

Rheological and Mechanical Properties of Polycarbonate–Liquid-Crystalline Polymer Blends with Controlled Chemical Reactions

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ABSTRACT: Chemical reactions can occur during the melt blending of polymers containing an ester group because ester groups are usually unstable at high temperatures; this instability generally deteriorates the mechanical properties of blends. Here, effects of chemical reactions on the rheological and mechanical properties of polycarbonate (PC)/liquid-crystalline polymer (LCP) blends are carefully investigated to determine a method for minimizing such undesirable impacts. For comparison, a physical blend, in which chemical reactions were minimized, was prepared at 300 °C in a twin-screw extruder. Both shear viscosity and complex viscosities of reactive blends were lower than those of physical blends, being almost proportional to $[\overline{M}_w]^{3.4}$ as a result of depolymerization and transesterification. Because of the enhanced miscibility, the tensile modulus of reactive blends increased compared with that of physical blend, according to the increase in the degree of incorporation (DI). It was also possible to increase tensile modulus if triester was added to the reactive blends. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2799–2807, 2001

Key words: polycarbonate; liquid-crystalline polymer; reactive blend; triester; transesterification

INTRODUCTION

When polymer blends are processed, miscibility between the components affects the properties of these blends. In immiscible blends, improvement of mechanical properties has been hampered by the poor interfacial adhesion between the matrix and the dispersed phase.¹ Therefore, interaction of the two separated phases should be introduced

to promote the interfacial adhesion. This effect can be achieved by introducing a third component into the system^{2–5} or by enhancing the macromolecular interaction between the separated phases.⁶ During reactive blending, chemical reactions such as transesterification, depolymerization, and repolymerization can occur. Depolymerization deteriorates the properties of the product because of the reduction in molecular weight. Furthermore, repolymerization arises from the fact that the small molecules generated by the depolymerization may again be polymerized in the presence of the catalyst, which increases molecular weight.⁷

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In this study, we used polycarbonate (PC) and LCP [*p*-hydroxybenzoic acid (PHB) 80/poly(ethylene terephthalate) (PET)20] as blending materials. The miscibility between PC and LCP (PHB80/PET20) is predicted to be unsatisfactory with no chemical reaction;^{8,9} therefore it is necessary to induce chemical reactions to enhance the properties. However, an excess of chemical reactions could bring about destruction of the liquid crystalline character and a large reduction of the molecular weight. Therefore, we were primarily concerned with identifying the chemical reactions during melt blending and secondarily with investigating optimal blending conditions and the corresponding mechanical properties of blends by means of controlling the chemical reactions.

EXPERIMENTAL

Materials

The polycarbonate used in this study was Lexan 121R manufactured by General Electric Plastics, which was end-capped with cumyl phenol as a terminal group for thermal stability. The chosen thermotropic liquid-crystalline polymer (TLCP), Novaccurate E322, was composed of 20 mol % PET and 80 mol % PHB and was manufactured by Mitsubishi Kasei. PC and LCP were dried under vacuum for 12 h at 100 °C to avoid possible degradation by hydration.

Blend Preparation

Reactive blends were prepared by melt-mixing in a cylindrical flask with varying preparation conditions; such as temperature, time, and the amount of catalyst. A schematic diagram of the reactor in the oil bath is shown in Figure 1. MgO in amounts of 0.1, 0.3, 0.5, and 0.7 wt % were added to the reactive blends as a catalyst, and then effects of chemical reactions on the properties were investigated.

To avoid a decrease in molecular weight during processing, Mark A0 412S and Irganox 1076 were added as a thermal stabilizer in the amounts of 0.1 wt % to reactive blends under a nitrogen atmosphere. Additionally, 0.5 wt % triester (trimethyl 1, 3, 5-benzene-tricarboxylate) was added to several reactive blends to facilitate the linking of polymers during blending. The structure of the triester is as follows:

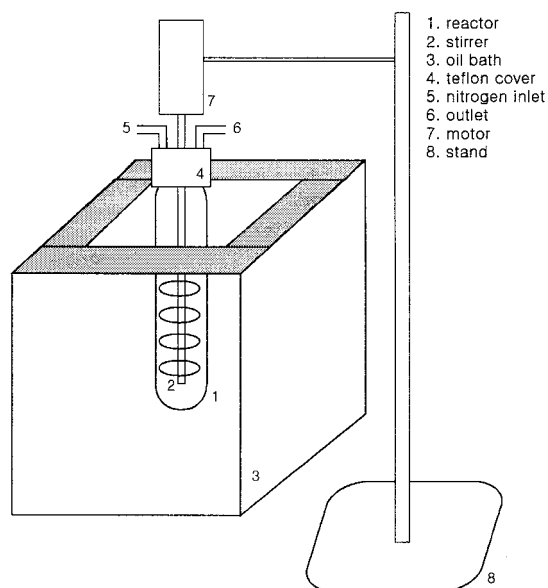
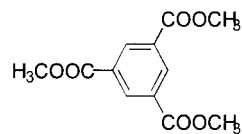


Figure 1 Schematic diagram of the reactor in the oil bath.



