Viscosity-Reducing Effects of Two Semiflexible Liquid-Crystalline Polyesters with Different Chain Rigidities in a Matrix of Polycarbonate

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Received 17 June 2003; accepted 16 October 2003

ABSTRACT: Two liquid-crystalline polyesters (LCPs) with different chain rigidities were synthesized and meltblended with polycarbonate (PC) at an LCP concentration of 2 wt %. The first LCP (LCP1) was based on hydroxybenzoic acid (HBA), hydroquinone (HQ), sebacic acid (SEA), and suberic acid (SUA) and contained a relatively high concentration of flexible units (SEA and SUA). The other one (LCP2) was based on HBA, hydroxynaphthoic acid, HQ, and SEA and contained a lower concentration of flexible units. LCP2 had a much lower melting point, a higher clearing temperature, and a lower shear viscosity than LCP1. The blending was carried out at 265, 280, and 300°C for both systems. The extent of the viscosity reduction induced by the addition of LCP1 depended on the compounding temperature, and the lowest viscosity was achieved with blending at 280°C. This was attributed to the large interfacial area and interactions between the flexible segments of LCP1 and PC chains at the interface. For PC/LCP2, the viscosity reduction was not significantly dependent on the compounding tem-

INTRODUCTION

In a previous publication,¹ we reported a liquid-crystalline polyester (LCP) based on 4-hydroxybenzoic acid (HBA), hydroquinone (HQ), sebacic acid (SEA), and suberic acid (SUA); denoted LCP1 in this article, it has a large viscosity reduction effect when blended with polycarbonate (PC) at a very low LCP concentration. An unusual phenomenon has been observed for this blend system: the relationship between the viscosity reduction and the miscibility is not monotonic. The largest viscosity reduction was achieved when the blend was compounded at a temperature (280°C) leading to a partially miscible morphology with a large interfacial area. In contrast, the viscosity reduction was less impressive with a nearly miscible or largely immiscible morphology that was obtained at a higher or lower compounding perature, and when it was compounded at 280°C, its viscosity was significantly higher than that of PC/LCP1 at high shear rates, even though LCP2 had lower viscosity. A scanning electron microscopy study revealed that, with compounding at 265 and 280°C, LCP2 was poorly dispersed in the PC matrix in comparison with LCP1, and the glasstransition-temperature depression caused by the addition of LCP2 was relatively small. This indicated that interfacial interactions in PC/LCP2 were weaker, thereby explaining their different rheological behavior in comparison with PC/ LCP1. With compounding at 300°C, the compatibility of both systems improved because of transesterification reactions, but this did not lead to a lower viscosity because of the lack of physical interfacial interactions. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 960–969, 2004

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

temperature. It was thus proposed that the large viscosity reduction achieved by compounding at 280°C was closely related to the large interfacial area of the blend. Both an interlayer slipping effect and the disentanglement of PC chains induced by the alignment of nematic domains were enhanced as the interfacial area increased. Several other groups have also reported similar phenomena regarding the relations between the rheological behavior and miscibility of blends containing liquidcrystalline polymers (LCPs). Their studies have demonstrated that the viscosity reduction effect of an LCP can be enhanced by an improvement in the miscibility if the blend is partially miscible.^{2,3} If an LCP is completely miscible with an isotropic polymer, the viscosity of the blend may even be higher than that of the pure components.4

In this article, we report a new LCP based on HBA, 2,6-hydroxynaphthoic acid (HNA), HQ, and SEA; denoted LCP2 in this article, it was specially designed for a comparison study with LCP1. LCP1 and LCP2 contain similar functional groups, and this gives them about the same solubility parameter, as well as chemical reactivity, in the isotropic state. However, LCP2

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Contract grant sponsor: Nanyang Technological University; contract grant number: RG35/99.

Journal of Applied Polymer Science, Vol. 92, 960–969 (2004) © 2004 Wiley Periodicals, Inc.



