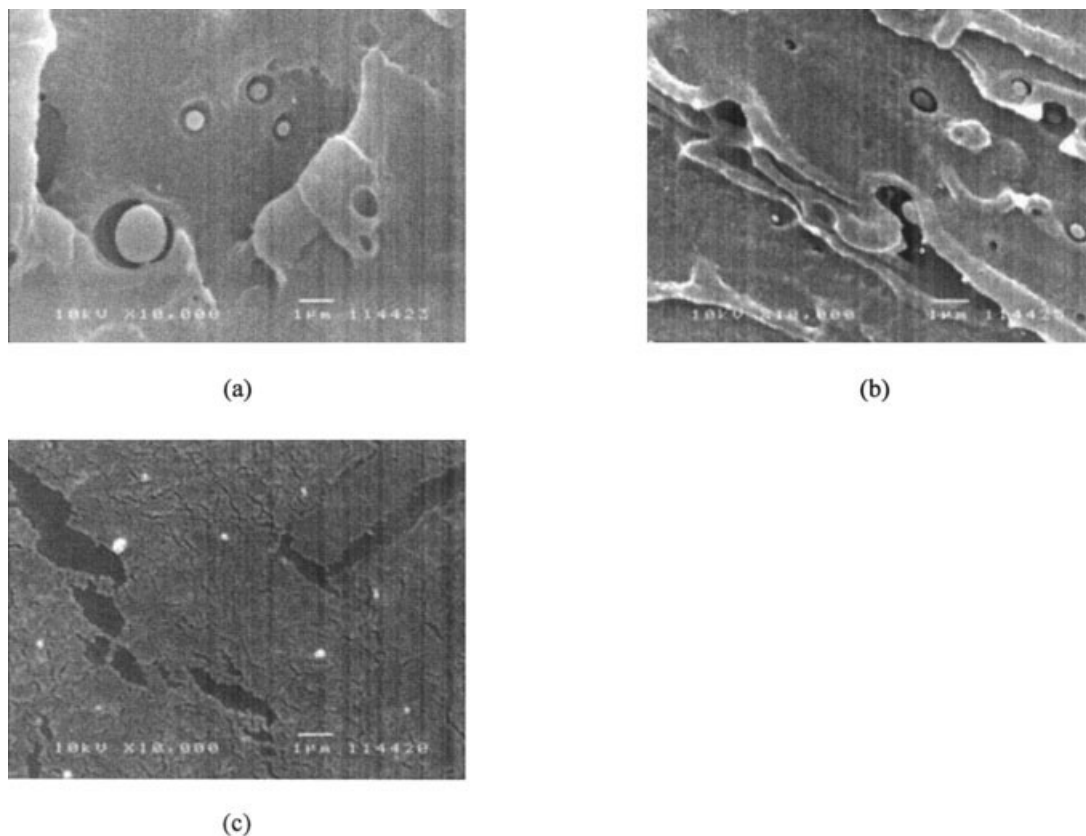
### Morphology of the blends

SEM micrographs of fractured surfaces of the blends are shown in Figure 5. For all three blends, phase separation was observed at this low TLCP concentration. The size of the dispersed TLCP particles decreases as the compounding temperature increases. For Blend-265, the particle size is about 1  $\mu\text{m}$  and the debonded particles and holes can be observed, as shown in Figure 5(a), which demonstrates the relatively poor miscibility between BQSESU and the PC matrix. For Blend-280, the particle size decreases to submicron level and there are many very small particles embedded in the matrix, as shown in Figure 5(b), which indicates a better miscibility than that in Blend-265. A nearly miscible morphology was obtained when compounded at 300°C, as seen in Figure 5(c). In this case both the particle size and population of the particles become very small, and the interface boundary is not very sharp. The SEM study indicates that the miscibility of the two components improves significantly as the compounding temperature increases. This may be closely related to the reduced rigidity of BQSESU at higher temperatures, especially at 300°C at which the nematic phase is very weak.