Triester (trimethyl 1, 3, 5-benzene-tricarboxylate)

For purposes of comparison, a physical blend was prepared at 300 °C in a twin screw extruder (Werner & Pfleiderer, L/D = 42, 25φ). The preparation conditions of PC/LCP blends are listed in Table I.

Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance (NMR) Spectroscopy

To investigate the change in molecular weights of PC/LCP blends, gel permeation chromatography (GPC) analysis was performed using a Waters 150C. Tetrahydrofuran (THF) was used as an eluent at 30 °C. Samples were dissolved in 0.1 wt % THF solutions; the insoluble substances were then filtered with a Teflon filter (mesh size = 0.45 μm). A GPC procedure was performed for the soluble portion of the blends. The system was calibrated with polystyrene standards.

Chemical structural changes resulting from transesterification can be identified by proton nuclear magnetic resonance (¹H NMR) spectroscopy. The solvent is deuterated chloroform (CDCl₃),

Table I Summary of Preparation Method in the PC90/LCP10 Blends (10 wt % LCP Blends)

Blend Type	Blend Code	Preparation Temperature (°C)	Preparation Time (min)	Catalyst (MgO, %)	Triester (wt %)	Thermal Stabilizer ^a
Physical blend ^b	LC10	300	1	—	—	—
Reactive blend ^c	280-60-01	280	60	0.1	—	0.2
	290-60-01	290	60	0.1	—	0.2
	290-60-03	290	60	0.3	—	0.2
	290-60-03T	290	60	0.3	0.5	0.2
	290-30-05T	290	30	0.5	0.5	0.2
	290-30-07T	290	30	0.7	0.5	0.2

^a Mark A0 412S and Igarnox 1076 were added in the amount of 0.1 wt % to reactive blends as a thermal stabilizer.

^b Physical blend was prepared in a twin-screw extruder.

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

which does not dissolve LCP but does dissolve PC and its derivatives. The transesterification between LCP and PC can therefore be confirmed by examining the chemical structural changes of PC in the blends. The 5 wt % solutions of the blends in deuterated chloroform (CDCl₃) were used as NMR solutions after insoluble portions, such as pure LCP, were filtered out with a Teflon filter (mesh size = 0.5 μm).

Rheological Measurements

Rheological experiments were carried out on the neat polymers and their blends using a rotational rheometer (Advanced Rheometric Expansion System, ARES) equipped with a cone-and-plate fixture of a cone angle of 0.1° and a diameter of 25 mm. The minimum gap was kept ~50 μm in all cases. Shear viscosity (η) was measured in the steady shear mode as a function of shear rate ($\dot{\gamma}$) under isothermal conditions. Dynamic storage modulus (G') and dynamic loss modulus (G'') were also measured in the oscillatory shear mode as a function of angular frequency (ω) under isothermal condition. Frequency sweeps were performed from 1 to 500 rad/s. 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.

Mechanical Measurements

A universal tensile tester (Instron model 4201) was used at room temperature. Cross head speed was 1 mm/min, and the load was 9800 N. The test specimens of the blends were prepared within 1 min at 290 °C in a MiniMax molder equipped with

a die for which detailed specifications are given in the ASTM D1708-96 (gauge length was 22 mm). At least five measurements were taken and averaged as results.

RESULTS AND DISCUSSION

Characterization of Chemical Reactions by GPC and NMR

To investigate the effects of chemical reactions on the molecular weight in reactive blends, the molecular weights of PC/LCP blends were measured by GPC and the results are shown in Table II. Samples were dissolved in 0.1 wt % THF solutions, then insoluble LCP portions were filtered out with a Teflon filter (mesh size = 0.45 μm). The molecular weight of LC10 (physical blend) was less than that of PC (as received) because of the depolymerization reaction of the PC phase during the preparation of physical blend at 300 °C. The molecular weights of reactive blends were lower

Table II Molecular Weights and Polydispersity of Dissolved Portions by THF in PC/LCP Blends

Blend Code	\overline{M}_n	\overline{M}_w	Polydispersity
PC (as received)	27,200	47,500	1.74
LC10	26,700	45,900	1.72
280-60-01	24,800	41,500	1.67
290-60-01	22,600	38,400	1.70
290-60-03	18,500	35,700	1.92
290-60-03T	18,300	33,400	1.83
290-30-05T	18,200	35,500	1.95
290-30-07T	16,000	31,300	1.95