Figure 1 Chemical structures of the repeat units of (a) LCP1 $(X + Y_1 + Y_2 + Z = 1, Y_1 + Y_2 = Z, \text{ and } X \ll X_1 + X_2)$ and (b) LCP2 $(X_1 + X_2 + Y' + Z' = 1, Y' = Z', \text{ and } X \ll X_1 + X_2)$.

was designed to be much more rigid than LCP1 through the partial replacement of HBA with HNA units and through an increase in the total concentration of rigid units (HBA and HNA). Thus, in its nematic state, LCP2 is less compatible with PC. This article describes how this change in compatibility brought by an increase in the LCP chain rigidity affects the rheological behavior of PC/LCP2 blends with respect to PC/LCP1 blends. The results of this work verify a claim that we made in our previous study:¹ physical interfacial interactions have a significant impact on viscosity reduction effects of LCPs for the studied blend systems. By manipulating LCP structures, we may be able to achieve a desirable degree of interfacial interaction between an LCP and an isotropic polymer matrix to maximize the viscosity reduction induced by the LCP. The knowledge that we gain could thus be used to design new LCPs as processing aids for various thermoplastics.

EXPERIMENTAL

Polymer synthesis

The chemical structures of the repeat units of LCP2 are shown in Figure 1 and compared with those of LCP1. The synthesis procedure for LCP1 has already been reported.⁵ LCP2 was synthesized by the melt-condensation polymerization of 4-acetoxybenzoic acid (ABA), 2,6-acetoxynaphthoic acid (ANA), *p*-phenylene diacetate (PDA), and SEA with the same procedure used for LCP1. SEA was purchased from Aldrich (Milwaukee, WI) without any further treatment. ABA, ANA, and PDA were prepared through the acetylation of HBA, HNA, and HQ, respectively, with acetic anhydride.⁶ HBA, HNA, and HQ were purchased from Aldrich. The acetic anhydride was reagent-grade, from Merck (Darmstadt, Germany).

¹³C-NMR analysis

¹³C-NMR spectra of LCP1 were obtained with a Bruker DRX 400 NMR spectrometer (Germany) at 27°C. The solvent was a 1:1 (v/v) mixture of CD₂ClCD₂Cl and phenol. The chemical shifts were referenced to tetramethylsilane (TMS).

Characterization of the thermal and rheological behaviors of the LCPs

The thermal properties and phase behaviors of LCP1 have already been reported.^{1,5} The glass-transition temperature (T_g), melting temperature (T_m), and degradation temperature of LCP2 were measured with a thermal dynamic mechanical analyzer, a differential scanning calorimeter, and a thermogravimetric analyzer, respectively, whereas its nematic-phase range was identified with polarized optical microscopy and melt viscosity measured with a parallel-plate rheometer. The instruments and experimental conditions were the same as those used for LCP1.^{1,5}

Blending and characterization of the blends

The matrix material used in this study was Lexan 141R-111, an injection-molding-grade PC, from GE Plastics (USA). PC and LCP2 were melt-blended at 2 wt % LCP2 with the same equipment, procedure, and conditions reported for the PC/LCP1 blends.¹ For simplicity, in this article the blends of LCP1 and LCP2



Figure 2 (a) Expanded ¹³C-NMR spectrum of an HBA/HQ/SEA/SUA polyester at an SEA/SUA molar ratio of 80:20 in a 1:1 (v/v) mixture of CD_2CICD_2CI and phenol and (b) chemical skeletons of dyads in an HBA/HQ/SEA/SUA polyester corresponding to resonance peaks 1–6.

with PC are called blends 1 and 2, respectively. The PC/LCP2 blends obtained at blending temperatures (metering zone temperatures) of 265, 280, and 300°C are named blend 2-265, blend 2-280, and blend 2-300, whereas the PC/LCP1 blends reported in ref. 1 are named blend 1-265, blend 1-280, and blend 1-300, respectively. The instruments and methods used for the characterization of the blend 2 system, which include capillary rheometry, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and modulated differential scanning calorimetry, were the same as those reported for LCP1 in ref. 1.

