

Effect of Transesterification on the Morphology and Mechanical Properties of a Blend Containing a Liquid Crystalline Polymer

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ABSTRACT: Transesterification of polymer blends containing polyesters is often utilized to improve the interfacial adhesion and mechanical properties of a phase-separated blend. However, in some circumstances, the transesterification can also modify the morphology (crystallinity or liquid crystallinity) of the blend components due to the disruption of the structure of a regular polymer. This, in turn, can deteriorate the mechanical properties of the blend. We present, in this article, results that correlate the extent of transesterification between a liquid crystalline polyester and polycarbonate to the change in the mechanical properties of the blend and the liquid crystallinity of the liquid crystalline polymer (LCP). The results exemplify the need to understand the role of transesterification on the morphology and mechanical properties of the blend so that the optimum processing conditions may be found. The experimental protocol can also be used as a guide to determine these optimal processing conditions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2583–2592, 2001

Key words: transesterification; liquid crystalline polymer; blends; interface; morphology

INTRODUCTION

Blending two or more polymers offers a method to create materials with novel properties. It also can afford an avenue by which the desired properties of an expensive material can be economically utilized. This is the case with liquid crystalline polymers (LCPs), which exhibited great promise of opening a new era of lightweight, high-strength materials when they were first introduced commercially. Unfortunately, these hopes and predictions have not come to fruition due to difficulties in processing and the high cost of the monomer

and polymerization. One method to overcome this economic factor is to mix the LCP with less expensive polymers to create a molecular composite. Unfortunately, this method also has difficulties, primarily due to the immiscibility of two polymers. The result is a two-phase system that does not retain the (desired) mechanical properties of the original components. The inferior properties are primarily the result of a weak interface between the two phases.

One method to improve the properties of a phase-separated polymer blend is to add an interfacial modifier to the blend that can improve the adhesion between the two phases and improve the properties of the resultant mixture.^{1–5} One type of interfacial modifier that has shown significant promise is a copolymer that consists of the two monomers that make up the homopolymers

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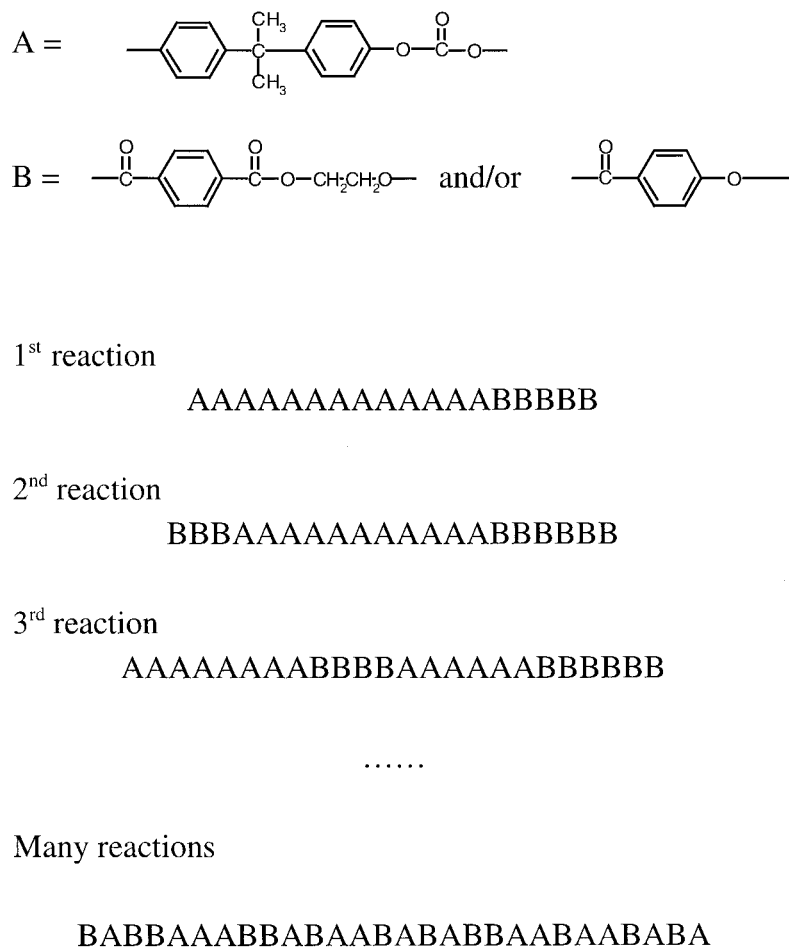


Figure 1 Representation of the transesterification process. This diagram is meant to exemplify the random nature of the resultant copolymers and disruption of polymer rigidity when one of the homopolymers is LC.