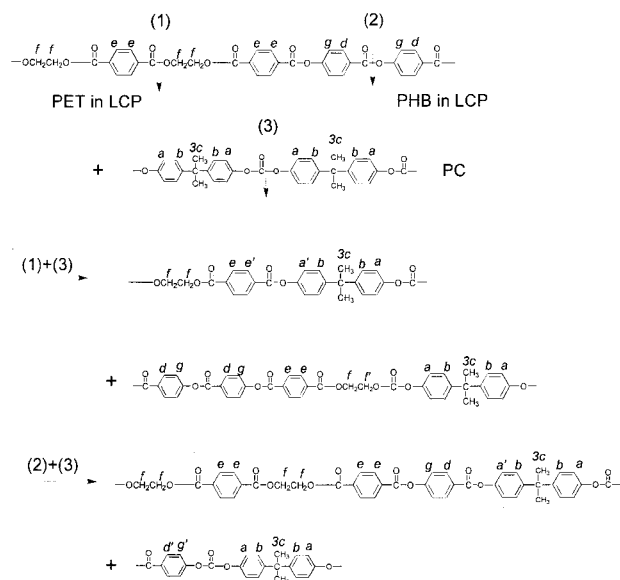


Figure 2 Scheme of transesterification reactions between PC and LCP.

than that of LC10 and decreased as preparation temperature and the content of catalyst increased. The blends with triester may have larger molecular weight because the polymers were linked together because of the triester, which would not be dissolved in THF. The molecular weights obtained by GPC were only the soluble portions in THF. Nevertheless, the molecular weights in these reactive blends were maintained to some extent without significant reduction compared with the molecular weights of previous reactive blends.⁷

To examine the extent of transesterification, a NMR experiment was conducted. NMR spectra were observed after the insoluble portions had been filtered. Because LCP would not be dissolved in CDCl_3 , the peaks of LCP segments that did not react with PC were not observed in the NMR spectrum. The scheme of transesterification reactions between PC and LCP is shown in Figure 2. As transesterification proceeded, LCP segments reacting with PC were dissolved in CDCl_3 . Accordingly, five new peaks appear at 3.66, 4.79, 7.42, 8.25 and 8.31 ppm in Figure 3 and 4, which are assigned to f' , f , g , e , and d in Figure 2, respectively.¹⁰

The spectrum of LC10 is similar to that of PC because only slight transesterification in LC10 occurred. The a'' peak at 6.68 ppm in reactive blends may be attributed to the depolymerization reaction of PC.⁷ Moreover, two new peaks appear

at 8.87 and 3.98 ppm in Figure 4, which are attributed to aromatic and aliphatic protons of triester, respectively.

It is difficult to quantify the extent of transesterification because the LCP did not be dissolved in CDCl_3 . Because not only transesterified portions but also segments linked with transesterified portions in LCP are observed in the NMR spectrum, the first reaction in Figure 2 is not distinct from the second reaction. Therefore, it is difficult to know which portions in LCP, PET, or PHB segments more easily participate in transesterification with PC. Instead, it is possible to roughly estimate the extent of transesterification by introducing the concept of "degree of incorporation" ($\text{DI} = \text{LCP portions soluble in } \text{CDCl}_3 \text{ incorporating with PC as a result of transesterification} / \text{total LCP added in the blend}$).

If all PET segments in LCP may incorporate with PC as a result of transesterification and be dissolved in CDCl_3 , the ratio of ($f + f'$) peak to c peak is 0.028, based on the mole ratio of blending materials. Hence, the degree of incorporation (DI) can be obtained from dividing the value of ($f + f'$

