Transesterification and Mechanical Properties of Blends of a Model Thermotropic Polyester and Polycarbonate

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ABSTRACT: Transesterification between a model thermotropic polyester (TTP) and polycarbonate (PC) was investigated during melt blending in a twin-screw mini-compounder at temperatures below and above the clearing temperature (T_{cl}) of the TTP. For the investigation, a model TTP, poly[(phenylsulfonyl)-*p*-phenylene hexamethylene-bis(4-oxybenzoate)] (PSHQ6), was synthesized that has a T_{cl} (206 °C) much lower than the thermal degradation temperature (ca. 350 °C). PSHQ6 was melt-blended with PC at temperatures below and above the T_{cl} of PSHQ6. In the preparation of the blends, temperature and residence time in the extruder were varied. It was observed from ^{13}C nuclear magnetic resonance (NMR) spectroscopy that negligible transesterification occurred when a blend was prepared at temperatures below the T_{cl} of PSHQ6, while the extent of transesterification increased steadily as the melt blending temperature increased above the T_{cl} of PSHQ6. The tensile strength of injection-molded specimens of PC/PSHQ6 blends prepared under various processing conditions was also investigated, showing that it first increased with increasing melt blending temperature, going through a maximum at a temperature above the T_{cl} of PSHQ6, and then decreased rapidly as the melt blending temperature increased further. The experimental observations indicate that there exists an optimum degree of transesterification that gives rise to the highest tensile and impact strengths of PC/PSHQ6 blends. That is, the effectiveness of PSHQ6 as a reinforcing agent for an improvement of the mechanical properties of injection-molded PC specimens begins to diminish when the extent of transesterification exceeds a certain critical level. This is attributed to the fact that the inherent liquid crystalline characteristics of PSHQ6 were lost when the extent of transesterification exceeded a certain critical level.

1. Introduction

In the past, investigations of transesterification between two otherwise immiscible thermoplastic polyesters (e.g., polycarbonate (PC) and poly(butylene terephthalate) (PBT)) attracted much attention from polymer researchers.[1−10] The investigations were motivated by the desire to obtain enhanced mechanical properties of a homogeneous random copolymer via transesterification between two thermoplastic polyesters. There are two different views on the sequence of events that produce a homogeneous blend system when two immiscible thermoplastic polyesters are mixed. It is the prevailing view that transesterification between two thermoplastic polyesters is a necessary step to obtain a homogeneous blend (or random copolymer), but others[11] argue that intermolecular mixing between two thermoplastic polyesters may first occur followed by transesterification; i.e., transesterification may not be a necessary step to obtain a homogeneous blend.

Some research groups[12−17] investigated transesterification between thermotropic polyester (TTP) and thermoplastic polyester (TPP), while others[18−25] reported on the mechanical properties and/or the morphology of such binary blends. For such purposes, two commercial TTPs have extensively been employed, namely, copolyesters of *p*-hydroxybenzoic acid (HBA) and poly(ethylene terephthalate) (PET), which were first developed by researchers[26] at Eastman Chemical Company and later commercialized by Unitika in Japan, and copolyesters of HBA and 6-hydroxy-2-naphthoic acid (HNA) (Vectra series), which were developed by researchers[27] at Celanese and then commercialized. The preparations of TTP/TPP blends by the investigations cited above were motivated by the expectation that the mechanical properties of a TPP (e.g., PET, PBT, or PC) would be improved by the orientation of the rigid or semiflexible chains of the TTP in the blend during processing. However, implicit in the expectation was that the TTP/TPP pair chosen would undergo a sufficient degree of transesterification between the ester groups in, for instance, HBA−PET or HBA−HNA copolyesters and the ester groups in the TPP. In the preparation of TTP/TPP blends, two methods were employed; some research groups[12,14−17] employed solution blending (i.e., coprecipitation in a common solvent) followed by isothermal annealing, and others[18−25] employed melt blending.

When the method of melt blending is employed, the extent of transesterification between TTP and TPP depends on melt blending conditions, which include melt blending temperature, duration of blending, and difference in melt viscosity between TTP and TPP. Note that melt viscosity depends on temperature, and the difference in melt viscosity between TTP and TPP would play a significant role in determining the extent of transesterification. It is worth pointing out that the melt viscosity of a TTP at temperatures below its clearing temperature (T_{cl}) is much higher than that at temperatures above its T_{cl}. In this regard, an interesting question may be raised as to whether melt blending temperature in relation to the T_{cl} of a TTP would influence greatly the extent of transesterification between the TTP and TPP chosen. This consideration will not be an issue when two TPPs are melt-blended. It is worth pointing out that the T_{cl} of TTP is much higher than its melting temperature (T_m) or glass

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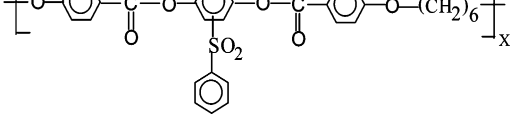
transition temperature (T_g), and often it is higher than the thermal degradation temperature. This is the case for HBA−PET and HBA−HNA copolyesters. Under such circumstances, it is not possible to choose a melt blending temperature above the T_{cl} of TTP, and thus it is anticipated that the extent of transesterification between HBA−PET or HBA−HNA copolyesters and TPP (e.g., PC, PBT, or PET) would be rather low owing to large differences in melt viscosity between the constituent components.

In this regard, the experimental evidence reported in the literature on the transesterification in TTP/TPP blends is very confusing. Radmard and Dadmun[17] investigated transesterification in solution-blended specimens composed of a HBA−PET copolyester and PC during isothermal annealing at 260 °C, which was below the T_{cl} of the HBA−PET copolyester, for a period up to 60 min, and reported a reasonable degree of transesterification as determined by ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Jo et al.[14] reported that a reasonable degree of transesterification occurred in solution-blended specimens composed of a specially synthesized TTP and PBT during isothermal annealing at 290 °C, which was below the T_{cl} (340 °C) of the TTP employed, for a period up to 90 min, as determined by ^{13}C NMR spectroscopy. Similar observations were also reported by Wei and co-workers.[15,16] Further, a number of research groups[18−25] reported on the morphology of TTP/TPP blends and/or an improvement in certain mechanical properties of a TPP (e.g., PC; PBT) when it was melt-blended with a commercial TTP (e.g., HBA−PET copolyester; HBA−HNA copolyester) at temperatures below its T_{cl}. Since the T_{cl}s of HBA−PET and HBA−HNA copolyesters are higher than their thermal degradation temperatures, it is not possible to anneal solution-blended specimens of those mixtures, or to conduct melt blending experiments, at temperatures above their T_{cl}s.

However, a question may be raised as to whether measurable transesterification can actually take place during isothermal annealing or melt blending of a TTP/TPP mixture at temperatures below the T_{cl} of the TTP in a reasonably short time, say within 10 min. This question is very pertinent to the achievement of a significant improvement in certain mechanical properties of TPP in the presence of a TTP because this can be realized only when a sufficient degree of transesterification takes place between the TTP and TPP chosen. Since the differences in melt viscosity between TTP and TPP are expected to be very high at melt blending temperatures below the T_{cl} of TTP, it is reasonable to speculate that the extent of transesterification between TTP and TPP might be insignificant under such processing conditions, while a significant degree of transesterification may occur when the same mixture is melt-blended at temperatures much higher than the T_{cl} of TTP. To test this speculation, one must employ a TTP whose T_{cl} is sufficiently below its thermal degradation temperature.

Very recently, we carried out an investigation to test the speculation made above by synthesizing a model TTP, poly[(phenylsulfonyl)-*p*-phenylene hexamethylene-bis(4-oxybenzoate)] (PSHQ6), with the chemical structure



Unlike HBA−PET and HBA−HNA copolyesters, PSHQ6 has a T_{cl} of 206 °C, which is far below its thermal degradation temperature (350 °C). We then prepared PC/PSHQ6 blends by melt blending, using a twin-screw mini-compounder, at temperatures below and above the T_{cl} of PSHQ6. In the preparation of PC/PSHQ6 blends we varied the residence time (2−20 min) inside the extruder. We determined, via ^{13}C NMR spectroscopy, the extent of transesterification of each blend prepared. Further, we investigated the tensile and impact properties of injection-molded specimens of PC/PSHQ6 blends as affected by the extent of transesterification. For comparison, we also prepared PC/(HBA−HNA copolyester) blends by melt blending at temperatures below the T_{cl} of the HBA−HNA copolyester. And then, the tensile properties of injection-molded PC/(HBA−HNA copolyester) blends were measured. In this paper we summarize the highlights of our findings.

2. Background for the Determination of the Randomness of Linear Copolycondensates

^{13}C NMR spectroscopy is a very useful experimental technique that enables one to determine quantitatively the extent of transesterification when the polyesters have significantly different chemical structures and they are soluble in a given solvent before and after transesterification occurs. Yamadera and Murano[28] were probably the first to evaluate the degree of randomness (B) and the mean sequence lengths for the structure characterization of three-component copolycondensates, based on the determination of three types of triads.