that are being blended. Additionally, it is well known that two polyesters can undergo exchange reactions at elevated temperatures to form copolymers of the two polymers.⁶⁻³¹ This process of transesterification is depicted in Figure 1, which exemplifies that the initial reaction between two homopolymers creates a diblock copolymer; however, as that diblock undergoes further transesterification reactions, the resultant copolymer attains a more random microstructure. It should also be noted that the later reactions in this scheme could be between two copolymers or a copolymer and either homopolymer. This reaction occurs at the interface between the two phases in a phase-separated system. Thus, the copolymer that can act as an interfacial modifier to strengthen the blend is created at the interface where it is needed. However, if transesterification is allowed to proceed for too long, it will lead to a change in the structure of the polymer due to the incorporation

the one monomer into the other polymer chain. This is most obvious in the case where one of the components is an LCP. The LCP possesses unique mechanical properties due to the rigid structure of the polymer chain; transesterification will incorporate flexible segments into an LCP chain, which can alter the rigid nature of the backbone and diminish the liquid crystalline and mechanical properties of the system. This article is a study of this trade-off and is meant to correlate the extent of transesterification between an LCP and an amorphous polymer to the liquid crystalline (LC) properties of the system and match both of those parameters to its mechanical properties.

EXPERIMENTAL

Polycarbonate (PC) ($M_w = 64,000$ g/mol), phenol, methanol, and tetrachloroethane (TCE) were pur-

chased from the Aldrich Chemical Co. (Milwaukee, WI). Poly(hydroxy benzoate-co-ethylene terephthalate) (PHB-PET; 40/60 molar ratio; $M_w = 50,000$ g/mol) was provided by the Eastman Chemical Co. (Kingsport, TN). PC was dissolved in toluene and was precipitated in methanol to remove any impurities. The blend of PC and PHB-PET (40/60, w/w %) was prepared by dissolving the polymers in a mixture of phenol and TCE 50/50 (w/w %) and then precipitated into methanol. The blends were kept *in vacuo* for 4 days at 100°C to remove any residual solvent. To examine the process of transesterification, the blends were annealed under nitrogen at 260°C for different times. The quantification of the transesterification that occurs in the blends was carried out by ^{13}C -NMR spectroscopy using a 400-MHz Bruker NMR spectrometer. A 10% (w/v %) solution of the annealed blend in a mixture of $\text{CDCl}_3/\text{CF}_3\text{COOD}$ (85/15, v/v %) was prepared for the ^{13}C -NMR studies. Optical microscopy of the blends was performed using an Olympus BH-2 microscope with polarizing and phase-contrast optics. Images of the morphology observed in the microscope were captured by a video camera connected to a PC with an image-capture card. Analysis of these images was completed using NIH image software. The tensile properties of the blends were obtained using an Instron instrument with a 2000-g load cell. The samples were prepared by melt-pressing unannealed and annealed blends to thin films (2.5 cm \times 2.5 mm). At least five samples of each blend were analyzed for the tensile measurement. The average Young's modulus of these samples is reported for each blend.

RESULTS AND DISCUSSION

It is well established that polyesters can undergo ester-ester interchange reactions or transesterification with itself or with other polymers at elevated temperatures.^{11,12} Although the blends of thermoplastic liquid crystalline (LC) polyesters and flexible coiled polymers are usually immiscible due to the low entropy of mixing, transesterification can be utilized to improve the interfacial adhesion or miscibility of the blends. It was the goal of this project to correlate the extent of transesterification as defined by the change in the mol fraction of dyads formed as a result of the transesterification to the LC nature and mechanical properties of the blend. The extent of transesterification between PHB-PET and PC in the blend was

monitored using ^{13}C -NMR after annealing at 260°C for various times. ^{13}C -NMR spectroscopy provided evidence of new bond formation between carbonate linkages and the bonds in the LCP, PET-PHB. This evidence is in the form of new peaks in the ^{13}C spectra, which can be analyzed to quantify the extent of transesterification that has taken place.

The ^{13}C -NMR spectra of the PC/PHB-PET blend (40/60, w/w%) upon annealing at 260°C for 0, 30, 45, and 60 min are shown in Figures 2-4 in the region of 120, 148, and 165 ppm, respectively. Examination of these spectra shows the appearance of new resonance signals at 120.9, 148.4, and 165.9 ppm after at least 30 min of annealing. These new signals can be attributed to the formation of bisphenol-A oxybenzoate and bisphenol-A terephthalate dyads resulting from transesterification between PC and PET-PHB. More specifically, the peak at 165.9 ppm corresponds to the carbonyl of the bisphenol-A oxybenzoate dyad, while the peaks at 148.3 and 120.9 ppm correspond to aromatic carbons in the bisphenol-A terephthalate dyad. The chemical structures and ^{13}C -NMR peak assignments of these dyads are shown in Figure 5.

