Effects of Chemical Reactions on the Properties of Polycarbonate/Liquid Crystalline Polymer Blends

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ABSTRACT: Effects of chemical reactions on the properties of the polycarbonate (PC)/ liquid crystalline polymer (LCP) blends are considered here. Not only thermal and rheological behaviors, but also morphology and molecular weight change are investigated. Reactive blends were prepared in a cylindrical flask at 300°C with varying processing time in the presence of a catalyst by the melt-phase reactions. For comparison, physical blends, in which chemical reactions were minimized, were also prepared at 300°C in a twin-screw extruder. It seems that transesterification and repolymerization did not occur, but depolymerization reaction took place slightly in PC/LCP physical blends. In reactive blends, however, transesterification and repolymerization as well as depolymerization reaction took place simultaneously. The depolymerization reaction occurred mainly at an early stage of processing; whereas, repolymerization reaction becomes especially dominant after some time (more than 30 min) in the presence of the catalyst, which had a great impact on its molecular weight. Also, chemical reactions changed the glass transition temperature and morphology as well as rheological behavior, which resulted in the enhanced miscibility in reactive blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2123-2133, 1999

Key words: transesterification; depolymerization reaction; reactive blending; miscibility; morphology

INTRODUCTION

From the economic viewpoint,¹ polymer blending is an outstanding tool to obtain new materials with desirable properties rather than synthesizing a novel polymer. Since the liquid crystalline polymers (LCPs) displaying good thermal and mechanical properties were introduced some 25 years ago, the new classes of high-performance polymers have received significant attention.² Blending LCP with thermoplastic polymers can offer improved melt processibility and enhanced mechanical properties, resulting from the rod-like conformation of LCP that exhibits an ordered structure in melt.³

A previous study⁴ indicated that the morphology and the properties of blends were affected by the interaction between the LCP and the matrix as well as by the properties of the individual polymeric components. Because the components in most polymer blends containing LCP are generally immiscible, interfacial interaction of the

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two separated phases should be introduced to make a successful polymer blend. It can be achieved by introducing a third component in the system to improve the adhesion between the separated phases, $^{5-8}$ or by enhancing the macromolecular interaction between them.

Co[poly(ethylene terephthalate-p-hydroxybenzoic acid)] (PET-PHB copolyester) was first developed by Tennessee Eastman Co.^{9,10} This copolyester, which contains $35 \sim 90\%$ of PHB is known as a thermotropic LCP. It is well known that transesterification can take place between ester groups in thermoplastic polyester/LCP (PHB/ PET) blends.^{11–13} As transesterification proceeds, the blends are first converted to block copolymers, and finally to random copolymers.¹⁴ Reactive blending is useful for preparation of new polymeric materials to introduce chemical reactions between two materials during the blending process. Hwang et al.^{11,12} have studied the reactive blend of PET and LCP (PHB60/PET40), in which transesterification reaction was monitored directly by the increase of nuclear magnetic resonance (NMR) peak area for PHB-PET dyad relative to PHB-PHB dyad. The high reactivity of acetate end groups in LCP was responsible for reducing molecular weight of products.

In this study, we used polycarbonate (PC) and LCP (PHB80/PET20) as blending materials. PC is partially miscible with the high PET phase of LCP; whereas, PC is immiscible with PHB phase of the LCP.^{15,16} Therefore, the miscibility between PC and LCP (PHB80/PET20) is predicted to be not as good without chemical reaction. The objectives of this study are to identify the chemical reactions during melt blending and to investigate the effect of such reactions on the properties of polycarbonate/LCP (PHB80/PET20). In the case of reactive blending, such chemical reactions as transesterification, depolymerization, and repolymerization reaction could take place during processing. The properties of the blend were investigated not only through thermal and rheological behaviors, but also because morphology and molecular weight change of the PC/LCP blends, depending on chemical reactions.

EXPERIMENTAL

Materials

Polycarbonate used in this work was Lexan 121R manufactured by General Electric Plastics, which

was end-capped with cumyl phenol as a terminal group for thermal stability. A thermotropic liquid crystalline polymer (TLCP), Novaccurate E322 was chosen, which was composed of 20-mole % PET and 80-mole % PHB, manufactured by Mitsubishi Kasei. Their structures are as follows.



PC and LCP were dried under vacuum for 12 h at 100°C to avoid possible degradation by hydration.