Devaux et al.[3] conducted a theoretical analysis of the structure of four-component copolycondensates resulting from transesterification between two polycondensates having different chemical natures. In their analysis, six parameters were used to describe a four-component system, as shown below, resulting from transesterification between two linear polycondensates, $(A_1B_1)_p$ and $(A_2B_2)_q$

$$[(A_1{-}B_1)_x{-}(A_2{-}B_1)_y]_m{-}[(A_1{-}B_2)_z{-}(A_2{-}B_2)_w]_n$$

where A_1 and A_2, and B_1 and B_2, represent the monomer units of different chemical structures but of the same functionality, and p and q denote the number-average degrees of polymerization; x, y, z, and w denote the mean lengths of the various sequences; and m and n denote the mean lengths of blocks having in common the same B_1 or B_2 unit. The mole fractions of A_i ($i = 1, 2$) and B_j ($j = 1, 2$) units are defined by the concentration ratios as

$$F_{A_i} = [A_i]/\sum_{i=1}^{2}[A_i] \tag{1}$$

$$F_{B_j} = [B_j]/\sum_{j=1}^{2}[B_j] \tag{2}$$

For dyad analysis, the fraction of dyads A_iB_j ($i, j = 1, 2$) is defined by

$$F_{A_iB_j} = [A_iB_j]/\sum_{i,j=1}^{2}[A_iB_j] = [A_iB_j]/\sum_{i=1}^{2}[A_i] \tag{3}$$

The probability of finding an A_i unit followed by a B_j unit is given by

$$P_{A_iB_j} = [A_iB_j]/\sum_{j=1}^{2}[A_iB_j] = [A_iB_j]/[A_i] \quad (i, j = 1, 2) \tag{4}$$

and the probability of finding a B_j unit followed by an A_i unit is given by

$$P_{B_jA_i} = [B_jA_i]/[B_j] = [A_iB_j]/[A_j] \quad (i, j = 1, 2) \qquad (5)$$

Thus, the degree of randomness B is defined by

$$B = P_{A_iB_j} + P_{B_jA_i} \quad (i, j = 1, 2; i \neq j) \qquad (6)$$

$B = 0$ is characteristic of a copolycondensate with long sequences or a mixture of the two polycondensates; $B < 1$ suggests that the units tend to cluster in homogeneous sequences A_1B_1 and A_2B_2; $B = 1$ indicates that the units are randomly distributed in the copolycondensate obeying Bernoulli statistics; $B > 1$ represents a tendency of A_1B_2 and A_2B_1 sequences to predominate over A_1B_1 and A_2B_2 sequences; $B = 2$ denotes the formation of very long alternate sequences A_1B_2 and A_2B_1 during transesterification.

3. Experimental Section

3.1. Materials and Preparation of Binary Blends. A model TTP, PSHQ6, employed in this study was synthesized following the procedures described in the literature.[29,30] Blends of PSHQ6 and PC (Dow Chemical Company, 22MFR) were prepared. For comparison, blends of PC and HBA-HNA copolyester (Celanese Company, Vectra A900) and blends of PC and high-density polyethylene (HDPE) (Dow Chemical Company, 25455N) were prepared.

70/30 PC/PSHQ6 blends were prepared by melt blending using a twin-screw mini-compounder (Haake), in which 70/30 refers to the weight percent of the component polymers. The choice of PC/PSHQ6 pair was made on the following basis. PC is a glassy polymer. According to Han et al.,[31] PC is so viscous that it hardly flows at temperatures below ca. 205 °C (T_g + 55 °C), and thus this temperature may be regarded as being equivalent to a melting point of a semicrystalline polymer, the so-called critical flow temperature of an amorphous polymer. On the other hand, PSHQ6 is very viscous below its T_{cl} (206 °C). Thus, the choice of the PC/PSHQ6 pair has enabled us to conduct melt blending at temperatures below and above the T_{cl} of PSHQ6 and yet well above the T_g of PC. During melt blending, the duration of blending was varied from 2 to 20 min at various temperatures below and above the T_{cl} of PSHQ6. The duration of melt blending within the twin-screw mini-compounder was controlled by recirculation before discharge and pelletizing. Also, blends of PC and HBA−HNA copolyester and blends of PC and HDPE with several different blend compositions were prepared using the same twin-screw mini-compounder.

3.2. Differential Scanning Calorimetry (DSC). Thermal transition temperatures of all blends prepared were determined using a differential scanning calorimeter (Perkin-Elmer 7). The instrument was calibrated for both heat flow and temperature using indium and zinc standards, and DSC runs were made under a nitrogen atmosphere with heating and cooling rates at 20 °C/min. To minimize variations of sample preparation history, all DSC runs were obtained from the second heating cycle. The peak position was taken as the transition temperature for melting or isotropization, and the inflection point was taken as the glass transition temperature. DSC thermograms for PC and PSHQ6 are given in Figure 1. It can be seen that (i) PC is a glassy polymer with a T_g of 152.1 °C and (ii) PSHQ6 is a semicrystalline liquid-crystalline polymer (LCP) with a T_g of 98.4 °C, a T_m of 174.7 °C, and a T_{cl} of 205.7 °C.

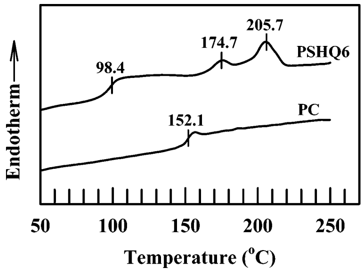


Figure 1. DSC thermograms at a heating rate of 20 °C/min in the second heating cycle for PC and PSHQ6.

3.3. ^{13}C Nuclear Magnetic Resonance (NMR) Spectroscopy. For solution-state ^{13}C NMR spectroscopy, samples were prepared by dissolving ca. 40 mg of PC/PSHQ6 blend in deuterated 1,1,2,2-tetrachloroethane placed in an NMR tube. ^{13}C NMR spectroscopy with proton broad-band decoupling at room temperature was conducted using a spectrometer (JEOL JNM-LA 400) operating at 100.5 MHz. As a measure of the extent of transesterification, the degree of randomness (B) of ester exchange was evaluated for the PC/PSHQ6 blends. The average of 16 384 acquisitions was used to produce an adequate signal-to-noise ratio. ^{13}C chemical shifts were expressed as values relative to tetramethylsilane (TMS). The pulse length was 4.7 μs. The ^{13}C NMR spectrum of the 70/30 PC/PSHQ6 specimen melt-blended at 240 °C for 20 min was measured using several "repetition times" in order to investigate the effect of spin−lattice relaxation on the peak intensities that were used for quantitative analysis. Since the relative peak intensities of the ^{13}C NMR spectrum were almost the same between the "repetition times" of 2 and 30 s, the "repetition time" of 2 s was used in this study. Methyl carbon and phenyl carbon have different nuclear Overhauser effects (NOEs). The apparent peak intensity multiplied by 0.889 as an NOE factor was used as the actual intensity of methyl carbon for the PC/PSHQ6 specimens. This NOE factor was estimated from the comparison between the peak intensities of the ^{13}C NMR spectrum for PC with proton broad-band decoupling and those without proton broad-band decoupling. The statistical analysis for evaluation of the degree of randomness (B) will be presented later in this paper.

3.4. Tensile Properties Measurement. Dumbbell-shaped specimens (ASTM D 638 type V) for tensile testing were prepared by injection-molding using a mini-injection molder (DSM). The tensile properties of the specimens were measured using an Instron tensile tester (Model 5567). The load cell used for tensile testing was an Instron static load cell with a 10 kN capacity. A cross-head speed of 5 mm/min was used for the tensile testing. The upper yield stress on the stress−strain curve was taken as the tensile strength of the specimens. The values of the tensile strength reported later in this paper are the average of at least three separate measurements.

3.5. Impact Properties Measurement. The specimens (ASTM standard, D 256) for impact testing were prepared by injection-molding using a mini-injection molder (DSM). The specimens were notched using a notching cutter (Model TMI 22-05) before impact testing. The Izod pendulum impact strength of blend specimens was measured using an impact tester (TMI No. 43-1). The values of the impact testing results reported later in this paper are the average of at least three separate measurements.

3.6. Birefringence Measurement. The birefringence ($\Delta n_{13} = n_1 - n_3$) between the flow direction (1) and the thickness direction (3) of an injection-molded slab (ASTM D 5023) was measured using an optical microscope (Leitz Laborlux 12 POL S) with cross-polarizers and a fourth-order compensator. The flow direction (1) was along the longitudinal direction of the slab. For the birefringence measurement, the following position on the surface in the longitudinal side was chosen: in the middle of the long side of the slab and 1/6th of the thickness of the slab from the edge. Birefringence measurements were conducted following the procedures described in the literature.[32]

3.7. Rheological Measurement. An Advanced Rheometric Expansion System (ARES, TA Instruments) was used in the oscillatory shear mode with a parallel-plate fixture (8 mm diameter) to conduct dynamic frequency sweep experiments, i.e., the dynamic storage modulus (G') and dynamic loss modulus (G'') were measured as functions of angular frequency (ω) ranging from 0.04 to 100 rad/s at various temperatures. Strain amplitude was varied from 0.01 to 0.06, which was found to be well within the linear viscoelasticity range of the materials investigated. The complex viscosity ($|\eta^*|$) was calculated from $|\eta^*(\omega)| = \{[G'(\omega)/\omega]^2 +$

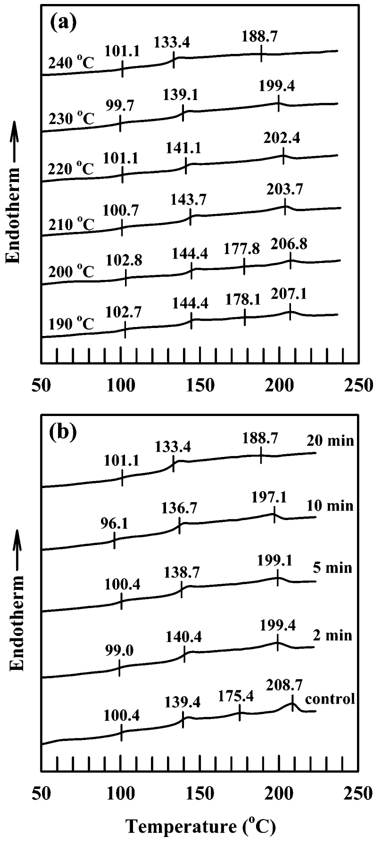


Figure 2. DSC thermograms at a heating rate of 20 °C/min in the second heating cycle for 70/30 PC/PSHQ6 blend specimens that were prepared by melt blending: (a) at various temperatures for 20 min and (b) for various durations at 240 °C.