Wei and Ho³² verified the assignments of these peaks by model compound studies of the reaction between PC and hydroxy benzoic acid or terephthalic acid (monomer units of PHB-PET) after heating each mixture to 300°C. The NMR analysis of PC/hydroxybenzoic acid and PC/terephthalic acid mixtures after heating also showed the appearance of new peaks at 120.9, 148.3, and 165.9 ppm, providing evidence that the new peaks are a result of the introduction of bisphenol-A oxybenzoate and bisphenol-A terephthalate dyads.

Note that the area under these peaks increases with the annealing time up to 60 min. This is expected because the amount of these dyads increases as transesterification proceeds. However, the integration of these peaks suggests no significant growth in the area under these peaks beyond 60-min annealing of the blend. This may be interpreted to denote that the formation of new bisphenol-A oxybenzoate and bisphenol-A terephthalate dyads has reached a steady state. Therefore, further transesterification results in the production and destruction of these dyads, that is, equilibrium.

Furthermore, a quantitative analysis of the formed copolymers in the PC/PHB-PET blend can be completed to quantify the amount of each

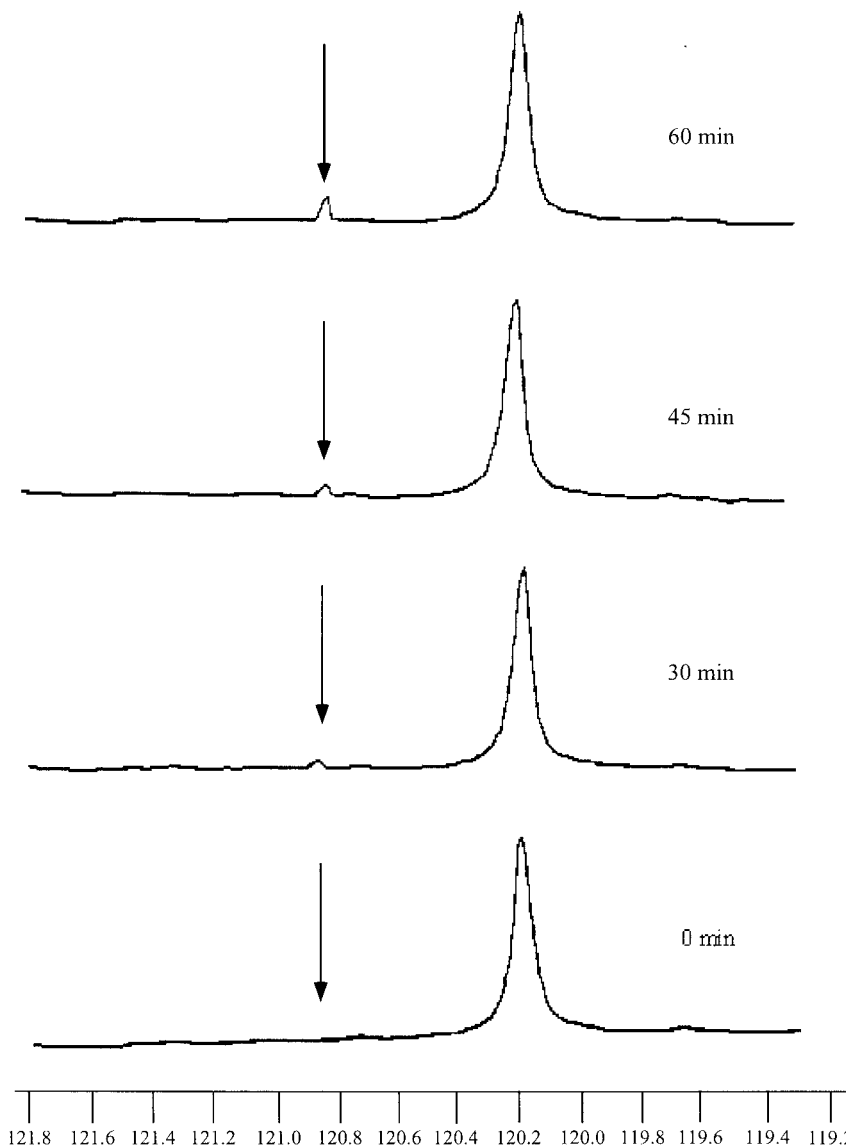


Figure 2 ^{13}C -NMR spectra of the blends in the region of 120 ppm as a function of annealing time at 260°C .

transesterification product by utilizing an analysis developed by Yamadera et al. and Devaux et al.^{30,31} From this analysis, one can obtain the mol fractions of the newly created dyads from knowledge of the mol fractions in the initial components in the blend and the probabilities of the formation of the dyads. In the analysis, the integrals under the peaks in the ^{13}C -NMR spectra are used as the probability of the formation of the respective dyads. Thus, the areas under the peaks of the formed copolymer dyads are directly proportional to the probability of the formation for the copolymer dyads.