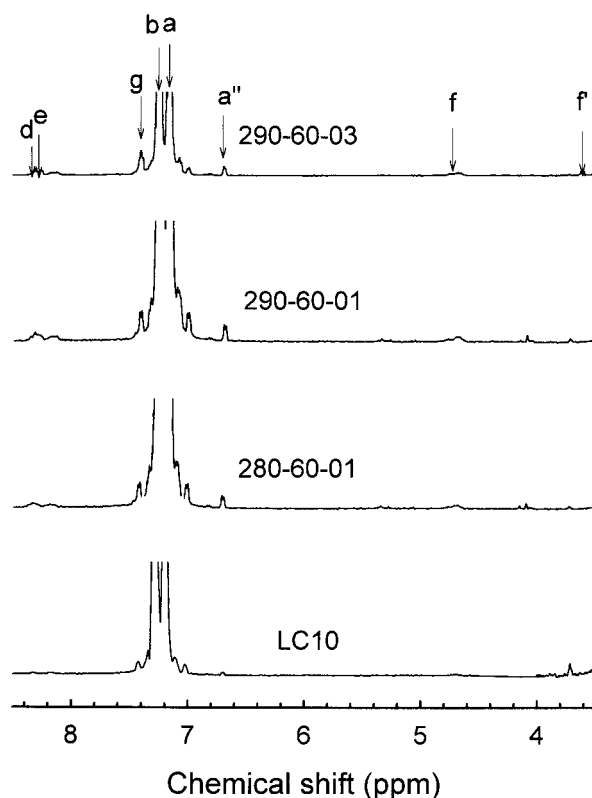


Figure 3 ^1H NMR spectra of only the dissolved portions by CDCl_3 in PC/LCP blends without triester ($\delta = 3.5\text{--}8.5$ ppm; d , e , f , and f' are shown in Figure 2).

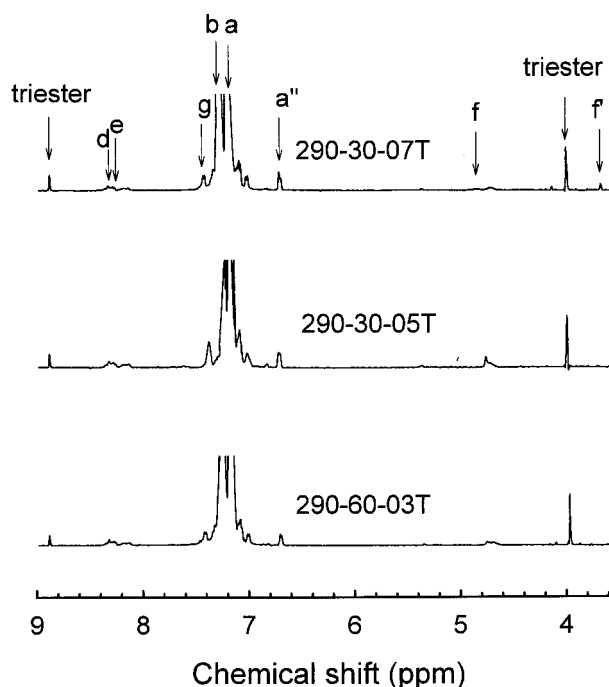


Figure 4 ^3H NMR spectra of only the dissolved portions by CDCl_3 in PC/LCP blends with triester ($\delta = 3.5\text{--}9$ ppm; d, e, f, and f' are shown in Figure 2).

peak/c peak) by 0.028. The DI for PC/LCP blends is listed in Table III. The DI increases in reactive blends as processing temperature and the content of catalyst increase. As expected, the 280-60-01 reactive blend has the lowest DI among the reactive blends because of the low processing temperature and the low amount of catalyst.

Moreover, the blends with triester have hardly f' peak at 3.60 ppm except for 290-30-07T. The f' peak is formed by transesterification between the PC and PET segments of LCP.¹¹ From this result, it may be said that the PET segment of LCP would not directly transesterify with PC but

would do so with triester in the case of 290-60-03T and 290-30-05T. Moreover, polymers linked together by triester did not be dissolved in CDCl_3 , which resulted in a decrease of DI. As a result, the DI of blends with triester was lower than that of 290-60-03 without triester. In the case of 290-30-07T, large amounts of catalysts might have noticeably promoted the transesterification reaction, resulting in the increase in DI.

Actually, more transesterification in reactive blends with triester seems to have occurred than in the NMR results. This result may be indirectly observed by analysis of the amount of triester added in the blends. The triester would have participated in forming polymers that were linked during reactive blending. The segments to have reacted with triester would not be dissolved in CDCl_3 , resulting in the reduced intensity of the NMR peak. If all triester added were shown in the NMR spectrum, the value of (aromatic proton peak at 8.87 ppm in triester/methyl proton peak at 1.68 ppm in PC) would be 0.31%. If we assume that the peak area of the methyl proton at 1.68 ppm in PC was 30, the peak area of the aromatic proton at 8.87 ppm in triester should have been 0.093. However, the peak intensities detected by NMR analysis were 0.073 in 290-60-03T, 0.056 in 290-30-05T, and 0.084 in 290-70-05T, which are lower than calculated value. Accordingly, it appears that many triester molecules participated in forming linked polymers that depreciated solubility in CDCl_3 .