$[G''(\omega)/\omega]^2\}^{1/2}$. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. The temperature control was satisfactory to within ±1 °C. All experiments were conducted under a nitrogen atmosphere to preclude oxidative degradation of the samples.

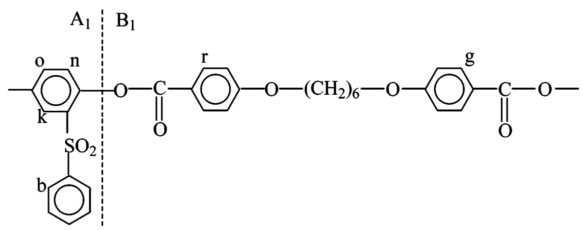
3.8. Optical Microscopy. The morphology of the blend samples prepared by melt blending, followed by compression-molding to obtain thin films, was observed using an optical microscope (Leitz Laborlux 12 POL S) equipped with a hot stage (Instec, HCS 302) and a digital camera (Diagnostic Instruments, Model 11.2 Color Mosaic).

4. Results and Discussion

4.1. Transesterification in PC/PSHQ6 Blends and Mechanical Properties of Injection-Molded PC/PSHQ6 Blend Specimens. (a) Thermal Transitions in PC/PSHQ6 Blends. Figure 2a gives DSC thermograms for 70/30 PC/PSHQ6 blend specimens prepared by melt blending for 20 min at various temperatures ranging from 190 to 240 °C. We obtained DSC thermograms for other blend ratios, but they are not presented for the reason of limited space available. The following observations are worth noting in Figure 2a. (i) The T_g (ca. 144 °C) of PC and the T_g (ca. 103 °C) of PSHQ6 in the blend remain more or less constant as the melt blending temperature is increased from 190 to 200 °C. (ii) The T_g of PC begins to decrease slowly, while the T_g of PSHQ6 changes very little as the melt blending temperature is increased above 200 °C. This observation seems to indicate that the miscibility between PC and PSHQ6 is enhanced as melt blending temperature is increased above the T_{cl} of PSHQ6, which is ca. 206 °C (see Figure 1). (iii) The T_{cl} of PSHQ6 begins to decrease noticeably as the melt blending temperature is increased from 200 to 210 °C and then continues to decrease as the melt blending temperature is increased further to 240 °C. This observation also suggests that an appreciable transesterification might occur at melt blending temperatures above the T_{cl} of PSHQ6, which is ca. 206 °C (see Figure 1), indicating that melt blending temperature relative to the T_{cl} of PSHQ6 plays an important role, at least qualitatively at this juncture, in understanding the circumstances under which a noticeable degree of transesterification occurs in 70/30 PC/PSHQ6 blend.

Chart 1

A_1B_1 dyad (in PSHQ6)



A_2B_2 dyad (in PC)

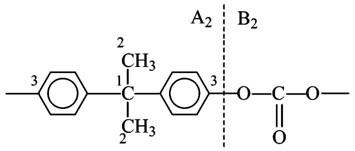


Figure 2b gives DSC thermograms for 70/30 PC/PSHQ6 blend specimens prepared by melt blending at 240 °C for various durations ranging from 2 to 20 min. Note that 240 °C employed for melt blending is higher than the T_{cl} (206 °C) of PSHQ6. Again, we also obtained DSC thermograms for other blend ratios, but they are not presented for the reason of limited space available. It is interesting to observe in Figure 2b that the T_{cl} of PSHQ6 continued to decrease as the melt blending at 240 °C continued for 20 min. It should be pointed out that an application of melt blending in an extruder brings about new interfaces between the constituent components, PC and PSHQ6. We hasten to point out, however, the renewal of interfaces during melt blending would not induce intermolecular mixing of the constituent components (thus a decrease in the T_{cl} of PSHQ6 in the 70/30 PC/PSHQ6 blend) when they are immiscible from a thermodynamic point of view.

(b) Transesterification in PC/PSHQ6 Blends as Determined from ^{13}C NMR Spectroscopy. To obtain direct evidence for transesterification between PC and PSHQ6, solution-state ^{13}C NMR spectroscopy for melt-blended PC/PSHQ6 blend specimens was conducted. The structures of the two dyads A_1B_1 and A_2B_2 before transesterification are shown in Chart 1 with various carbons coded. Upon transesterification, two additional dyads A_1B_2 and A_2B_1 are formed with various carbons being coded as shown in Chart 2.

Figure 3 describes ^{13}C NMR spectra of neat PC, in which we observe a very large peak at 30.81 ppm corresponding to C(2), methyl carbon in the A_2B_2 dyad for neat PC. Figure 4 describes ^{13}C NMR spectra of neat PSHQ6, in which we observe peaks at 128.92, 128.43, 132.58, and 132.40 ppm corresponding to C(b), C(o), C(r), and C(g), respectively, in the A_1B_1 dyad for neat PSHQ6. The ^{13}C NMR spectra for neat PC and neat PSHQ6 are presented as reference and for the purpose of comparison later with the ^{13}C NMR spectra for 70/30 PC/PSHQ6 blends prepared at different melt blending temperatures and for different durations of melt blending.

Chart 2

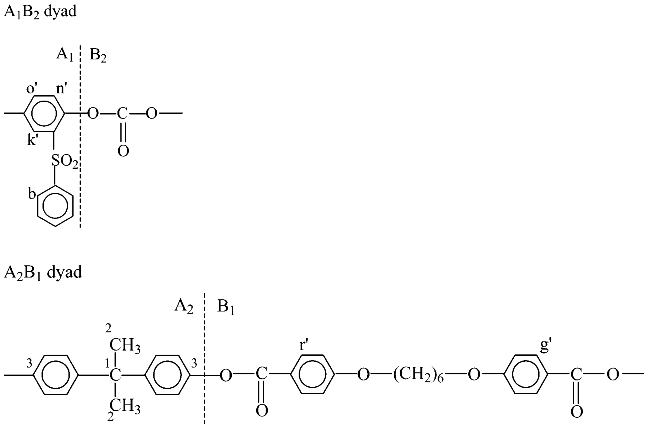


Figure 5 describes variations of ^{13}C NMR spectra for 70/30 PC/PSHQ6 specimens that were prepared by melt blending for 20 min at various temperatures. Referring to Figure 5, the peaks at 132.57, 132.39, and 128.41 ppm correspond to C(r), C(g), and C(o), respectively, in the dyad A_1B_1 in PSHQ6. The appearance of new peaks at 132.23, 132.13, and 129.60 ppm, which are assigned to C(r′) and C(g′) in the new dyad A_2B_1 and to C(o′) in the new dyad A_1B_2, respectively, confirms the occurrence of transesterification between PC and PSHQ6.

Figure 6 describes variations of ^{13}C NMR spectra for 70/30 PC/PSHQ6 blend specimens that were prepared for various durations of melt blending ranging from 2 to 20 min at 240 °C. The peaks at 132.57, 132.39, and 128.41 ppm and the new peaks at 132.23, 132.13, and 129.60 ppm in Figure 6 have the same assignments as those given in Figure 5. The emergence of the new peaks in the ^{13}C NMR spectra confirms the occurrence of transesterification between PC and PSHQ6 during melt blending at 240 °C.

To evaluate the degree of randomness *B* from the ^{13}C NMR spectra given in Figures 5 and 6, we have employed the following statistical method. The relative peak intensities (*I*) for C(r), C(g), C(r′), and C(g′) in various dyads, which were obtained by integrating the respective NMR peaks followed by the normalization of various NMR peak intensities by the peak intensity of a γ-CH_2 carbon in the hexamethylene unit of PSHQ6, were found to be very small, as compared to the relative peak intensities (*I*) for C(o), C(o′), and C(2) in various dyads. It should be mentioned that PSHQ6 showed many ^{13}C NMR peaks, and the intensity of each peak for PSHQ6 was much weaker than that for PC. Thus, in the present study, we have decided to use only the relative peak intensities (*I*) for C(o), C(o′), and C(2) in various dyads for calculation, which are summarized in Tables 1 and 2. Referring to the chemical structures of the four dyads presented above, we have used the relative peak intensities for various carbons given in Tables 1 and 2 to estimate the concentration of each dyad and each monomer unit as $[A_1B_1] = I_o$, $[A_1B_2] = [A_2B_1] = [B_2A_1] = [B_1A_2] = I_{o'}$, $[A_2B_2] = 0.5I_2$, $[A_1] = [B_1] = [A_1B_1] + [A_1B_2]$,

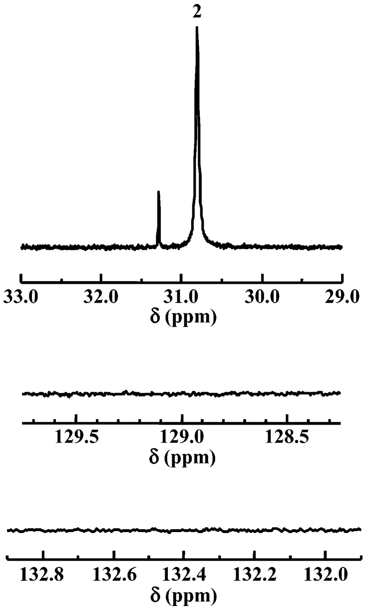


Figure 3. ^{13}C NMR spectra for PC.