Knowing the initial amount of PC and PHB-PET (or the initial amount of the starting com-

ponents) in the blend, the mol fraction of bisphenol-A terephthalate and bisphenol-A oxybenzoate dyads in the PC/PHB-PET blends can thus be calculated. Table I shows the calculated mol fractions of bisphenol-A oxybenzoate and bisphenol-A terephthalate dyads in the PC/PHB-PET blends after 30, 45, and 60 min of annealing at 260°C .

The tabulated values of mol fractions of bisphenol-A oxybenzoate and bisphenol-A terephthalate dyads are plotted in Figure 6. The data indicate that, as the annealing time of the blend increases, the mol fraction of each of the dyads produced from the transesterification between PC and PHB-PET increases. A steeper increase is observed for the

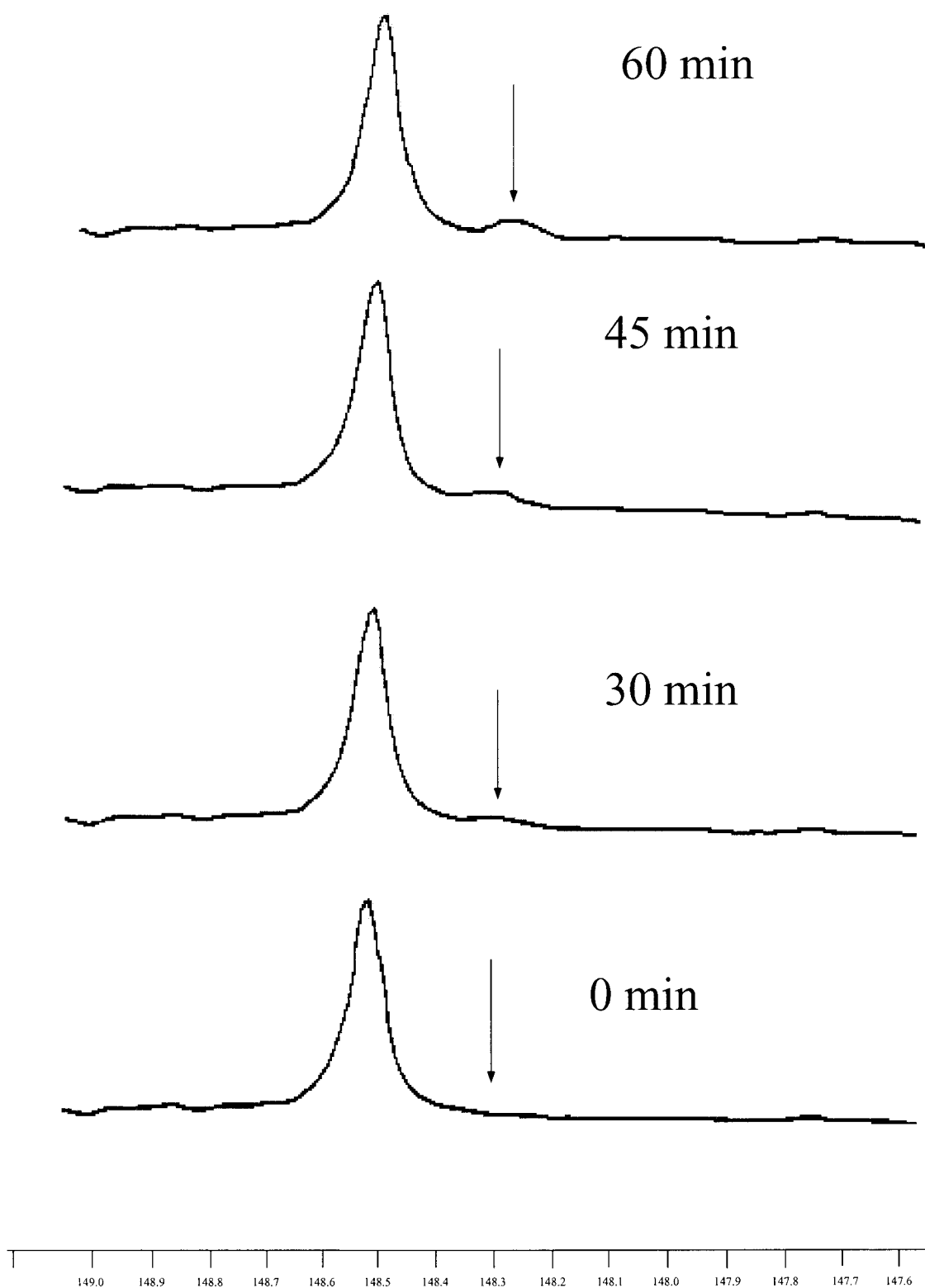


Figure 3 ^{13}C -NMR spectra of the blends in the region of 148 ppm as a function of annealing time at 260°C.

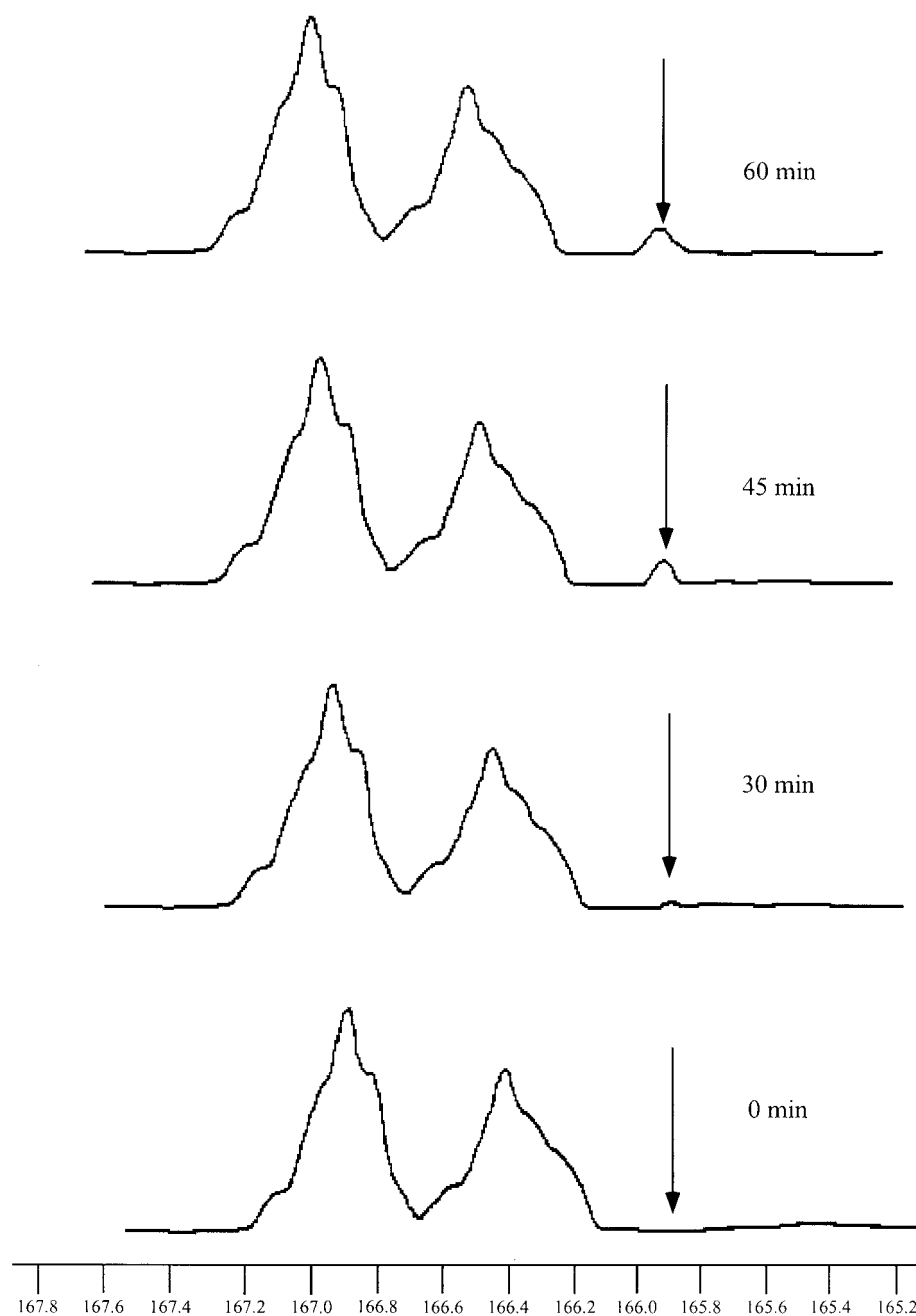
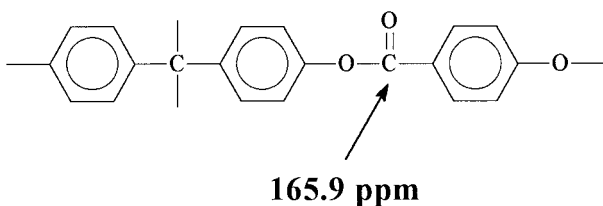