Blend Preparation

Physical blends of PC and LCP were prepared by using a twin-screw extruder (Werner & Pfleiderer, L/D = 42, 25ϕ) at 300°C. LCP contents were 3, 5, 7, and 10 wt % each (LC03, LC05, LC07, and LC10). The extrusion was done for less than 1 min to minimize any chemical reaction. The extruded products were cooled in water, pelletized, and dried in a vacuum oven for 12 h at 100°C. Reactive blends were prepared at 300°C by melt-mixing in a cylindrical flask with a vacuum distillation head, a stainless steel agitator, and a condensate trap. To diminish depolymerization, the pressure was kept at 0.05 torr during the preparation. A catalyst, di-n-butyltin-dilaurate in the amounts of 0.5 wt % was added to the reactive blends to accelerate the chemical reactions. The preparation conditions are listed in Table I.

Measurements

Scanning Electron Microscopy (SEM)

The morphological state of the blends was examined by scanning electron microscopy (SEM). SEM experiment was carried out using a Phillips 535 M microscope. Samples were prepared at 290°C by compression molding and fractured at cryogenic temperature after immersion in liquid nitrogen for 5 min. The fractured surfaces were coated with gold palladium for the SEM observation.

	LCP Content (wt %)	Blend Code	Preparation Time (min)	Preparation Pressure (torr)	Preparation Temperature (°C)
Physical Blends ^a	3	LC03	1	760	300
	5	LC05	1	760	300
	7	LC07	1	760	300
	10	LC10	1	760	300
Reactive Blends ^b	10	LC10-15	15	0.05	300
		LC10-30	30	0.05	300
		LC10-60	60	0.05	300

 Table I
 Summary of Preparation Method for the PC/LCP Blends

^a Physical blends were prepared in a twin-screw extruder.

^b Reactive blends were prepared in a cylindrical flask by the melt-phase reactions adding the catalyst.

Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analysis was performed using a Waters 600 to investigate the change in molecular weights of the PC/LCP blends. Tetrahydrofuran (THF) was used as an eluent at 30°C. Samples were dissolved into 0.1 wt % THF solutions. After the insoluble substances were filtered with a teflon filter (mesh size = 0.5 μ m), GPC experiment was performed. The system was calibrated using polystyrene standards.

¹H-Nuclear Magnetic Resonance (NMR) Spectrometer

To study the extent of the transesterification reaction between the PC and LCP, proton nuclear magnetic resonance (¹H-NMR) experiment was carried out. A solvent is deuteriated chloroform (CDCl₃), which does not dissolve LCP but does dissolve PC. The 5 wt % solutions of the blends were used as NMR solutions after the insoluble portions were filtered with a teflon filter (mesh size = 0.5 μ m). The spectra were calibrated by tetramethylsilane (TMS) as an internal standard. A Bruker AMX FT-NMR spectrometer (600 MHz) was used for this study.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to characterize the thermal behaviors of the blends. DSC measurements were carried out in a Dupont DSC cell equipped with a Dupont 2010 thermal analyst system. Samples were heated to 300°C at a heating rate of 20°C/min under a nitrogen atmosphere and then quenched in liquid nitrogen. The quenched samples were heated again to 300°C at the heating rate of 10°C/min. All curves and data were obtained from the second scanning.

Rheological Measurements

Rheological experiments were carried out on the neat polymers and blends using rotational rheometer (PHYSICA Rheo-Lab MC120) equipped with a cone-and-plate fixture having a cone angle of 1° and a diameter of 50 mm. The minimum gap was kept approximately 50 μ m in all cases. Before any measurement, all samples were allowed to relax at measuring temperature for 2 min and then sheared at a low shear rate (0.01 s⁻¹) for 3 min under a nitrogen atmosphere. Dynamic storage modulus (G') and dynamic loss modulus (G'') were measured in the oscillatory shear mode as a function of angular frequency (ω) under isothermal conditions. The frequency sweeps were performed from 1 ~ 500 rad/s.

Thermogravimetric Analyzer (TGA)

A 951 thermogravimetric analyzer of Dupont Instrument was used to investigate the thermal stability of the blends. Experiments were carried out on about $10 \sim 15$ -mg samples under the nitrogen atmosphere. The weight loss of samples was measured, while they were heated at a rate of 10° C/min up to 600°C from room temperature.

RESULTS AND DISCUSSION

Figure 1 shows SEMs of the fractured surface of the PC/LCP physical blends. The graphs show the



(a)

(b)



Figure 1 SEMs for PC/LCP physical blends: (a) LC03; (b) LC05; (c) LC07; and (d) LC10 (\times 5000).