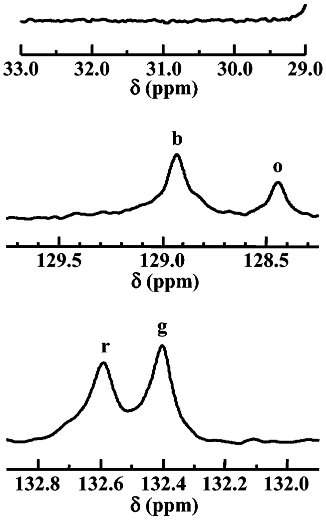


Figure 4. ^{13}C NMR spectra for PSHQ6.

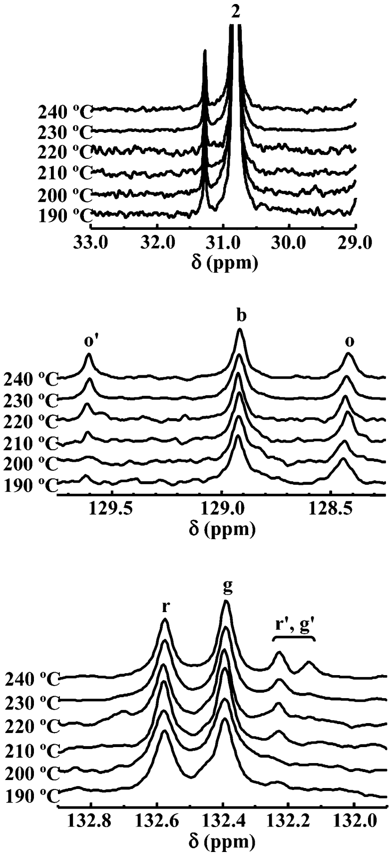


Figure 5. ^{13}C NMR spectra for 70/30 PC/PSHQ6 blend specimens that were prepared by melt blending for 20 min at various temperatures indicated in the NMR spectra.

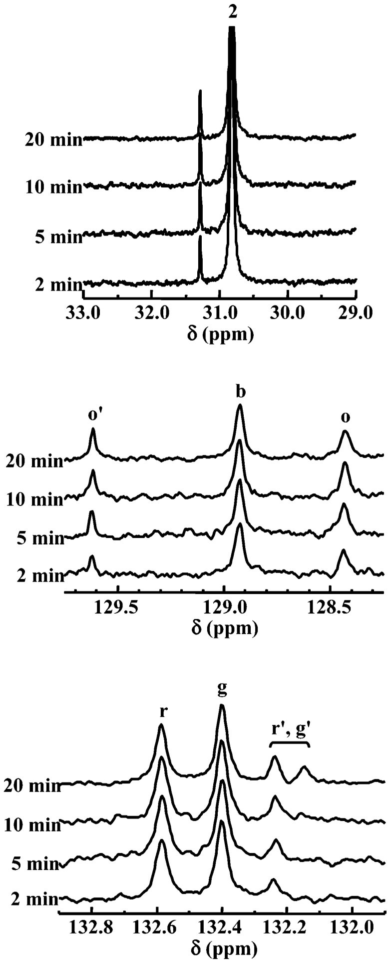


Figure 6. ^{13}C NMR spectra for 70/30 PC/PSHQ6 blend specimens that were prepared by melt blending at 240 °C for various durations indicated in the NMR spectra.

Table 1. Dependence of Relative Intensities of ^{13}C NMR Peaks for 70/30 PC/PSHQ6 Blend Specimens on Melt Blending Temperature for 20 min

melt blending temp (°C)	relative intensities o 128.41 ppm	 o′ 129.60 ppm	 2 30.81 ppm
190	0.43	0.00[a]	5.41
200	0.29	0.00[a]	4.55
210	0.33	0.06	5.27
220	0.26	0.10	5.49
230	0.24	0.14	5.20
240	0.28	0.20	5.21

[a] Since the relative peak intensities for the carbons at positions r′ and g′ at 190 and 200 °C are negligibly small (see Figure 5), we regard the relative peak intensity for the carbon at position o′ at the same temperatures to be within the range of noises. Thus, we did not use the relative peak intensity for the carbon at position o′ to calculate values of *B* at 190 and 200 °C, as summarized in Table 3.

Table 2. Dependence of Relative Intensities of ^{13}C NMR Peaks for 70/30 PC/PSHQ6 Blend Specimens on the Duration of Melt Blending at 240 °C

duration of melt blending (min)	relative intensities o 128.41 ppm	 o′ 129.60 ppm	 2 30.81 ppm
2	0.27	0.15	5.40
5	0.30	0.13	5.20
10	0.32	0.16	5.47
20	0.28	0.20	5.21

Table 3. Dependences of Probability $P_{A_iB_j}$ and Degree of Randomness *B* for 70/30 PC/PSHQ6 Blend Specimens on Melt Blending Temperature for 20 min

melt blending temp (°C)	$P_{A_1B_1}$	$P_{A_1B_2}$	$P_{A_2B_1}$	$P_{A_2B_2}$	*B*
190	1.00	0.00	0.00	1.00	0.00
200	1.00	0.00	0.00	1.00	0.00
210	0.85	0.15	0.02	0.98	0.17
220	0.72	0.28	0.04	0.96	0.32
230	0.63	0.37	0.05	0.95	0.42
240	0.59	0.41	0.07	0.93	0.48

Table 4. Dependences of Probability $P_{A_iB_j}$ and Degree of Randomness *B* for 70/30 PC/PSHQ6 Blend Specimens on the Duration of Melt Blending at 240 °C

duration of melt blending (min)	$P_{A_1B_1}$	$P_{A_1B_2}$	$P_{A_2B_1}$	$P_{A_2B_2}$	*B*
2	0.72	0.28	0.04	0.96	0.32
5	0.70	0.30	0.05	0.95	0.35
10	0.66	0.34	0.06	0.94	0.40
20	0.59	0.41	0.07	0.93	0.48

and $[A_2] = [B_2] = [A_2B_1] + [A_2B_2]$. Using eqs 1−6, we have evaluated the degree of randomness *B* for 70/30 PC/PSHQ6 specimens, and they are summarized in Tables 3 and 4.

In Figure 7a we observe that an appreciable degree of randomness *B* occurs only when the melt blending temperature is higher than the T_{cl} of PSHQ6 (206 °C). It should be mentioned that at 190 and 200 °C the calculated values of *B* based on the ^{13}C NMR spectra (see the footnote of Table 1) turn out to be extremely small, and thus we have concluded that, for all intents and purposes, *B* is virtually zero (see Table 3). This conclusion suggests that discernible transesterification did not occur between the PC and PSHQ6 in the blend when they were melt-blended at 190 and 200 °C, below the T_{cl} of PSHQ6. Referring to Figure 7b, at the melt blending temperature of 240 °C, above the T_{cl} of PSHQ6, the degree of randomness *B* increased rapidly in the first 2 min after melt blending began and then continued to increase slowly as the melt blending continued.

The results of ^{13}C NMR spectroscopic study presented above clearly support our speculation, stated in the Introduction section, that a discernible degree of transesterification between TTP and TPP would occur only when melt blending of the component polymers is conducted at temperatures above the clearing

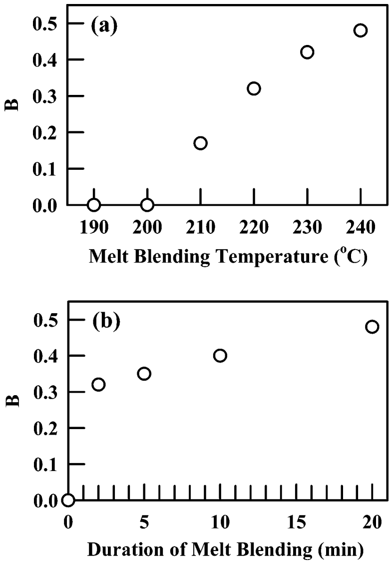


Figure 7. Degree of randomness *B* determined from ^{13}C NMR spectroscopy of the 70/30 PC/PSHQ6 blend specimens: (a) effect of melt blending temperature for 20 min and (b) effect of the duration of melt blending at 240 °C.