RESULTS AND DISCUSSION

Chain structure of the LCPs

The chain rigidity of an LCP consisting of rigid and flexible units is affected by its sequence distribution. If the LCP has a random sequence distribution, statistical calculations show that its average mesogen length will increase as the content of the rigid units increases. For example, the average mesogen length of HBA/HQ/SEA terpolyesters increases as the HBA concentration increases.⁷ Therefore, to establish that LCP2 is more rigid than LCP1, we need to study their sequence distributions first.

Moore and Stupp⁸ and Hsiue et al.⁷ studied the sequence distributions of terpolyesters based on HBA, HQ, and an aliphatic diacid with ¹³C-NMR and confirmed that they were random terpolymers. On the basis of their results and the fact that HBA and HNA can form random copolymers,⁹ we can conclude that LCP2 is a random polyester. For LCP1, as its monomers include two types of aliphatic diacids, ¹³C-NMR was conducted to determine if the two diacid units are distributed randomly. A series of HBA/HQ/SEA/ SUA polyesters (including LCP1) with different SEA/ SUA ratios were tested. For all the samples, six relatively strong carbonyl resonance peaks were observed, which were labeled 1-6, as shown in Figure 2(a). As the intensities of the other peaks in this range are fairly low, the six strong peaks can be approximately taken as the signals corresponding to six dyads. The assignments for peaks 1–6 are given in Figure 2(b). A general observation is that as the SEA concentration increases from 0 to 100 mol %, the C1/C2 and C3/C4 intensity ratios change from 100:0 to 0:100 accordingly, and for a given sample, the intensity ratio is close to its SEA/ SUA molar ratio. This indicates that the distribution of SEA and SUA units along the chains is random, as expected from their similar chemical structures. From this and the results of Moore and Stupp⁸ and Hsiue et al.,⁷ we can conclude that LCP1 also has a randomchain structure.

From the chemical structures of LCP1 and LCP2, we know that LCP2 contains HNA units, which have a higher aspect ratio than HBA and thus tend to increase the chain rigidity of LCP2. LCP1 contains SUA units, which are slightly shorter than SEA units. As both SEA and SUA have an even number of CH₂ units and the length difference between them is small, replacing a small percentage of SEA units with SUA units would not affect chain rigidity too much.⁵ More importantly, LCP2 has a much higher total concentration of rigid units (HNA and HBA) than LCP1. These would give LCP2 a longer average mesogen length and, therefore, higher chain rigidity than LCP1 because both LCP1 and LCP2 have random sequence distributions. According to the Flory lattice theory, this would also cause LCP2 to have a much higher nematic-to-isotropic transition temperature than LCP1, which is exactly what we observed. The details are given in the next section.

Phase and rheological behaviors of the LCPs

Important thermal properties of LCP2 are summarized in Table I and compared with those of LCP1. LCP2 has a much broader nematic-phase range than LCP1. LCP1 is dominantly nematic in the temperature range of 220–310°C.¹ The LCP2 melt is dominantly nematic from 155 to 340°C, and birefringence persists until 375°C, as shown in Figure 3, above which ther-

TABLE I					
Important Properties of LCP1	and	LCP2			

Property	LCP1 (°C)	LCP2 (°C)
T _g ^a	56	63
T ^b _g	—	59
$T_m^{\mathbf{b}}$	185	148
Temperature range for the nematic		
dominant structure ^c	220-310	155-340
Clearing temperature ^c	340-350	>375
Degradation temperature (at 5%		
weight loss)	378	400

^a Measured with a dynamic mechanical analyzer in a heating process.

^b Measured with a differential scanning calorimeter in a heating process.

^c Measured with a polarized optical microscope in a cooling process.

mal degradation becomes significant. The much broader nematic range of LCP2 is due to its lower melting temperature and higher nematic-to-isotropic transition temperature with respect to those of LCP1. The higher nematic-to-isotropic transition temperature of LCP2 proves its higher chain rigidity, which was predicted from the chemical structures and compositions of LCP1 and LCP2.