LCP phase as a form of the spherical droplet dispersed in PC matrix,¹⁶ and the interfaces between PC matrix and LCP droplet are observed clearly. The size of LCP droplets increases with increasing LCP content. The graphs of fractured surfaces of PC90/LCP10 blends (10 wt % LCP blends) with processing time are shown in Figure 2. Because transesterification reaction proceeds with processing time, resulting in the enhanced miscibility of the blends, the size of the LCP droplets in the reactive blends decreased and finally showed a cocontinuous morphology.

To confirm the changes of the molecular weight in reactive blends, the molecular weight for PC/ LCP blends from GPC analysis was measured. The results are shown in Figure 3 and Table II. Samples were dissolved into 0.1 wt % THF solutions, and then insoluble LCP portions were filtered out with a teflon filter (mesh size = 0.5μ m). In this way, the molecular weight of the dissolved portions by THF could be measured. The molecular weight in LC05 and LC10 (physical blend) is smaller than that of PC (as received) as a result of the depolymerization reaction of PC phase during the preparation of physical blend at high temperature 300°C.

In principle, transesterification reaction will not change the number average molecular weight but will make some influence on the weight average molecular weight in the case of homogeneous polyesters. Hence, the decrease of the weight average molecular weight in reactive blends may result not only from depolymerization but also from transesterification reaction. As it appears in Figure 3, LC10-30 has a lot of small molecules, because depolymerization reaction occurs dominantly, as compared to repolymerization, in LC10-30. However, the molecular weight of LC10-60 is higher than that of LC10-30, because the small molecules generated by the depolymerization reaction may be polymerized again in the presence of the catalyst. In other words, small molecular portions of LC10-60 have been tremendously reduced because of the repolymerization. Accordingly, depolymerization reaction is dominant up to 30 min (LC10-15, LC10-30);





(b)



Figure 2 SEM for PC90/LCP10 blends: (a) LC10 (physical blend); (b) LC10–15; (c) LC10–30; and (d) LC10–60 (\times 5000).

whereas, repolymerization is dominant after $30 \min (LC10-60)$.

The scheme of transesterification reactions between PC and LCP is shown in Figure 4. Two possible transesterification reactions were considered in this study: reactions between (1) PC and PET segment in LCP; and (2) PC and PHB segment in LCP. To examine the extent of transesterification reaction, NMR experiment was carried out. ¹H-NMR spectra of PC and LC10 (PC90/ LCP10 physical blend) by using $CDCl_3$ as an NMR solvent. NMR spectra were observed after the insoluble portions had been filtered. Because LCP would not dissolve in CDCl₃, the peaks of LCP segments unreacted with PC were not observed in NMR spectrum. A solvent peak overlaps with b peak of PC and LC10 at around 7.26 ppm. The spectrum of LC10 is similar to that of PC, which shows that transesterification in LC10 would hardly occur. The NMR spectra of PC90/ LCP10 blends are shown in Figure 6. The a" peak at 6.68 ppm may be attributable to the depolymerization reaction of PC. As transesterification



Figure 3 The molecular weight distributions for PC90/LCP10 blends from GPC experiment (LC10 indicates physical blend and the others reactive blends).

LCP Content (wt %)	Blend Code	$ar{M}_n$	${ar M}_w$
0	PC	17,600	39,200
5	LC05	15,500	38,400
10	LC10	15,100	36,800
	LC10-15	12,700	27,200
	LC10-30	12,200	25,500
	LC10-60	14,600	29,300

Table IIMolecular Weight of PC/LCP BlendsDissolved by THF

reaction proceeds, LCP segments reacted with PC are dissolved in CDCl₃. Accordingly, five new peaks appear at 3.66, 4.79, 7.42, 8.25, and 8.31 ppm in NMR spectra, which are assigned to f', f, g + satellite peak of PC, e, and d in Figure 4, respectively.^{11,17}

It is difficult to quantify the extent of transesterification, because the LCP would not dissolve in $CDCl_3$. Because segments linked with transesterified portions as well as transesterified portions in LCP are seen in NMR spectrum, the first reaction in Figure 4 is not distinct with the second reaction in NMR spectrum. Therefore, it is difficult to know which portions in LCP, PET or PHB segments, participate in transesterification reaction with PC more easily. Instead, it is possible that the extent of transesterification is estimated roughly by introducing the concept of "degree of incorporation."



Figure 4 Scheme of transesterification reaction between PC and LCP.