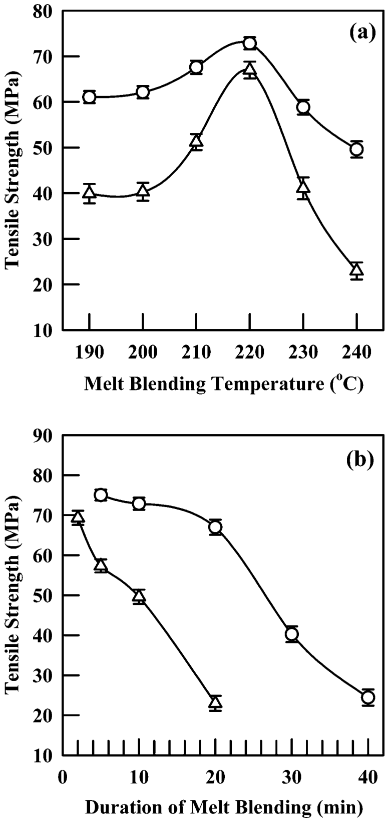


Figure 8. Tensile strength of injection-molded 70/30 PC/PSHQ6 blend specimens. (a) Effect of melt blending temperature: (○) melt-blended for 10 min and (△) melt-blended for 20 min. (b) Effect of the duration of melt blending: (○) melt-blended at 220 °C and (△) melt-blended at 240 °C.

temperature of the TTP. It should be mentioned at this juncture that the observations made above on transesterification, based on the DSC thermograms presented in Figure 2, must be regarded as being suggestive rather than conclusive.

(c) Tensile and Impact Strengths of Injection-Molded PC/PSHQ6 Blends. Figure 8 describes the tensile strength of injection-molded specimens of 70/30 PC/PSHQ6 blend obtained (a) at various melt blending temperatures ranging from 190 to 240 °C for 10 and 20 min, respectively, and (b) for various durations of melt blending at 220 and 240 °C, respectively. In Figure 8a we observe that the tensile strength remains more or less constant when the blend was melt-blended for 10 and 20 min respectively at 190 and 200 °C, which are below the T_{cl} of PSHQ6, begins to increase when the melt blending temperature was increased further, going through a maximum at a melt blending temperature of ca. 220 °C, and then decreases rapidly as the melt blending temperature was increased further. At first glance, such a dependence of tensile strength of injection-molded specimen of 70/30 PC/PSHQ6 blend on melt blending temperature may seem strange, but this can be explained in terms of the extent of transesterification evidenced from the results of ^{13}C NMR spectroscopy. Namely, notice from Figure 7a that the degree of randomness *B* of the 70/30 PC/PSHQ6 blend is virtually zero at melt blending temperatures below the T_{cl} (206 °C) of PSHQ6, indicating that very little miscibility between PC and PSHQ6 took place under such a processing condition. It is then clear that the two-phase (incompatible) mixture of PC and PSHQ6 cannot be expected to enhance the tensile strength of PC under such circumstances. However, Figure 7a shows that as the melt blending temperature exceeded the T_{cl} of PSHQ6, the degree of randomness *B* begins to increase, indicating that partial miscibility between PC and PSHQ6 took place. In the presence of partial miscibility owing to transesterification between PC and PSHQ6, the tensile strength of PC/PSHQ6 blend is expected to be higher than that of neat PC. Indeed, we found that the tensile strength of 70/30 PC/PSHQ6 blend prepared by melt blending at 220 °C for 10 min is 72.8 MPa, while the tensile strength of neat PC prepared by melt blending under the identical condition is 60.4 MPa. This is attributed to the fact that the nematic phase in PSHQ6 helps enhance the tensile strength of PC. The rapid decrease in the tensile strength of 70/30 PC/PSHQ6 blend when the melt blending continued for 10 or 20 min at temperatures higher than ca. 220 °C (Figure 8a) is attributed to the fact that PSHQ6 in the 70/30 PC/PSHQ6 blend has lost too much of its liquid crystallinity as the degree of randomness *B* exceeded a certain critical value during melt blending. In other words, the 70/30 PC/PSHQ6 blend has been randomized to an extent that PSHQ6 could no longer function effectively as a reinforcing agent for PC. The above observations suggest that an optimum processing condition exists, which gives rise to the highest tensile strength of the 70/30 PC/PSHQ6 blend.

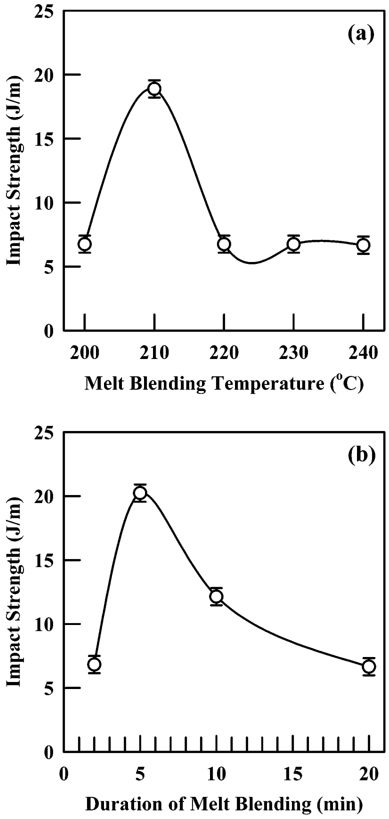


Figure 9. Izod impact strength of injection-molded 70/30 PC/PSHQ6 blend specimens: (a) effect of melt blending temperature for 20 min and (b) effect of the duration of melt blending at 240 °C.

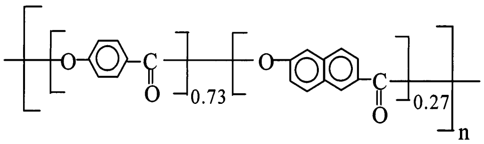
The above observations are reinforced by Figure 8b in that the tensile strength of the injection-molded specimen of 70/30 PC/PSHQ6 blend decreases when melt blending continues beyond about 10 min at 220 °C, and it decreases at a much faster rate when melt blending continues at 240 °C. The above observations can be explained by Figure 7b, showing that the degree of randomness *B* keeps increasing as the melt blending continues at 240 °C, and thus the ability for PSHQ6 to function as a reinforcing agent for PC continues to decrease when the degree of randomness *B* exceeds a certain critical level.

Very interestingly, in Figure 9 we can make very similar observations on the effects of processing conditions (melt blending temperature and the duration of melt blending) on the impact strength of the injection-molded specimen of 70/30 PC/PSHQ6 blend. It should be mentioned that impact strength of 70/30 PC/PSHQ6 blend is not a straightforward indicator of miscibility because the blend can contain numerous defects. Therefore, there is no guarantee that the blend after melt blending at a temperature above the T_{cl} of PSHQ6 for a predetermined period (i.e., partially transesterified blend) would not give rise to a brittle interlayer between the component phases. It is worth noting that a maximum in impact strength of the injection-molded specimen of 70/30 PC/PSHQ6 blend occurs when it was prepared by melt blending at 210 °C (see Figure 9a), while a maximum in tensile strength occurs when injection-molded 70/30 PC/PSHQ6 specimen was prepared by melt blending at 220 °C (see Figure 8a). At first glance the two results may seem inconsistent, but this can be explained in terms of the differences in sensitivity between tensile strength and impact strength to the extent of transesterification and thus the morphological state of the specimens. Namely, the tensile strength is very sensitive to the degree of randomness (i.e., to an enhancement in miscibility), while the impact strength is very sensitive to the sharpness of the interface between the discrete PSHQ6 phase and the continuous PC phase. Specifically, the impact strength of injection-molded specimens might decrease with increasing melt blending temperature when the interface between the discrete PSHQ6 phase and the continuous PC phase is diffuse owing to a higher degree of randomness B. According to Figure 7a, the 70/30 PC/PSHQ6 blend prepared by melt blending at 220 °C has a higher degree of randomness B (thus a diffuse interface) as compared to that prepared by melt blending at 210 °C. We can then conclude that a maximum in impact strength of 70/30 PC/PSHQ6 blend observed at a melt blending temperature of 210 °C, given in Figure 9a, may be attributable to a sharp interface between the discrete PSHQ6 phase and the continuous PC phase having an optimum degree of randomness B.

(d) Birefringence of Injection-Molded PC/PSHQ6 Blends. The nematic mesophase of PSHQ6 in an injection-molded PC/PSHQ6 blend specimen is expected to exhibit birefringence under cross-polarized light. However, an injection-molded specimen of PC alone would also exhibit birefringence. Thus, it is very difficult, if not impossible, to separate the contribution of the nematic phase of PSHQ6 from the overall birefringence measured for a PC/PSHQ6 blend. But, it is very reasonable to state that the contribution to the birefringence from the nematic phase of PSHQ6 would decrease as the extent of transesterification increases because the liquid crystallinity of PSHQ6 will gradually be lost as transesterification between PC and PSHQ6 progresses. To help understand the effect of processing variables (melt blending temperature and the duration of melt blending) on the tensile and impact strengths observed in Figures 8 and 9, we conducted birefringence measurement of injection-molded 70/30 PC/PSHQ6 blend specimens using polarized optical microscopy by following the procedures described in the literature,[32] the results of which are summarized in Figure 10. Note that the values of birefringence given in Figure 10 were obtained from the expression $\Delta n_{13} = \Gamma/d$, in which subscript 1 refers to the flow direction (i.e., in the longitudinal direction of a rectangular specimen), subscript 3 refers to the thickness direction of the specimen, Γ is the optical retardation, and d is the thickness of a tested film cut from the specimen. It should be mentioned that there is a contribution to the birefringence given in Figure 10 not only from the degree of orientation but also from the amount of orientation of the PSHQ6 phase.