Shear Rate Sweeps for PC/LCP Blends

To investigate the effects of chemical reactions on rheological properties, the shear viscosities of PC/LCP blends are shown as a function of shear rate in Figure 5. PC shows Newtonian viscosity below

Table III Degree of Incorporation in PC/LCP Blends Determined by ^1H NMR Analysis

Blend Code	c Peak (1.68 ppm)	f' Peak (3.60 ppm)	f Peak (4.79 ppm)	Triester (8.87 ppm)	Degree of Incorporation (DI)
PC (as received)	30	—	—	—	0
LC10	30	0.06	—	—	0.07
280-60-01	30	0.02	0.07	—	0.10
290-60-01	30	0.02	0.09	—	0.13
290-60-03	30	0.06	0.18	—	0.28
290-60-03T	30	—	0.15	0.073	0.18
290-30-05T	30	—	0.14	0.056	0.17
290-30-07T	30	0.09	0.11	0.084	0.25

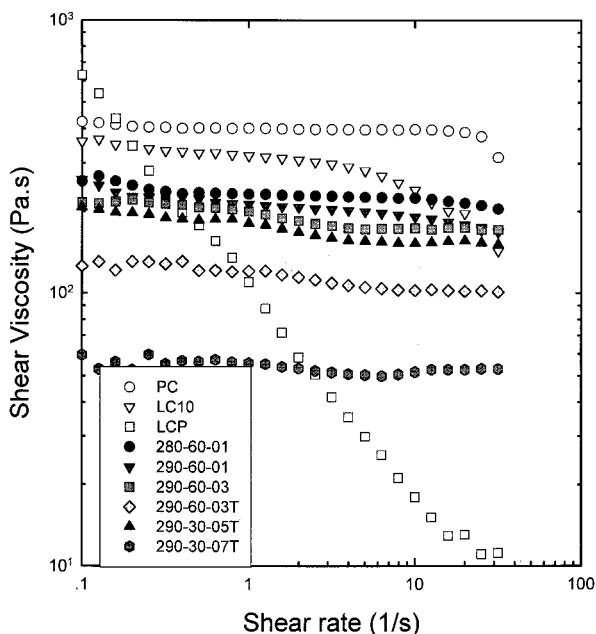


Figure 5 Shear viscosities as a function of shear rate for PC/LCP blends at 290 °C.

a shear rate of 20 (1/s), whereas the LCP shows shear thinning behavior over the entire shear rate. Reactive blends have lower viscosities than LC10, physical blend, because of their lower molecular weight and enhanced miscibility. It is noteworthy that the 290-30-07T blend has the lowest shear viscosity in all the PC/LCP blends because of the transesterification due to the large amount of catalyst. The shear viscosities at shear rate = 1 (1/s) are shown as a function of molecular weight in Figure 6, where the shear viscosities are almost proportional to $[\overline{M}_w]^{3.4}$, which is in accord with eq. 1.^{12,13} For a linear polymer and concentrated solutions or melt,

$$\log \eta_0 = 3.4 \log \overline{M}_w + A \quad \text{if } \overline{M}_w > M_{cr}$$

where M_{cr} is critical molecular weight (M_{cr} of PC is 3000 g/mol), and A is empirical constant.

However, the 290-30-07T blend deviates from this linearity because it has significantly enhanced miscibility as a result of the increase in transesterification. Hence, the change of shear viscosity depends on the combined effect of the reduced molecular weight due to depolymerization and the enhanced miscibility due to transesterification.

Frequency Sweeps for PC/LCP Blends

The storage moduli and loss moduli as a function of frequency at 290 °C during frequency sweeps

for PC/LCP blends are shown in Figure 7. The storage modulus G' is seen to scale with frequency as $G' \sim \omega^2$, whereas the loss modulus, G'' is also found to scale with frequency as $G'' \sim \omega^1$ in PC/LCP reactive blends. However, storage modulus of LC10, physical blend shows deviation from this tendency because of the contribution of the interfaces between PC and LCP as adding the LCP.

The complex viscosities obtained from the frequency sweeps at 290 °C ($\omega = 10$ rad/s) are shown as a function of molecular weight in Figure 8. The complex viscosities are almost proportional to $[\overline{M}_w]^{3.4}$, as was shear viscosity. 290-30-07T shows the lowest complex viscosity among all PC/LCP blends because of its reduced molecular weight and enhanced miscibility.

Logarithmic plots of $G'(\omega)$ and $G''(\omega)$ at 290 °C during frequency sweeps are shown in Figure 9. The slope of PC is 2 because PC is homogeneous at this temperature, as is generally known.¹⁴ However, storage modulus relative to loss modulus in LCP increases, especially at low frequency, due to the nematic phase of LCP at 290°C. The slope of the LC10 physical blend is <2 because of the increase in interfaces between PC and LCP. Moreover, the reactive blend shows more homogeneous behavior than LC10, physical blend because of enhanced miscibility as a result of transesterification.