Figure 4 shows the shear viscosity of LCP2 measured with parallel-plate rheometry at 280°C in comparison with that of LCP1. At 280°C, both LCP1 and LCP2 are in the nematic state. In the tested shear rate range, the viscosity of LCP2 is only about 1 Pa s, which is significantly lower than that of LCP1. The nematicphase range (155–340°C) of LCP2 matches the processing temperature windows of many important thermoplastics, and it has a combination of excellent thermal stability and extremely low melt viscosity. It thus has great potential to be used as a processing aid for a wide range of thermoplastics.

Rheological behaviors of the blends

Figure 5 shows the apparent viscosity of the blend 2 system as a function of the apparent shear rate in comparison with that of neat PC and the blend 1 system at a testing temperature of 280°C. The blend 2 system also shows a significant viscosity reduction in comparison with neat PC, whereas its dependence on the compounding temperature is quite different from that of the blend 1 system. As mentioned earlier, for the blend 1 system, there are significant differences in the viscosity among the blends compounded at different temperatures. At high shear rates, the viscosity of blend 1-280 is significantly lower than those of blend 1-265 and blend 1-300. The trend is, however, not seen for the blend 2 system; its blends, compounded at



Figure 3 Optical textures exhibited by LCP2 upon cooling: (a) the appearance of birefringence at 375° C, (b) the appearance of a threadlike structure at 350° C, (c) the threadlike texture at 332° C, (d) the threadlike texture at 168° C, and (e) the disappearance of the threadlike texture at 143° C.

different temperatures, have about the same viscosity. In addition, even though LCP2 has lower viscosity than LCP1 at 280°C, all three PC/LCP2 blends have higher viscosities than blend 1-280 at high shear rates when tested at 280°C. This difference can be attributed to their different levels of compatibility with PC; this is discussed in detail in later sections.

Effect of the molecular weight reduction on the viscosity reduction

In our previous study on blend 1, we established that there is a decrease in the molecular weight of the PC matrix after compounding, and the higher the compounding temperature is, the lower the molecular weight is of the PC matrix.¹ Also, the reduction in the zero-shear viscosity (η_0) caused by a weight-average molecular weight (M_w) reduction, estimated as $\eta_0 = KM_w^{0.34}$ (where *K* is a constant), is much smaller than the corresponding viscosity reduction observed experimentally, and the effect of the compounding temperature on the viscosity reduction cannot be correlated to the corresponding molecular weight change. Thus, a conclusion made for blend 1 is that molecular weight reduction is not



Figure 4 Melt viscosity of LCP1 and LCP2 measured with parallel-plate rheometry at 280°C.



Figure 5 Apparent viscosity of blends (\blacktriangle) 2-265, (\blacksquare) 2-280, and (\diamondsuit) 2-300, blends (\triangle) 1-265, (\Box) 1-280, and (\diamondsuit) 1-300, and (\bigcirc) neat PC versus the apparent shear rate measured with a capillary rheometer at 280°C.

a major contributor to the viscosity reduction observed. In this study, the molecular weight of the PC matrix of blend 2-300 was measured and compared with that of blend 1-300. The results, as shown in Table II, demonstrate that the two systems have comparable molecular weights. The aforementioned conclusion for blend 1 can thus be extended to the blend 2 system. The aforementioned rheological differences between the two systems are, therefore, not a result of the molecular weight reduction of the PC matrix.

Morphology of the blends

SEM micrographs of fractured surfaces of blends 2-265, 2-280, and 2-300 are shown in Figure 6(a–c), and SEM micrographs of the blend 1 system are shown in Figure 6(d–f). A typical island-sea morphology can be observed for all three PC/LCP2 blends at this low LCP concentration. The dispersed LCP2 particles are up to 2 μ m in size when compounded at 265 and 280°C and up to 1 μ m in size when compounded at 300°C; these values are significantly larger than that of the blend 1 system. This clearly indicates poorer compatibility be-

TABLE II Molecular Weight Measurement

Material	M_n	M_w	Polydispersity
PC (extruded at 300°C)	27,700	52,300	1.9
PC Matrix of Blend 1–300	24,100	44,000	1.8
PC Matrix of Blend 2–300	25,800	40,300	1.6

tween PC and LCP2. The solubility parameters of PC, LCP1, and LCP2, calculated with the group molar attraction constants determined by Small,¹⁰ are 16.4, 17.0, and 17.2 MPa^{1/2}, respectively. In the isotropic state, LCP1 and LCP2 should, therefore, have similar levels of compatibility with PC. The observed difference in the morphology is obviously due to the higher chain rigidity of LCP2 in the nematic state.