In Figure 10a we observe that the birefringence of the specimens first increases, going through a maximum at a melt blending temperature of ca. 220 °C, and then rapidly decreases as the melt blending temperature increases further to 240 °C. Of particular interest in Figure 10a is that the melt blending temperature at which a maximum in birefringence occurs is very close to the melt blending temperature at which the tensile strength goes through a maximum (see Figure 8a). Such an observation is not merely a coincidence for the following reasons. The initial increase in birefringence observed in Figure 10a is attributable primarily to the enhanced orientation of the nematic phase of PSHQ6 owing to a progressive decrease in melt viscosity with increasing melt blending temperature (see Figure S1 in the Supporting Information). On the other hand, a rapid decrease in birefringence when the melt blending temperature exceeded ca. 220 °C is attributable to the loss of the orientation of PSHQ6 chains due to the progressive increase in the extent of transesterification between PSHQ6 and PC. The reason is that when the randomization between PSHQ6 and PC due to transesterification has progressed to a critical level, the nematic phase of PSHQ6 can orient less along the flow direction as a consequence of a significant loss of liquid crystallinity in PSHQ6. This explanation is reinforced by the dependence of birefringence on the duration of melt blending at 220 °C, summarized in Figure 10b. Namely, as melt blending continues at 220 °C, the extent of transesterification increases and thus the availability of nematic phase in PSHQ6 decreases. Consequently, the birefringence of the injection-molded 70/30 PC/PSHQ6 blend specimen is expected to decrease with an increase in the duration of melt blending at 220 °C. It is worth mentioning at this juncture that earlier Radmard and Dadmun[17] observed a loss of birefringence of solution-blended specimens composed of PC and HBA-PET copolyester during isothermal annealing at 260 °C for an extended period up to 60 min.

4.2. Transesterification of PC/Vectra A900 Blends and Their Tensile Strength. For comparison, in the present study we also prepared blends of PC and HBA−HNA copolyester (Vectra A900, Celanese) by melt blending. Vectra A900 has 73 mol % HBA and 27 mol % HNA, the chemical structure of which is given below:



There are different grades of Vectra series, depending upon copolyester composition. Figure 11 gives DSC thermograms in the second heating cycle for PC, Vectra A900, and 70/30 PC/Vectra A900 blend specimens that were prepared by melt blending for 10 min at various temperatures ranging from 280 to 320 °C, which was annealed at 220 °C for 2 h in the first cooling cycle. In Figure 11 we observe that PC has a T_g of ca. 151 °C, Vectra A900 has a low T_m of ca. 254 °C and a high T_m of ca. 281 °C, and the value of T_m of Vectra A900 in the 70/30 PC/Vectra A900 blend is little affected by the melt blending temperature employed. Notice further in Figure 11 that the value of T_g (ca. 149 °C) for PC in the 70/30 PC/Vectra A900 blend remains more or less constant, independent of the melt blending temperatures employed. This observation is quite different from that made for 70/30 PC/PSHQ6 blend (see Figure 2a). Therefore, it is very reasonable to conclude that little or no transesterification between PC and Vectra A900 has taken place during melt blending for 10 min at temperatures ranging from 280 to

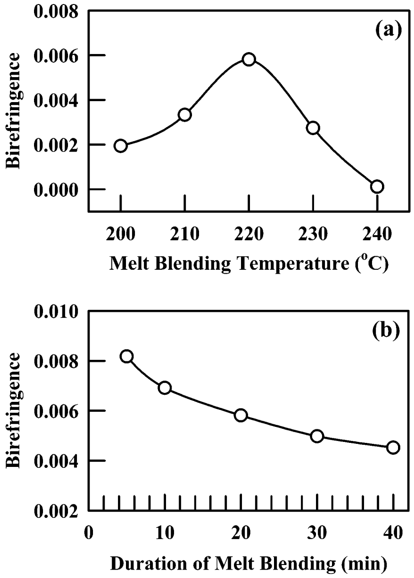


Figure 10. Birefringence of injection-molded 70/30 PC/PSHQ6 blend specimens: (a) effect of melt blending temperature for 20 min and (b) effect of the duration of melt blending at 220 °C.

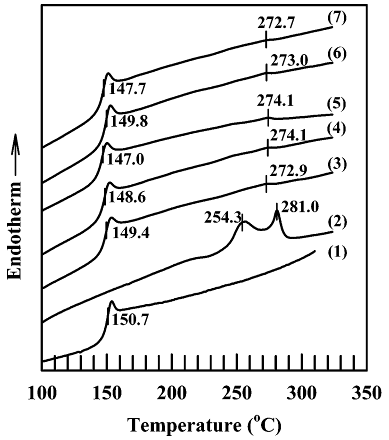


Figure 11. DSC thermograms at a heating rate of 20 °C/min in the second heating cycle for (1) PC, (2) Vectra A900, and 70/30 PC/Vectra A900 blend specimens that were prepared by melt blending for 10 min at various temperatures (°C): (3) 280, (4) 290, (5) 300, (6) 310, and (7) 320, which were annealed at 220 °C for 2 h in the first cooling cycle.

320 °C. This conclusion is consistent with that made for the 70/30 PC/PSHQ6 blend in that the melt blending temperatures employed to prepare PC/Vectra A900 blends were below the $T_{\rm cl}$ of Vectra A900. Note that the $T_{\rm cl}$ of Vectra A900 is higher than its thermal degradation temperature (ca. 350 °C). Thus, we could not prepare PC/Vectra A900 blends by melt blending at temperatures above the $T_{\rm cl}$ of Vectra A900. It should be mentioned that owing to a great difficulty with finding a suitable solvent that could dissolve both PC and Vectra A900, we were not able to conduct ^{13}C NMR spectroscopy for PC/Vectra A900 blends.

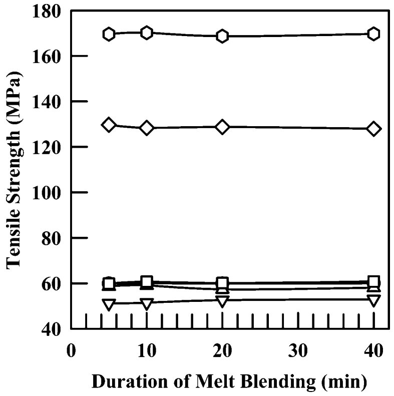


Figure 12. Effect of the duration of melt blending on the tensile strength of injection-molded PC/Vectra A900 blend specimens that were melt-blended at 290 °C: (○) PC, (△) 85/15 PC/Vectra A900 blend, (□) 70/30 PC/Vectra A900 blend, (▽) 50/50 PC/Vectra A900 blend, (◇) 25/75 PC/Vectra A900 blend, and (⬡) Vectra A900. The data points for neat PC cannot be seen because they overlap the data points for 70/30 PC/Vectra A900 blend.

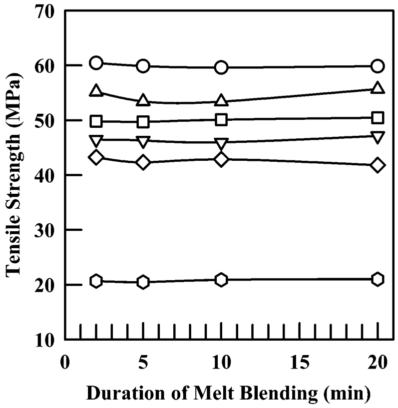


Figure 13. Effect of the duration of melt blending on the tensile strength of injection-molded PC/HDPE blend specimens that were melt-blended at 240 °C: (○) PC, (△) 95/5 PC/HDPE blend, (□) 90/10 PC/HDPE blend, (▽) 80/20 PC/HDPE blend, (◇) 70/30 PC/HDPE blend, and (⬡) HDPE.

Figure 12 describes the effect of the duration of melt blending on the tensile strength of injection-molded PC/Vectra A900 blend specimens having four different blend compositions, which were prepared by melt blending at 290 °C. It is seen in Figure 12 that the duration of melt blending had no effect on the tensile strength of injection-molded specimens of PC/Vectra A900 blends, indicating clearly that no transesterification took place between PC and Vectra A900 during the preparation of the blends by melt blending; i.e., PC and Vectra A900 formed two-phase mixtures without randomization between the constituent components. This observation is consistent with the conclusion drawn above from the DSC thermograms given in Figure 11. Thus, we conclude that Vectra A900 has not reinforced the tensile strength of PC when both components were melt-blended under the processing conditions employed. In the past, some investigators[18,19,22−24,33,34] employed HBA−HNA copolyester (Vectra series) to prepare binary blends with TPP (PC, PET, PBT) and investigated their mechanical properties. On the basis of the results presented above, it is fair to state that blends of HBA−HNA copolyester with TPP would not yield a noticeable improvement in mechanical properties of TPP, since little or no transesterification can take place during compounding simply because melt blending would not be possible at temperatures above the $T_{\rm cl}$ of the copolyester. Simply put, no discernible improvement in mechanical properties can be expected from immiscible polymer blends. In this regard, blends of TTP and TPP cannot be an exception as long as there is no compatibility, via transesterification, between the component polymers.