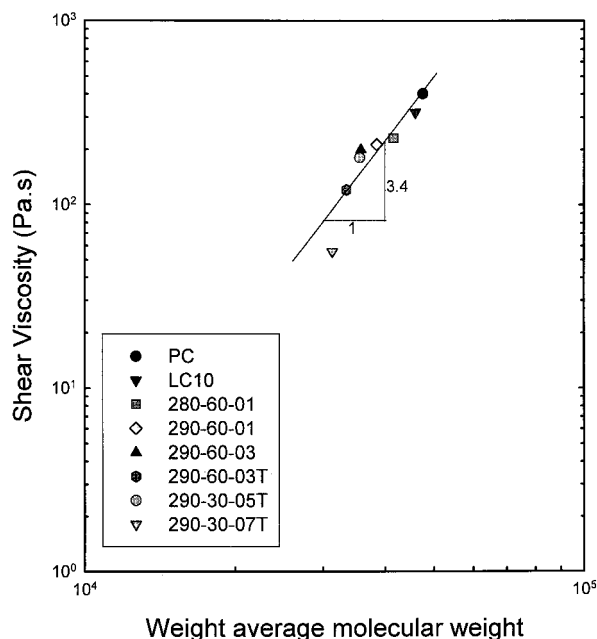


Figure 6 Shear viscosities at 290 °C.

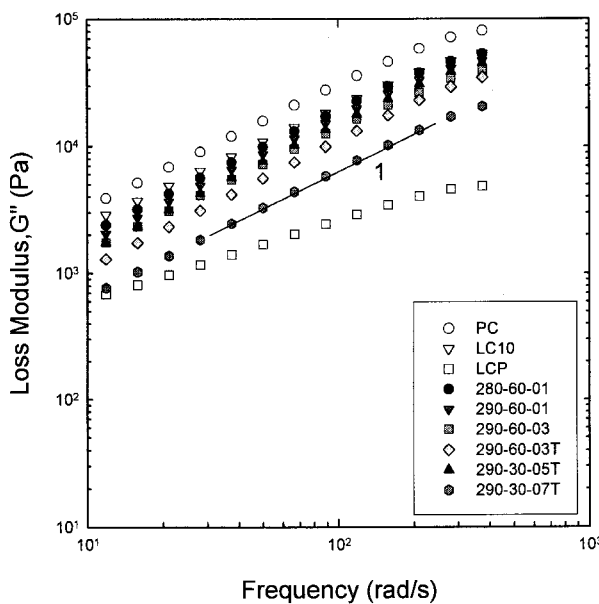
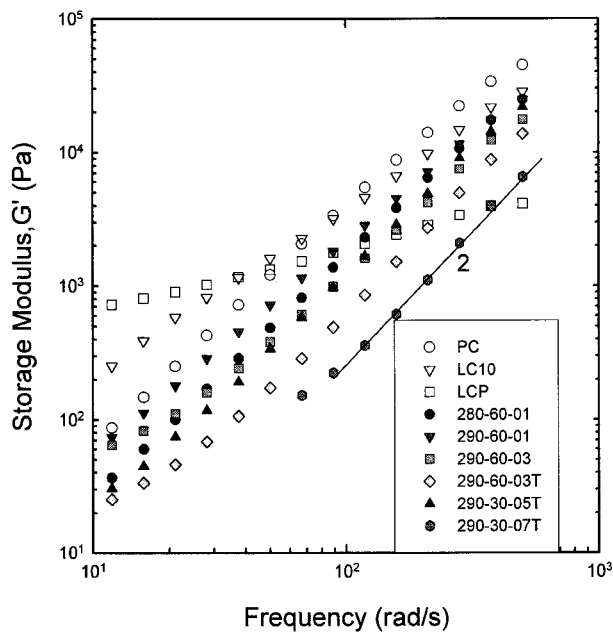


Figure 7 Storage moduli and loss moduli as a function of frequency for PC/LCP blends at 290 °C.

Mechanical Properties

To investigate the effects of chemical reactions on the mechanical properties, a tensile test by Instron was performed. The mechanical properties for blends including PC have been investigated by many researchers. Kunori et al.^{15,16} reported that in the case of PC/polystyrene (PS) blends, there is an appreciable interfacial adhesion between the PC matrix and the PS inclusion, which affects tensile and dynamic mechanical properties. Lee