Figure 6 shows FTIR spectra of the three blends compared with those of PC and BQSESU. The band at around 1750  $\text{cm}^{-1}$  corresponds to the carbonate group, which is very sharp for PC but very broad for BQSESU because of its random structure. For the blends, as the compounding temperature increases the carbonate band broadens significantly, which indi-

**TABLE II**  
Molecular Weight Measurement Results

Material	$M_n$	$M_w$	$P$
Before rheological tests			
Pure PC (raw materials)	31,500	54,500	1.73
Pure PC (extruded at 300°C)	27,700	52,300	1.89
PC Matrix of Blend-265	27,900	48,100	1.73
PC Matrix of Blend-280	26,600	43,300	1.63
PC Matrix of Blend-300	24,100	44,000	1.83
After rheological tests			
PC Matrix of Blend-300 (tested at 260°C)	23,700	42,000	1.77
PC Matrix of Blend-300 (tested at 280°C)	22,900	42,100	1.84
PC Matrix of Blend-300 (tested at 300°C)	20,100	35,900	1.79



**Figure 5** SEM micrographs of fractured surfaces of (a) Blend-265, (b) Blend-280, and (c) Blend-300.

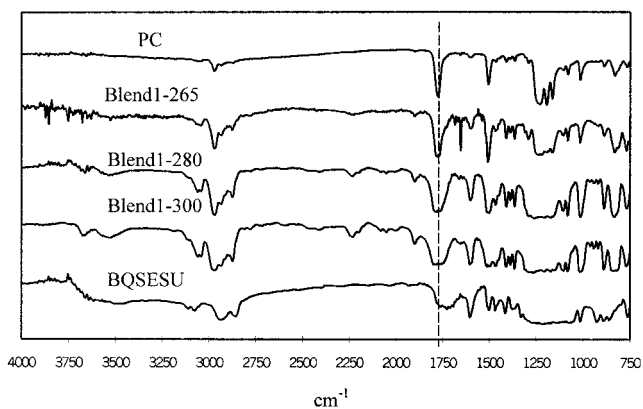
cates an increase in reaction between BQSESU and PC. The more vigorous transesterification at higher compounding temperatures is thus also responsible for the improved miscibility.

Figure 7 shows the morphology of Blend-265 after a capillary rheometer test. The sample was collected at the measuring temperature of 260°C and shear rate of 500 s<sup>-1</sup>. Compared to the blend before the capillary rheometer test, the particle shape obviously becomes irregular. It implies that the TLCP droplets might have been deformed into fibrils during the rheological test and after passing through the die they quickly relaxed

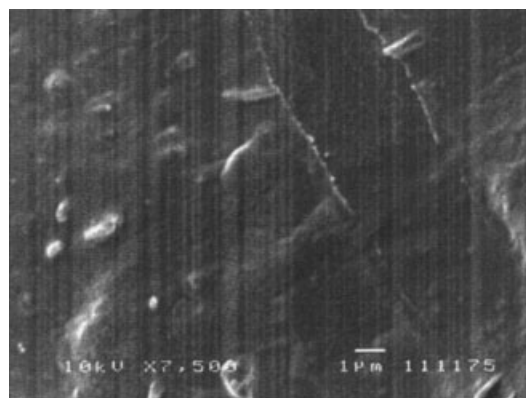
and coalesced into irregular-shape particles. This observation indicates that deformation of TLCP domains under extensional flow contributes to the viscosity reduction observed.

#### Miscibility of the blends

To evaluate the miscibility of the system,  $T_g$  values of the blends were measured using MDSC and the results are listed in Table III. For the pure PC,  $T_g$  does



**Figure 6** FTIR spectra of PC, BQSESU, and their blends.



**Figure 7** SEM micrographs of fractured surface of Blend-265 after rheological test at 260°C and apparent shear rate of 500 s<sup>-1</sup>.

TABLE III  
Glass-Transition Temperature ( $T_g$ ) of the Materials and  $T_g$  Depression of the Blends

Material	$T_g$ (°C)	$T_g$ depression <sup>a</sup> (°C)	$M_n$	$T_g$ depression due to molecular weight reduction <sup>b</sup> (°C)
PC (extruded at 300°C)	145.7 ± 0.8		27,727	
Blend-265	141.1 ± 1.2	4.6	27,852	-0.02
Blend-280	139.3 ± 1.4	6.4	26,585	0.16
Blend-300	145.4 ± 1.8	0.3	24,077	0.55
Blend-280 (annealed at 310°C)	145.6 ± 0.2	0.1		
LCP-SESU	55.5			

<sup>a</sup>  $T_g$  depression =  $T_g$  (PC) -  $T_g$  (blend).

<sup>b</sup>  $T_g$  depression due to molecular weight reduction =  $10^5 \times [1/M_n$  (blend) -  $1/M_n$  (PC)].

not have a noticeable change after the compounding, whereas compared to that of the pure PC all the blends show significant  $T_g$  depression and the extent of the  $T_g$  depression changes with the compounding temperature.