To demonstrate the validity of the above statement, in this study we also prepared binary blends of PC and HDPE having four different blend compositions, and subsequently they were injection-molded. Figure 13 describes the effect of the duration of melt blending on the tensile strength of injection-molded specimens of PC/HDPE blends having four different blend

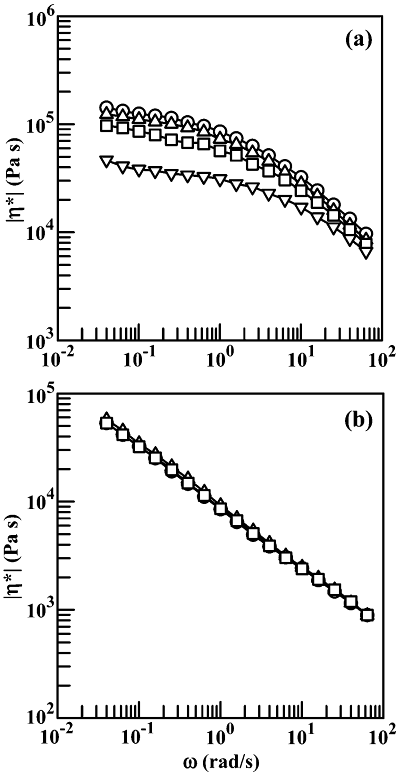


Figure 14. (a) Plots of log |η*| vs log ω at 180 °C for 70/30 PC/PSHQ6 blend specimens, which were prepared by melt blending at 240 °C for different periods (min): (○) 2, (△) 5, (□) 10, and (▽) 20. (b) Plots of log |η*| vs log ω at 310 °C for 70/30 PC/Vectra A900 blend specimens, which were prepared by melt blending at 290 °C for different periods (min): (○) 5, (△) 10, and (□) 20.

compositions, which were prepared by melt blending at 240 °C. It is seen in Figure 13 that the tensile strength of injection-molded specimens of PC/HDPE blends remains constant regardless of how long each blend was melt-blended. This observation is the same as that made above from Figure 12 for PC/Vectra A900 blends. It is well established that PC and HDPE are completely immiscible. The similarity in tensile strength behavior between PC/HDPE blends (Figure 13) and PC/Vectra A900 blends (Figure 12) reassures us that the PC/Vectra A900 blends prepared under the processing conditions described in reference to Figure 12 are immiscible two-phase mixtures, just like PC/HDPE mixtures.

4.3. Rheological Signature for the Onset of Transesterification in PC/PSHQ6 and PC/Vectra A900 Blends. To demonstrate further the difference between PC/PSHQ6 and PC/Vectra A900 blends in their ability to undergo transesterification during melt blending, in the present study we employed rheological measurements as a characterization tool. Specifically, we conducted oscillatory shear flow measurements for (i) PC/PSHQ6 blend specimens at temperatures below the T_{cl} (206 °C) of PSHQ6, which were prepared by melt blending at various temperatures ranging from 190 to 240 °C for different durations, and (ii) PC/Vectra A900 blend specimens at 310 °C, which were prepared by melt blending at 290 °C for different durations. Note that for the reason of thermal degradation, it was not possible to prepare PC/Vectra A900 blends by melt blending at a temperature above the T_{cl} (>350 °C) of Vectra A900. The rationale behind the use of such rheological measurements as a characterization tool lies in that the duration of melt blending should not affect the linear dynamic viscoelastic properties of the blends as long as their morphological states are not changed during melt blending.

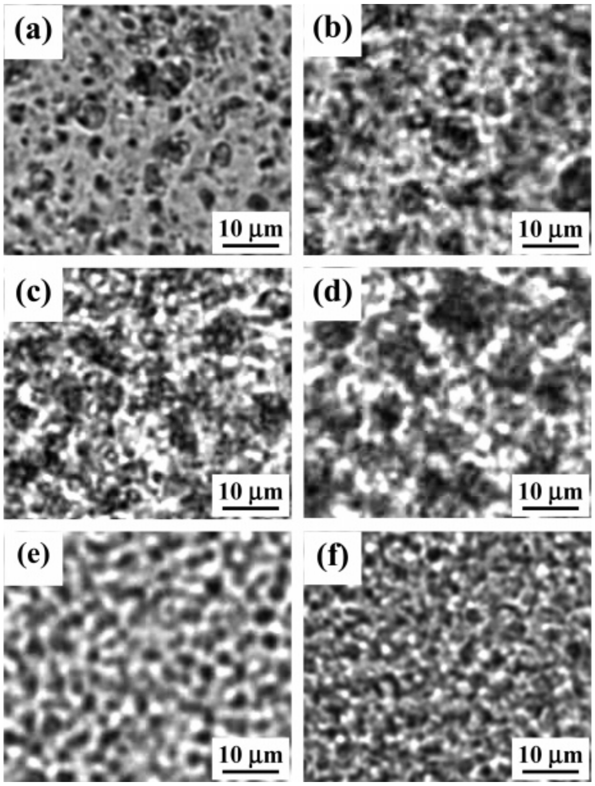
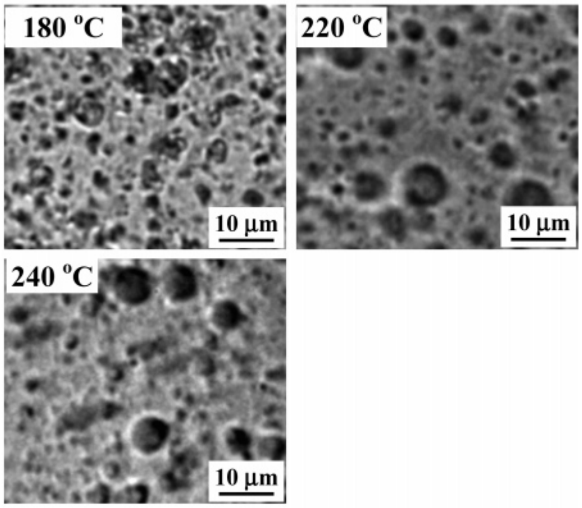


Figure 15. Optical micrographs taken at 180 °C of 70/30 PC/PSHQ6 blend specimens that were prepared by melt blending for 20 min at various temperatures (°C): (a) 190, (b) 200, (c) 210, (d) 220, (e) 230, and (f) 240, in which the bright areas represent the PC phase and the dark areas represent the PSHQ6 phase.

Figure 14 gives log |η*| vs log ω plots for (a) 70/30 PC/PSHQ6 blend specimens at 180 °C, which were prepared by melt blending at 240 °C for different periods ranging from 2 to 20 min, and (b) 70/30 PC/Vectra A900 blend specimens at 310 °C, which were prepared by melt blending at 290 °C for different periods ranging from 5 to 20 min. It should be mentioned that we measured the |η*| of 70/30 PC/PSHQ6 blends at 180 °C (below the T_{cl} of PSHQ6) in order to prevent transesterification during rheological measurements. It can be seen very clearly from Figure 14 that the duration of melt blending affected considerably the values of |η*| for the 70/30 PC/PSHQ6 blend but did not affect values of |η*| for the 70/30 PC/Vectra A900 blend. Since it is well-established today that the |η*| of a polymer blend is very sensitive to its morphological state, we can infer from the above observation that the morphological state of the 70/30 PC/PSHQ6 blend varied due to transesterification as melt blending continued at 240 °C (above the T_{cl} of PSHQ6) for 20 min, whereas the morphological state of the 70/30 PC/Vectra A900 blend did not vary as melt blending continued at 290 °C for 20 min. From this observation we can conclude that no transesterification between PC and Vectra A900 occurred during melt blending at 290 °C for 20 min. Other linear dynamic viscoelastic properties of 70/30 PC/PSHQ6 and 70/30 PC/Vectra A900 blends measured under different melt blending conditions are presented in the Supporting Information.

4.4. Morphology of PC/PSHQ6 and PC/Vectra A900 Blends. Figure 15 gives optical micrographs taken at 180 °C, which is far below the T_{cl} (206 °C) of PSHQ6, of 70/30 PC/PSHQ6 blend specimens that were prepared by melt blending for 20 min at various temperatures ranging from 190 to 240 °C. Note in Figure 15 that the dark areas represent the PSHQ6 phase and the bright/gray areas represent the PC phase. The micrographs were taken at 180 °C in order to avoid any

(a) melt-blended at 190 °C (< T_{cl})



(b) melt-blended at 240 °C (> T_{cl})

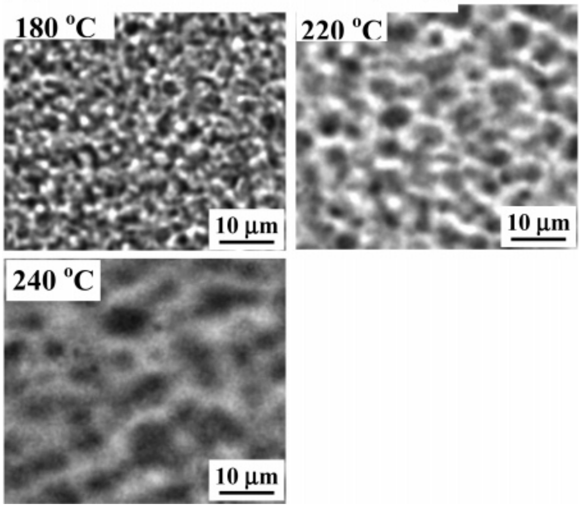


Figure 16. (a) Optical micrographs, taken at various temperatures indicated in the images, of the 70/30 PC/PSHQ6 blend specimen prepared by melt blending at 190 °C for 20 min. (b) Optical micrographs, taken at various temperatures indicated in the images, of the 70/30 PC/PSHQ6 blend specimen prepared by melt blending at 240 °C for 20 min. In both (a) and (b), the bright areas represent the PC phase and the dark areas represent the PSHQ6 phase.