Figure 5 (a) ¹H-NMR spectra of PC dissolved portions by $CDCl_3$ and (b) ¹H-NMR spectra of LC10 (PC90/ LCP10 physical blend) dissolved portions by $CDCl_3$.

Degree of Incorporation (DI) = LCP portions soluble in $CDCl_3$ incorporating with PC as a result of transesterification/Total LCP added in the blend

As for the degree of incorporation, the area ratio of $(f + f^{-})$ peak to *c* peak can be considered. If all PET segments in LCP may incorporate with PC as a result of transesterification and dissolve in CDCl₃, the ratio of $(f + f^{-})$ peak to c peak comes to be 0.028 based on mole ratio of blending material. Therefore, the degree of incorporation (DI) can be obtained from dividing the value of (f+ f^- peak/c peak) by 0.028. The degree of incorporation (DI) for PC/LCP blends is listed in Table III. It seems that the degree of incorporation increases with processing time until 30 min, but decreases thereafter. The degree of incorporation of LC10-60 is smaller than that of LC10-30, which may be attributable to the solubility difference as a result of the change in molecular weight.

Figure 7 shows the glass transition temperature (T_g) of PC phase by DSC in physical blend with LCP contents. The transition peaks of the LCP phase in the PC/LCP blends are too weak to observe. The T_g of PC phase in physical blends is



Figure 6 ¹H-NMR spectra of PC90/LCP10 blends dissolved portions by CDCl₃ according to reaction time: (a) LC10; (b) LC10–15; (c) LC10–30; and (d) LC10–60.

not remarkably changed with the LCP contents. This confirms that physical blends are immiscible. To study effects of chemical reactions on miscibility, the T_g 's of PC90/LCP10 blends with reaction time were investigated. DSC heating curves for PC90/LCP10 blends are shown in Figure 8, where the T_g of the PC phase in the reactive blends decreases up to 30 min (LC10–15, LC10–30). Especially, the T_g of LC10–30 is lower than that of LC10 (physical blend) by 25°, resulting from depolymerization of PC and transesterification between PC and LCP. These chemical

Table IIIThe Degree of Incorporation in PC/LCP Blends

Code	Relative Intensity of c Peak	Relative Intensity of $f + f^-$ Peak	Degree of Incorporation (DI)
PC	30	0	0
LC10	30	0.06	0.07
LC10–15	30	0.22	0.26
LC10–30	30	0.35	0.42
LC10-60	30	0.27	0.32



Figure 7 DSC-determined glass transition temperatures of PC phase with LCP contents in PC/LCP physical blends.

reactions result in the decrease of molecular weight and improved miscibility in PC/LCP blends, respectively. This agrees with the results of Friedrich et al.,¹⁸ who reported that a single T_{g} in PC/LCP (PHB35/PET65) = 50/50 blends (wt %) was observed in DSC heating curve after annealing at 300°C for 10 min. On the other hand, the T_{σ} of LC10–60 was higher than that of LC10–30. It is consistent with the fact that LC10-60 has higher molecular weight than LC10-30. This may imply that the small molecules formed by depolymerization are repolymerized in the presence of the catalyst. Yoon et al.¹⁹ reported that the increase of molecular weight attributable to the end-to-end reaction as well as transesterification should be considered in reaction blend of polyesters.

In many cases, the rheological behavior of polymer blend can serve as not only a key property in processing but also as a piece of evidence in investigating the miscibility. The log G' versus log G'' plots suggested by Han et al.^{20,21} to investigate the miscibility of PC/LCP physical blends are shown in Figure 9. Furthermore, it has been demonstrated that the change of temperature does not affect the plots. If the polymer blends have the same miscibility, a superposition of the rheologi-



Figure 8 DSC heating curves for PC and PC90/ LCP10 blends at a heating rate of 10°C/min (LC10 indicates physical blend and the others reactive blends).

cal data will be obtained in the log G'-log G'' plots. As seen in the Figure 9, the slope of PC is about 2, which is consistent with that of linear



Figure 9 Log G' versus log G'' plots for PC/LCP physical blends at 290°C.