The following equation is often employed to represent the relationship between  $T_g$  and molecular weight:

$$T_g = T_g(\infty) - \frac{K}{M_n}$$

where  $T(\infty)$  is the  $T_g$  at infinite molecular weight,  $M_n$  is the number-average molecular weight, and  $K$  is a constant. Generally,  $K$  is in the scale of  $1-5 \times 10^5$ .<sup>12</sup>  $T_g$  depression caused by the molecular weight reduction

was estimated using this equation (assume  $K = 10^5$ ). The result is plotted in Figure 8 compared against the experimental values of  $T_g$  depression. It shows that the  $T_g$  depression resulting from the molecular weight reduction is relatively small compared to the experimental values. More important, the experimental  $T_g$  depression value reaches the maximum at 280°C, whereas the value attributed to molecular weight reduction increases slightly as the compounding temperature increases and reaches the maximum at 300°C. The molecular weight reduction is thus not the major reason for the  $T_g$  depression of the blends observed. The  $T_g$  depression can thus be attributed to partial miscibility between BQSESU and PC.

In terms of chemical functional groups, PC and BQSESU are fairly similar to each other. They can-

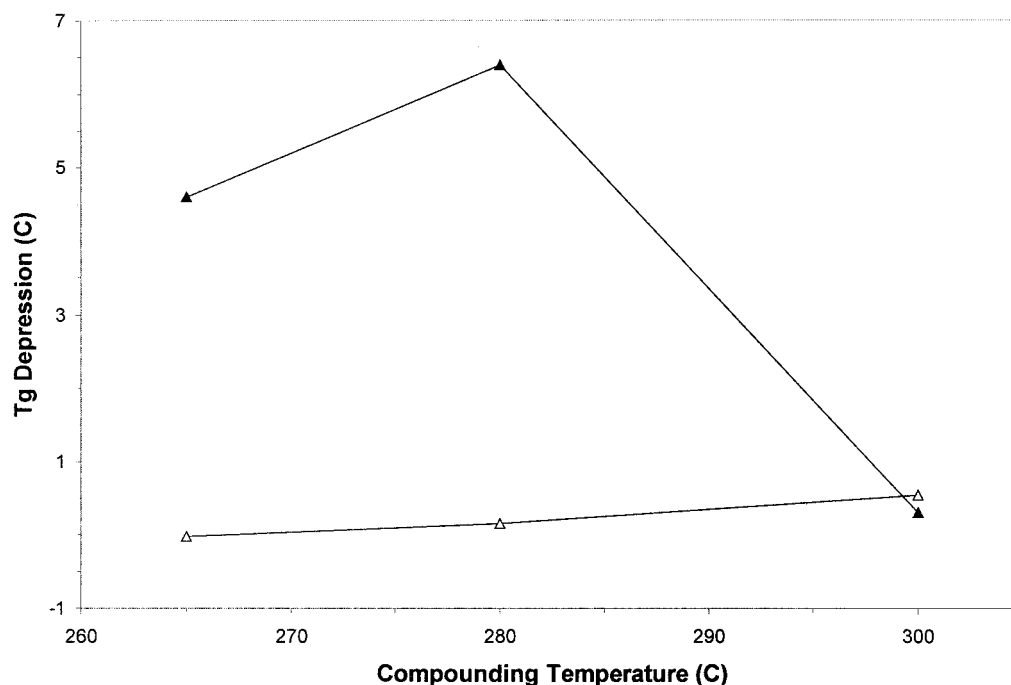
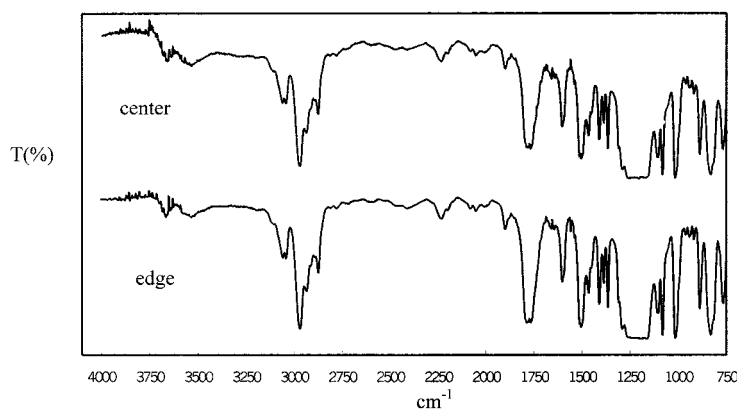


Figure 8  $T_g$  depression of the blends as a function of compounding temperature. ▲ represents the  $T_g$  depression obtained from DSC experiments; △ represents the  $T_g$  depression caused by the molecular weight reduction based on the calculation stated in the caption of Table III.