For the blend 1 system, the LCP1 particle size is reduced significantly when the compounding temperature is increased from 265 to 280°C, whereas for the blend 2 system, the LCP2 particle size remains the same with the same temperature change. The significantly enhanced compatibility in blend 1-280 can be attributed to the relatively high concentration of flexible diacid units in LCP1, which make a considerable number of segments become flexible at 280°C and thus facilitate the formation of an interface between PC and LCP1. For the blend 2 system, because of its lower concentration of flexible units, far fewer segments are flexible enough to mix with PC chains to form an interface at 280°C. The significant morphological difference between blend 1-280 and blend 2-280 leads to their significantly different rheological behaviors, which further verify that the larger interfacial area in blend 1-280 is responsible for its lower viscosity.

When compounded at 300°C the LCP2 particles become significantly smaller, and the population of the particles is also reduced significantly in comparison with those of blends 2-265 and 2-280. In addition, on the fractured surface of blend 2-300, no debonded particles and holes can be observed; this is in contrast



(d) (f)

Figure 6 SEM micrographs of fractured surfaces of (a) blend 2-265, (b) blend 2-280, (c) blend 2-300, (d) blend 1-265, (e) blend 1-280, and (f) blend 1-300.

to what was observed for fractured surfaces of blends 2-265 and 2-280. From our early discussion, we know that LCP2 remains nematic-dominant at temperatures well above 300°C. The significantly improved compatibility at 300°C should, therefore, mainly be attributed

to a transesterification reaction between PC and LCP2 chains rather than the reduced chain rigidity of LCP2. The observed morphology change is, therefore, likely to be caused by chemical bonding between PC and LCP2 chains, which is similar to but less pronounced



Figure 7 T_g of the neat PC and blends as a function of the compounding temperature: (×) neat PC, (\blacktriangle) blend 1 system, and (\triangle) blend 2 system.



Figure 8 FTIR spectra of PC, LCP1, LCP2, and their blends.

than what happens in blend 1-300. This does not promote an interlayer slipping effect¹¹ and the disentanglement of PC chains at the interface induced by LCP domain alignment,¹² and this is probably why blend 2-300 still possesses a relatively high viscosity at high shear rates in comparison with that of blend 1-280, although the two blends have apparently similar morphological features. This shows the importance of physical interfacial interactions to the viscosity reduction effect for the systems under study.

Interfacial interaction between PC and the LCPs

The relationship between the viscosity reduction effect and interfacial interactions was also probed through the changes in T_g with the compounding temperature. As shown in Figure 7, a very large T_g depression can be observed from blend 1-280 due to the plasticized interface (by the flexible segments of LCP1), and T_g of blend 1-300 is much higher because of the contribution of the rigid segments of LCP1 brought by the nearly miscible morphology.¹ For the blend 2 system, the T_{g} depression is much smaller with compounding at 265 and 280°C because of the smaller interfacial area. A further increase in the compounding temperature to 300°C increases the compatibility but does not cause any significant increase or decrease in T_{g} . T_{g} of blend 2-300 is not increased as much as that in blend 1-300 because phase separation is still fairly pronounced and the rigid segments of LCP2 may still largely remain in the dispersed phase. T_g is not significantly reduced either because the interface is not significantly plasticized on account of the lower concentration of flexible segments in LCP2. To summarize, we can say that the relatively small T_{g} depression observed for the blend 2 system indicates a weak physical interfacial interaction in this system.