Figure 10 Complex viscosities for PC/LCP physical blends with LCP contents at 290°C ($\omega = 10$ rad/s).

homopolymer in the terminal region. However, the slope of LCP is not 2, because LCP forms nematic orientation at 290°C. Storage modulus relative to loss modulus increases especially at low frequency with increasing LCP content in PC/LCP physical blends. This is because of the increase of the interfaces between PC and LCP with adding the LCP, which confirms that physical blends are truly immiscible. Figure 10 shows the complex viscosity of PC, LCP, and physical blends at $\omega = 10$ rad/s in a frequency sweep experiment. PC has the highest complex viscosity, and physical blends have lower one than PC; whereas, LCP acts as a processing agent. In particular, the LC05 has a minimum complex viscosity. The minimum viscosity in the incompatible blend systems suggests the presence of microstructure of the LCP, which is consistent with results of other researchers.^{22–24}

To investigate the effects of chemical reactions on the rheological properties, the storage modulus (G') and loss modulus (G'') of PC90/LCP10 blends were measured at 250°C and shown in Figure 11. The moduli of reactive blends at 290°C are too low to measure. Because the LCP droplets in reactive blends were destroyed by transesterification reaction as confirmed by SEM analysis, reactive blends can be considered as miscible blends. Hence, the rheological behavior of reactive blends



Figure 11 Storage modulus and loss modulus for PC90/LCP10 blends at 250°C (LC10 indicates physical blend and the others reactive blends).

at 250°C would resemble the rheological behavior at 290°C, because there is no reason to expect any phase change within this temperature range. All reactive blends show almost $G' \sim \omega^2$ and $G'' \sim \omega^1$ trends, as expected. Moreover, all reactive blends have lower storage modulus and loss modulus than LC10 because of the decrease of molecular weight and the enhanced miscibility. These results from depolymerization and transesterification, respectively. The complex viscosity ($\omega = 10$ rad/s at 250°C) obtained from storage modulus and loss modulus, and weight average molecular weight with processing time in the PC90/LCP10 blends are plotted in Figure 12. The complex viscosity of the reactive blends decreases with processing time until 30 min, but increases thereafter. The depolymerization of PC and transesterification reaction occur dominantly in LC10-15 and LC10-30, which results in the decrease of the molecular weight and enhanced miscibility, respectively. These are responsible for the decrease of complex viscosity in LC10-15 and LC10-30. However, repolymerization besides transesterification occurs in LC10-60, which results in the increase of the molecular weight. This results in the increase of complex viscosity in LC10-60. This kind of trend in the complex viscosity is almost similar to that of the weight average molecular weight, as shown in Figure 12. LC10-60 has higher complex viscosity than LC10-30 owing to the increase of weight average molecular weight resulting from repolymerization. Moreover, the complex viscosity of LC10-60 is slightly lower than that of LC10–15, which is attributable to the effect of more compatibilizer formed by transesterification.

It is important to study the thermal stability of the blends for industrial applications. Thermogravimetric curves of PC/LCP physical blends are shown in Figure 13. As it appears, PC has the



Figure 12 Complex viscosity at 250°C ($\omega = 10$ rad/s) and weight average molecular weight for PC90/LCP10 blends with processing time.

best thermal stability in PC/LCP blends in early stage. Although LCP undergoes a more rapid thermal decomposition than does PC in the early stages, afterward, it has more residual weight above 495°C. This is because the PET segment in LCP that has poor thermal stability degrades preferentially, and the PHB segment in LCP that has good thermal stability does so thereafter. PC/ LCP physical blends show a higher weight loss than PC. Moreover, LC05 shows better thermal resistance than other physical blends. Figure 14 shows the effects of chemical reactions on thermal stability. Thermal stability of PC90/LCP10 reactive blends is inferior to that of physical blend LC10. This may be attributed not only to the decrease in molecular weight resulting from depolymerization but also the destruction of PC and LCP segment by transesterification in the presence of the catalyst. LC10-60 has better thermal resistance than LC10-30, which results from the increase of the molecular weight attributable to repolymerization. Therefore, although depolymerization reaction should be restricted at a minimum, transesterification and repolymerization should be controlled properly for the purpose of good thermal stability.



Figure 13 Thermogravimetric curves of PC/LCP physical blends at a heating rate of 10°C/min under nitrogen flow.



Figure 14 Thermogravimetric curves of PC90/LCP10 blends at a heating rate of 10°C/min under nitrogen flow.

CONCLUSIONS

In PC/LCP reactive blends, such chemical reactions as repolymerization and transesterification in addition to depolymerization reaction were successfully identified in the presence of the catalyst, which resulted in a change of molecular weight and miscibility. However, the mechanical properties may deteriorate because of excessive chemical reactions. Therefore, we can conclude that chemical reactions should be carefully controlled for optimal properties, considering such factors as blending temperature, time, and amount of catalyst, which are currently under investigation.

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