**Figure 9** FTIR spectra of Blend-265 at different locations of an extrudate collected after a capillary rheometer test at 280°C and 1000 s<sup>-1</sup>.

not be completely miscible mainly because of their very different chain rigidity. A plausible explanation for the nonlinear relation between the  $T_g$  depression and the compounding temperature is that, although phase separation occurs in Blend-265 and Blend-280, in the interfacial regions relatively flexible segments of BQSESU have strong interaction with PC chains. These flexible segments cause the interfacial regions to have a very low  $T_g$ . Because BQSESU particle sizes are very small, the interfacial area could be considerably large, especially in Blend-280. The interfacial regions thus make a large contribution to the  $T_g$  depression. In Blend-300, BQSESU is mixed with PC nearly at the molecular level, such that  $T_g$  becomes higher as a consequence of the contribution of the rigid segments. Similar behavior was also reported for other PC/TLCP blends.<sup>13</sup>

Blend-280 was also kept in an MDSC cell at 310°C for 5 min, which is closer to the clearing temperature of BQSESU, to achieve molecular-level miscibility. After the annealing, the  $T_g$  of the blend was indeed increased to the value close to that of Blend-300, as shown in Table III, which gives strong evidentiary support to our explanation above.

### Proposed mechanisms

The compounding causes a decrease in molecular weight, which is partially responsible for the viscosity reduction of the blends, mainly at the low shear rate end, although it cannot explain the effect of the compounding temperature on the viscosity reduction.

Figure 9 shows FTIR spectra of Blend-280 collected after a capillary rheometer test at 260°C and 1000 s<sup>-1</sup>. Across the diameter of the extrudate, the shape of the carbonate band remains unchanged from the center to the edge, which implies that BQSESU has no tendency to migrate to the surface so that the external lubrication effect can be ruled out.

Because the trend for  $T_g$  depression coincides well with the trend for viscosity reduction of the blends (i.e., both achieved the maximum at the compounding temperature of 280°C), here we try to correlate the rheological difference among the three blends to their differences in miscibility.

The effect of the compounding temperature on viscosity reduction is likely to be an interfacial phenomenon. When compounded at 265°C, the flexible segments of BQSESU are able to interact with the PC chains forming an interface. Transesterification also occurs in the interfacial regions. Under extensional flow at the die entrance, the TLCP droplets are deformed and aligned along the flow direction. This may induce disentanglement of PC chains in the interfacial regions. Because of the very low viscosity of the TLCP it may also act as an internal lubricant to induce interlayer slipping of PC. The viscosity reduction effect can be enhanced when the compounding temperature is increased from 265 to 280°C, which is attributed to the large increase in interfacial area caused by the much smaller particle size. When compounded at 300°C the miscibility of the two phases has reached such an extent that the two phases are nearly mixed at the molecular level. In this situation, BQSESU mainly act as plasticizers. Thus the viscosity is higher than that of the blends compounded at 265 and 280°C.

### CONCLUSIONS

1. BQSESU has extremely low shear viscosity in its nematic state. When blended with polycarbonate at the LCP concentration of 2 wt %, the viscosity reduction effect of BQSESU in PC depends on the compounding temperature. At the testing temperature of 280°C and relatively high shear rates, the blend compounded at 280°C has significant lower viscosity than blends compounded at 265 and 300°C.

2. Molecular weight reduction induced by the compounding contributes to the viscosity reduction at low shear rates but is not a major contributor. An external lubricating effect was not observed.
3. The miscibility of the blends increases as the compounding temperature increases. When compounded at 280°C the particle size of the blend is at the submicron level, and there are strong interactions between the flexible segments of BQESU and PC in the interfacial regions. The largest viscosity reduction achieved by blending at 280°C is thus proposed as an interfacial phenomenon. When compounded at 300°C, a nearly miscible morphology was achieved, which explains the diminished viscosity reduction observed.

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