morphological change, via transesterification, during the optical microscopy experiment. Note in Figure 15 that the PSHQ6 phase (the dark areas) is dispersed in the PC matrix (the bright areas). It is very interesting to observe in Figure 15 that a very sharp interface between the PSHQ6 and PC phases can be seen when the blend was melt-blended at temperatures below 210 °C, but the interface became progressively diffuse as the melt blending temperature was increased from 210 to 240 °C. This observation clearly demonstrates that the 70/30 PC/PSHQ6 blend has undergone transesterification during melt blending at temperatures above 210 °C, inducing randomization between the component polymers, PC and PSHQ6. It is not surprising to observe in Figure 15 that the temperature (ca. 210 °C) at which a diffuse interface begins to appear in the micrograph is very close to the T_{cl} (206 °C) of PSHQ6. We have already observed in Figure 7a that at 210 °C the degree of randomness B has progressed sufficiently, giving rise to a noticeable enhancement in the tensile strength (see Figure 8a) of the 70/30 PC/PSHQ6 blend.

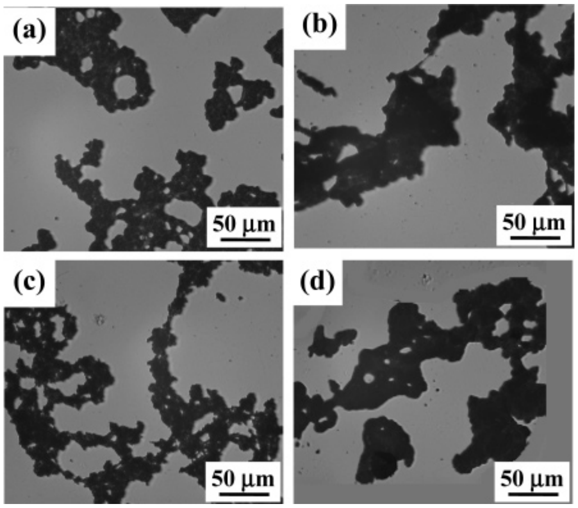


Figure 17. Optical micrographs taken at 300 °C of 70/30 PC/Vectra A900 blend specimens that were prepared by melt blending at 290 °C for different periods (min): (a) 5, (b) 10, (c) 20, and (d) 40, in which the gray areas represent the PC phase and the dark areas represent the Vectra A900 phase.

It is worth mentioning, in reference to Figure 15, that when the 70/30 PC/PSHQ6 blend was mixed at temperatures below the T_{cl} (206 °C) of PSHQ6, it was composed of the nematic phase of PSHQ6 that was suspended in the matrix of PC. Under such mixing conditions, the interface between the PC and PSHQ6 phases is very sharp because little or no transesterification occurred. However, when the 70/30 PC/PSHQ6 blend was mixed at temperatures above the T_{cl} of PSHQ6, the blend became a two-phase liquid mixture, in which the minor component PSHQ6 formed liquid drops that were dispersed in the major component PC forming the continuous phase, like any pair of immiscible polymers.[35,36] Under such mixing conditions, in Figure 15 we observe a diffuse interface between the PC and PSHQ6 phases, indicating that compatibilization occurred, via transesterification, during melt blending. Had there been no transesterification between the PC and PSHQ6 phases during melt blending at temperatures above the T_{cl} of PSHQ6, we would have not observed a diffuse interface between the PC and PSHQ6 phases.

Figure 16a gives optical micrographs taken at three different temperatures (180, 220, and 240 °C) of the 70/30 PC/PSHQ6 blend specimen that was prepared by melt blending at 190 °C (below the T_{cl} of PSHQ6) for 20 min. Figure 16b gives optical micrographs taken at three different temperatures (180, 220, and 240 °C) of the 70/30 PC/PSHQ6 blend specimen that was prepared by melt blending at 240 °C (above the T_{cl} of PSHQ6) for 20 min. Referring to Figure 16a, owing to the absence of transesterification during melt blending at 190 °C, when the specimen was heated from 180 to 220 and to 240 °C, we still observe a sharp interface between the discrete PSHQ6 phase and the continuous PC phase, indicating that no discernible change in blend morphology occurred during such a short period of heating to 220 and 240 °C. That is, heating the blend from 180 to 220 and to 240 °C did not induce miscibility between the discrete PSHQ6 phase and the continuous PC phase. On the other hand, referring to Figure 16b, the morphology of the specimen at 180 °C shows a diffuse interface due to transesterification taken place during melt blending at 240 °C for 20 min. As the temperature of the blend specimen was increased to 220 °C, the interface became very blurred, showing evidence that a certain degree of coalescence of the discrete PSHQ6 phase took place. As the temperature of the blend specimen was increased further to 240 °C, we observe evidence that a greater degree of coalescence of the discrete PSHQ6 phase took place, showing larger drops of PSHQ6 phase.

Figure 17 gives optical micrographs taken at 300 °C, which is far below the T_{cl} (>350 °C) of Vectra A900, of 70/30 PC/Vectra A900 blend specimens that were prepared by melt blending at 290 °C for different periods ranging from 5 to 40 min. Note in Figure 17 that the dark areas represent the Vectra A900 phase and the gray areas represent the PC matrix. In Figure 17 we observe that the interface between the discrete Vectra A900 phase and the continuous PC phase is very sharp; also, the shape of the discrete Vectra A900 phase did not change much as the duration of melt blending was increased from 5 to 40 min. This observation clearly indicates that no compatibilization, via transesterification, between Vectra A900 and PC occurred during melt blending at 290 °C, which is far below the T_{cl} of Vectra A900. This observation now explains why the tensile strength of PC/Vectra A900 blends remains constant, irrespective of the duration of melt blending (see Figure 12).

5. Concluding Remarks

In this paper we have summarized the results of our recent investigation on transesterification and the mechanical properties of blends composed of a model thermotropic polyester (TTP), PSHQ6, and PC. PSHQ6 was chosen as a model TTP because it has a clearing temperature (T_{cl}) much lower than its thermal degradation temperature, which enabled us to prepare PC/PSHQ6 blends at temperatures below and above the T_{cl} of PSHQ6. We employed ^{13}C NMR spectroscopy to determine the extent of transesterification, placing emphasis on the effect of melt blending temperature relative to the T_{cl} of PSHQ6 on the mechanical properties of PC/PSHQ6 blends. We have found that the extent of transesterification is very low when melt blending temperature was below the T_{cl} of PSHQ6, and consequently little enhancement in the tensile strength of PC was observed. This observation suggests that melt blending must be conducted at temperatures above the T_{cl} of PSHQ6 in order to achieve a significant degree of transesterification and thus a noticeable enhancement in the tensile strength of PC. However, we also have observed that the tensile strength of PC/PSHQ6 blends decreases when the extent of transesterification exceeded a certain critical level, indicating that there exists an optimum range of transesterification that gives rise to a significant improvement in the tensile strength of PC/PSHQ6 blends. This is interpreted as being the result of an appreciable degree of liquid crystallinity of PSHQ6 lost when the extent of transesterification exceeds a certain critical level. The existence of an optimum range of transesterification is corroborated by independent measurements of birefringence of injection-molded PC/PSHQ6 blends. Also investigated in this study was the effect of the duration of melt blending on the tensile and impact strengths of injection-molded PC/PSHQ6 blends. We have found that intricate relationships exist between melt blending temperature and the duration of melt blending, which can give rise to a significant improvement in the tensile and impact strengths of PC. In this study we have been able to correlate qualitatively the extent of transesterification to the tensile and impact strengths of binary blends composed of a model TTP, PSHQ6, and PC. To our knowledge, to date no such investigation has ever been reported.

For comparison, in this study we also investigated the tensile strength of blends of PC and HBA−HNA copolyester (Vectra A900). It was not possible to prepare the blends by melt blending at temperatures above the T_{cl} of Vectra A900 because the T_{cl} of Vectra A900 lies above its thermal degradation temperature (ca. 350 °C). We have observed evidence that no transesterification had occurred between PC and Vectra A900 during melt blending, and thus the two polymers remained as an incompatible blend over the entire range of melt processing conditions employed. From the present investigation we conclude that a noticeable improvement in the tensile strength and most likely other mechanical properties of TPP/TTP blends cannot be expected as long as the blends are prepared by melt blending at temperatures below the T_{cl} of the TTP chosen.

In the past, some investigators[12,14−17] reported on the effect of transesterification of blends of TTP and TPP, which were prepared by solution blending followed by an isothermal annealing, on their mechanical properties and/or morphology. Solution blending followed by an isothermal annealing is not an option for industrial polymer processing operations. Thus, in this study we have not addressed the subject of solution blending of TTP and TPP.

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Supporting Information Available: Linear dynamic viscoelastic properties of 70/30 PC/PSHQ6 blends measured under different melt blending conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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