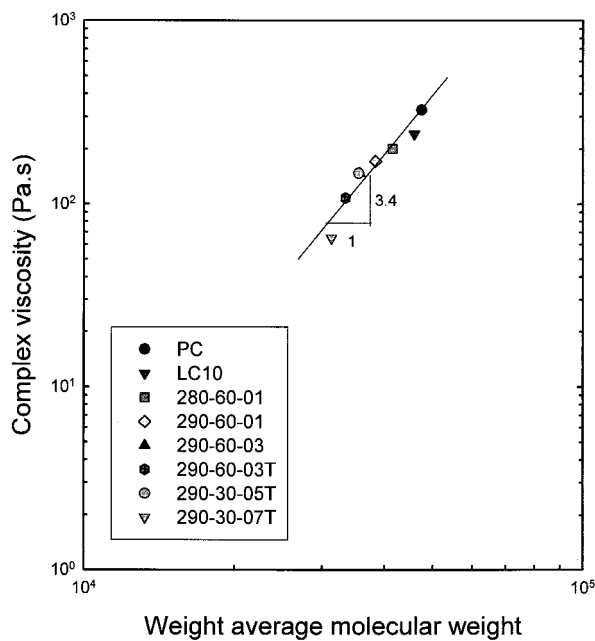


Figure 8 Complex viscosities at 290 °C with weight-average molecular weights for PC/LCP blends ($\omega = \text{rad/s}$).

et al.¹⁷ investigated the reactive compatibilized PC/PS blends where impact strength increased with addition of styrene-butadiene-styrene (SBS) copolymer as an impact modifying agent of PS

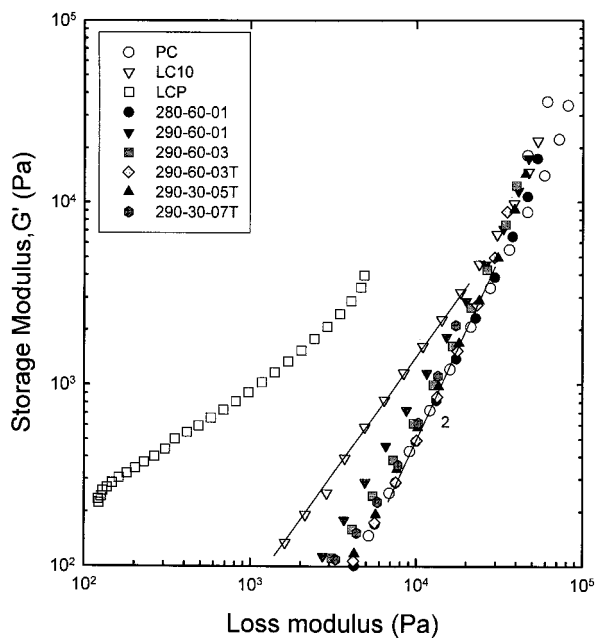


Figure 9 Log G' versus log G'' plots for PC/LCP blends at 290 °C.

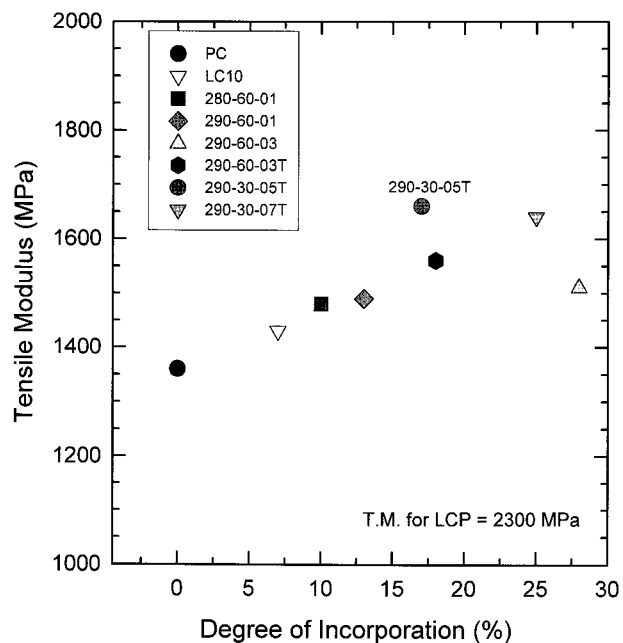


Figure 10 Tensile moduli for PC/LCP blends as a function of dumbbell with degree of incorporation.

phase. Moreover, Nunes et al.¹⁸ reviewed the literature on polymer mechanical properties as a function of molecular weight and molecular weight distribution. In their studies, mechanical properties generally increased as the molecular weight increased. However, above a limiting molecular weight, the mechanical property was usually unaffected.

The mechanical properties such as tensile modulus, strength, and elongation after tensile tests by Instron were measured. The tensile modulus as a function of DI is shown in Figure 10. The tensile modulus of LCP is 2300 MPa, which is significantly higher than that of PC, which is 1360 MPa. The tensile modulus of LC10 is 1430 MPa, which is slightly higher than that of PC because of the high modulus of the added LCP.