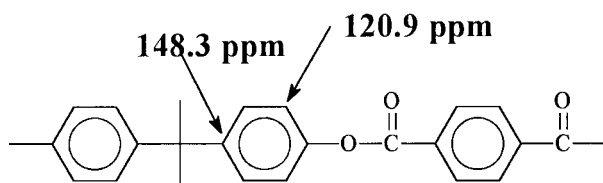
Figure 4 ^{13}C -NMR spectra of the blends in the region of 165 ppm as a function of annealing time at 260°C.

165.9-ppm peak that corresponds to the carbonyl group of a bisphenol-A oxybenzoate dyad, especially after 30-min annealing. This suggests that the rate of formation of the bisphenol-A oxybenzoate dyad is faster than that of the bisphenol-A terephthalate dyad at this temperature. A feasible explanation for this behavior may be related to the rigid structure of the PHB segments in the PHB-PET chain. The more rigid PHB segment has a larger size than that

of the flexible PET segment. Based on simple collision theory, the collision frequency in chemical reactions is proportional to the square of the size of the reacting species.³³ Therefore, one possible explanation for these results is that the more rigid PHB segments have a higher probability of collision with PC to form bisphenol-A oxybenzoate dyads than that of the PET segments simply due to its larger size.



Bisphenol-A-Oxybenzoate Dyad



Bisphenol-A-Terephthalate Dyad

Figure 5 Structures and ^{13}C -NMR peak assignments for the new dyad formed by the transesterification process.

Thus, the incremental formation of transient bisphenol-A oxybenzoate and bisphenol-A terephthalate dyads up to 60 min of annealing has been confirmed and quantified by ^{13}C -NMR spectroscopy. The NMR data provides the chemical signature for the transesterification between PC and PHB-PET upon annealing at 260°C . The objective of this study was to correlate the changes in the microstructure of the PC/PHB-PET blend due to transesterification to its macroscopic properties such as the blend morphology and mechanical properties. It is known that transesterification can alter the morphology of polymer blends.¹ In the case of PC/PHB-PET, the chemical structure of the LC PHB-PET is dramatically altered as transesterification proceeds. As a consequence of successive transreactions between the LCP and PC, random copolymers are formed in the blend. This, in turn, results in a loss of the LC character of the PHB-PET as the backbone linkages of the LCP become less rigid as more carbonate groups are incorporated into the chains.

The LC domains in a blend exhibit birefringence under cross-polarized light. However, the birefringence emanating from the LC domains under cross-polarized light in the blend diminishes as the PHB-PET undergoes transesterification with PC upon annealing. This is due to the

breakdown of the rigid structure of the PHB-PET chain as the transesterification proceeds. The loss of liquid crystallinity in the PC/PHB-PET blends can be quantified using polarized optical microscopy and image analysis. The parameter of interest in this quantification process is the integrated density of the image, which is related to the birefringence of the blend images. The integrated density is defined as the intensity of the birefringent LC domains in the image minus the intensity of the isotropic background and is essentially a measure of how bright the micrograph is. Figure 7 shows a plot of the measured integrated density of the annealed PC/PET-PHB blends at different annealing times. As seen in Figure 7, the measured integrated density shows a decrease as annealing time increases due to the expansion of isotropic domains at longer annealing times. Note that the darker isotropic regions have lower pixel intensities than that of the brighter LC domains, which results in the negative values for the measured integrated intensities. This plot also shows that the integrated density declines sharply in the early stages of the annealing process, indicating a sharp decrease in the birefringence of the LC domains during the first 30 min of the annealing process. This is presumably due to the rapid destruction of the LC structure of PHB-PET chains during their initial reaction with PC molecules. However, the integrated density levels off after the first 30 min, up to 60 min. These data demonstrate that the transesterification process alters the LC nature of the LCP during the early stages of the annealing process. This, in turn, suggests that to retain the LC character of the LCP and its associated advantageous properties scrambling reactions must be limited to short times.