Transesterification

Figure 8 shows FTIR spectra of PC/LCP2 blends and PC/LCP1 blends. Similarly to the blend 1 system, for



Figure 9 FTIR spectra of (a) blend 1-265 and (b) blend 2-265 extrudates (at different locations) collected after capillary rheometry tests at 260° C and 1000 s^{-1} .

the blend 2 system, as the compounding temperature increases, the carbonate band around 1750 cm⁻¹ also broadens, and this indicates an increase in the reaction between LCP2 and PC. However, the increase in the band broadness with the compounding temperature for the blend 2 system is less pronounced than that of the blend 1 system, although the two LCPs have similar chemical structures and are, therefore, expected to have similar reactivities. This is because the transesterification reaction is affected by the dispersion of the

LCPs. The better the dispersion is, the more vigorous the reaction is. The extent of transesterification is thus also highly influenced by the chain rigidity of the LCPs.

Figure 9 shows FTIR spectra of blend 1-265 and blend 2-265 extrudates collected after capillary rheometer tests at 260°C and 1000 s⁻¹. For blend 1-265, across the diameter of the extrudate, the shape of the carbonate band remains almost unchanged from the center to the edge, and this implies that LCP1 has no

tendency to migrate to surface; therefore, an external lubrication effect can be ruled out. For blend 2-265, the carbonate band for the edge region is slightly broader than that detected from the center of the extrudate. This implies that during capillary tests of PC/LCP2 blends, LCP2 may migrate toward the wall, at least at relatively low compounding and testing temperatures, because of the relatively poor compatibility between PC and LCP2. However, even if migration and, therefore, external lubrication occur in PC/LCP2 blends to some extent, they cannot explain the major rheological difference between the two blend systems, that they differ in the dependence of the viscosity reduction on the compounding temperature.

CONCLUSIONS

- 1. Both LCP1 and LCP2 are random polyesters, but LCP2 is more rigid than LCP1. LCP2 has a much lower T_m , a higher nematic-to-isotropic transition temperature, and a lower viscosity than LCP1.
- 2. The viscosity reduction induced by the addition of LCP2 to PC is not significantly dependent on the compounding temperature; this is in contrast to LCP1. This phenomenon can be attributed to the poorer physical interfacial interactions between LCP2 and PC due to the higher chain rigidity of LCP2.
- 3. The transesterification reaction is more vigorous in the blend 1 system than in the blend 2 system because it highly depends on the degree of the

LCP dispersion. The more vigorous reaction with compounding at 300°C leads to a nearly miscible morphology for blend 1 and better compatibility for blend 2, whereas the viscosity reduction effect is not enhanced for either.

4. This comparison study demonstrates that rodcoil liquid-crystalline polymers with a proper degree of chain rigidity are useful in creating physical interfacial interactions that can facilitate the dispersion of LCPs in flexible polymer matrices and at the same time not lead to molecular-level mixing. The viscosity reduction effect can thus be enhanced.

References

- 1. Zhao, W.; Chua, Y. C.; Lu, X. J Appl Polym Sci 2003, 90, 3051.
- 2. Seo, Y.; Kim, B.; Kim, K. U. Polymer 1999, 40, 4483.
- Kil, S. B.; Park, O. O.; Yoon, K. H. J Appl Polym Sci 2001, 82, 2799.
- Hsieh, T. T.; Tiu, C.; Simon, G. P.; Wu, R. Y. J Non-Newtonian Mech 1999, 86, 15.
- 5. Liu, L.; Lu, X. Plast Rubber Compos 2002, 31(7), 1.
- Tsai, H. B.; Lee, C.; Chang, N. S.; Chen, M. S.; Chang, S. J. J Appl Polym Sci 1990, 40, 1499.
- Hsiue, L.-T.; Ma, C.-C. M.; Tsai, H.-B. J Appl Polym Sci 1995, 56, 471.
- 8. Moore, J. S.; Stupp, S. I. Macromolecules 1987, 20, 27.
- Donald, A. M.; Windle, A. H. Liquid Crystalline Polymers; Cambridge University Press: London, 1992.
- 10. Small, P. A. J Appl Chem 1953, 3, 71.
- 11. Yi, X.-S.; Zhao, G. J Appl Polym Sci 1996, 61, 1655.
- 12. Chan, C. K.; Whitehouse, C.; Gao, P.; Chai, C. K. Polymer 2001, 42, 7847.