Reactive blends have higher tensile moduli than LC10. Notably, the tensile modulus in reactive blends increases as the DI increases on the whole. Because of the polymers linked, the blends with triester also have higher tensile modulus than the others. From these results, the primary factor that affects tensile modulus is thought to be miscibility due to transesterification, as well as, to the amount of linked polymer. In particular, the tensile modulus of 290-30-05T blend, where transesterification has occurred without significant reduction of molecular weight, is 1660 MPa.

This value is 22% higher than that of PC and 16% higher than that of LC10.

Tensile strength is also shown as a function of weight-average molecular weight in Figure 11. On the whole, tensile strength of reactive blends except 290-30-07T is almost maintained without severe reduction of molecular weight because the tensile strength of LCP is similar to that of PC (the tensile strength of LCP is 65 MPa and that of PC is 66 MPa). In the case of 290-30-07T, tensile strength is 31 MPa, which is remarkably lower than that of other blends. This result indicates that the failure mode might be changed from ductile to brittle because of the severe reduction in molecular weight. Gardner and Martin reported that tensile strength dropped off rapidly below a critical value ($\bar{M}_n = 14,300$, $\bar{M}_w = 33,800$) and that the failure mode changed from ductile to brittle.¹⁹

The tensile elongation as a function of degree of incorporation in PC/LCP blends is shown in Figure 12. The tensile elongation of PC is 34% whereas other blends have significantly lower tensile elongation than PC. This result can be attributed to the low elongation of LCP. However, the 290-60-03 and 290-30-05T in reactive blends have higher elongation than other reactive blends, which is likely because of the increase of DI in the absence of severe reduction of molecular weight.

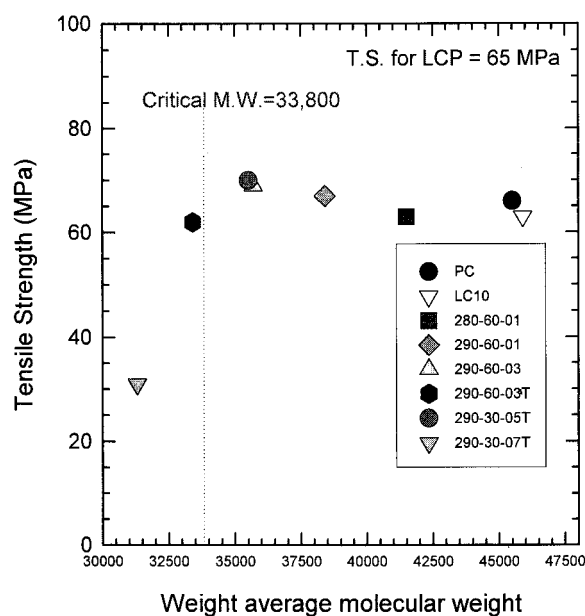


Figure 11 Tensile strengths for PC/LCP blends as a function of dumbbell with weight-average molecular weights.

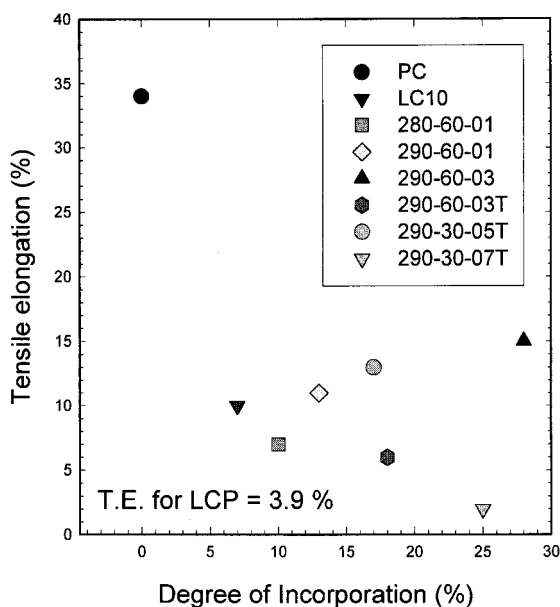


Figure 12 Tensile elongations for PC/LCP blends as a form of dumbbell with weight average molecular weights.

CONCLUSIONS

Chemical reactions such as transesterification and depolymerization affected miscibility, molecular weight, and mechanical properties in PC/LCP blends. In particular, excessive chemical reactions reduced molecular weight of reactive blends severely and deteriorated the mechanical properties of blends, even though miscibility was improved. 290-30-05T in all prepared reactive blends can be considered the optimal reactive blend in which chemical reactions were adequately controlled without severe reduction of molecular weight. Therefore, it can be concluded that the properties of the reactive blends can be controlled by means of the chemical reactions through consideration of several factors, such as preparation time, temperature, and the amount and type of catalyst and other additives.

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