Table I Mol Fraction of Bisphenol-A Oxybenzoate and Bisphenol-A Terephthalate Dyads in PC/PHB-PET Blends Upon Annealing at 260°C

| Annealing Time (min) | Dyad Mole Fraction at 120.9 ppm (mol) | Dyad Mol Fraction at 148.39 ppm (mol) | Dyad Mol Fraction at 165.9 ppm (mol) |
|----------------------|---------------------------------------|---------------------------------------|--------------------------------------|
| 0 | 0.000 | 0.000 | 0.000 |
| 30 | 0.003442 | 0.010614 | 0.006844 |
| 45 | 0.007720 | 0.018038 | 0.029348 |
| 60 | 0.011136 | 0.025781 | 0.033524 |

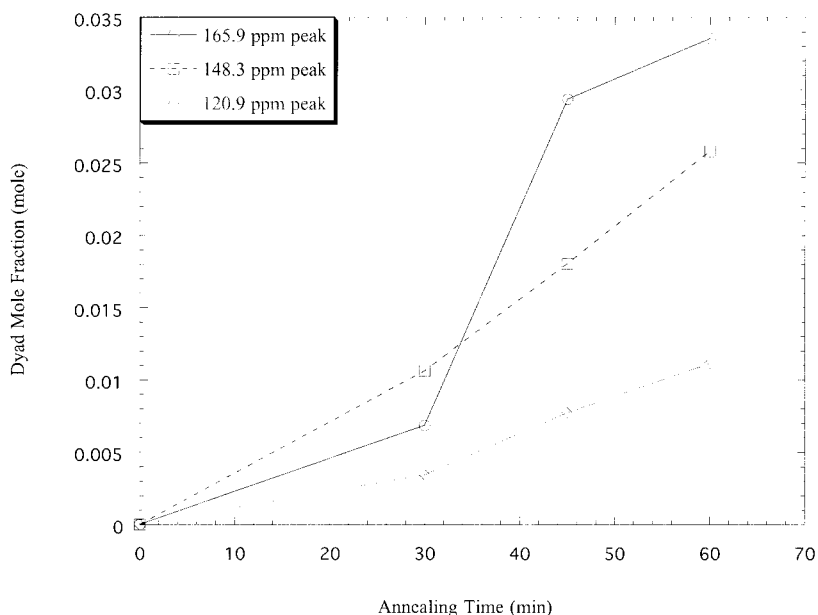


Figure 6 Time evolution of the dyads formed by transesterification. This analysis provides a quantitative measure of the extent of transesterification.

Lastly, the correlation of the extent of transesterification and the LC nature of the PHB-PET chains to the mechanical properties of the PC/PET-PHB blend is presented. Generally, the formation of copolymers at the interface by transesterification reactions should promote interfacial adhesion between the two phases and improve the mechanical properties of the blend. To exam-

ine this in the current system, the Young's modulus of the PC/PHB-PET blend was measured as a function of the annealing time. These data are presented in Figure 8, which shows a plot of the Young's modulus of the blend as a function of the annealing time.

These data show an initial decrease in the Young's modulus of the blend after 30 min of

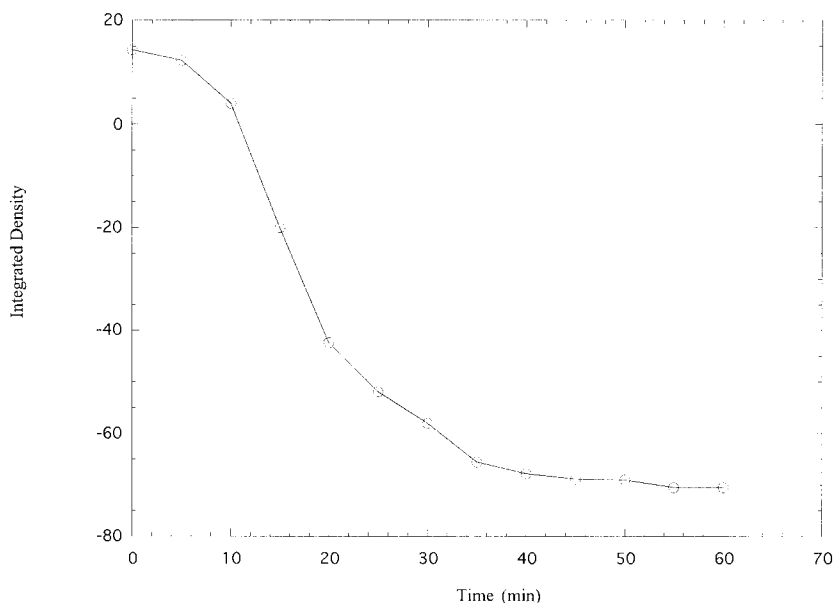


Figure 7 Loss of birefringence in the blend as a function of annealing time at 260°C.

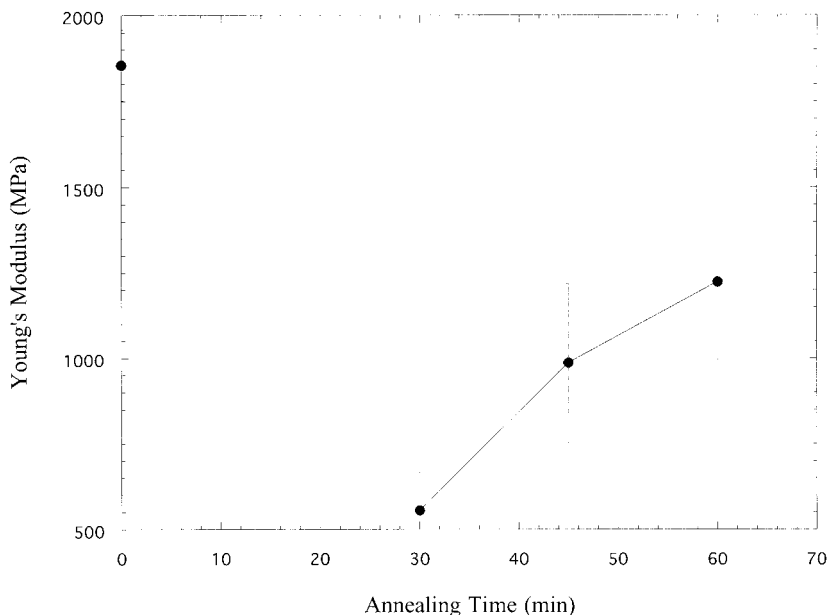


Figure 8 Change in the Young's modulus of the blend as a function of annealing time at 260°C. Comparison of Figures 5, 6, and 7 provide the information needed to understand the trade-off between interfacial modification and structure alteration during transesterification.

annealing and then further increases in the modulus with annealing time up to 60 min. The initial decrease in the modulus in the first 30 min of annealing may be explained as due to the disruption of the LC nature and rigid structure of PHB-PET upon transesterification between PC and PHB-PET, as shown in Figure 7. However, as the transesterification proceeds for more than 30 min, the interfacial adhesion between the PC phase and the PHB-PET phase will increase due to increased formation of copolymers at the interface. As a result, a recovery trend in the Young's modulus is observed up to 60-min annealing time. Note that the overall Young's modulus of the blend after 60 min of annealing is still lower than that of the unannealed sample. This is further evidence of the importance of the loss of the LC nature of the blend.

This interpretation of the data can lead to the expectation that there is a point during transesterification where the Young's modulus of the blend can be optimized without major destruction of the LC structure of PHB-PET. In other words, a compromise between the detrimental loss of the LC character within the blend and the beneficial interfacial modification of the annealed blends can be obtained. Optical microscopy and tensile measurement results suggest that this point can

be reached in the annealed PC/PET-PHB blend with an annealing time of less than 30 min.

Based on our ^{13}C -NMR results, the first signatures of the formed bisphenol-A oxybenzoate and bisphenol-A terephthalate dyads were observed in the blend that has been annealed for 30 min. Thus, it was difficult for us to verify the formation of bisphenol-A oxybenzoate and bisphenol-A terephthalate dyads by NMR spectroscopy in the annealed blends for less than 30 min. This is presumably due to limited sensitivity (signal/noise ratio) of the NMR instrument used in this study. The future study of these blends with more sensitive NMR instruments (600 MHz or higher) with a higher resolution will help in the determination of the optimal point in these blends.

CONCLUSIONS

The formation of copolymers at the interface of a blend containing an LCP and an amorphous polymer was characterized using ^{13}C -NMR spectroscopy and quantified by dyad analysis of the bisphenol-A oxybenzoate and bisphenol-A terephthalate dyads. The mol fraction of these dyads increases with the annealing time up to 60 min as a result of transesterification reactions between

PC and PHB–PET. A loss of LC character was also observed on these same timescales as a result of the disruption of the rigid structure of PHB–PET in the blend and quantified by video microscopy. These measurements were also correlated to the Young's modulus of the PC/PHB–PET blend. The results of these complimentary studies exemplify a trade-off between the loss of the LC character of the blend and the improved interfacial adhesion resulting from transesterification between the two components in the blend. More broadly, this article described a set of complimentary experiments that can be utilized to correlate the microscopic changes in a blend due to scrambling reactions that can occur during processing to the morphology and ultimate properties of the final multicomponent product.

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