 doi:10.20944/preprints201805.0052.v1

Article

Chemical Interaction–Induced Evolution of Phase Compatibilization in Blends of Poly(hydroxy ether of bisphenol-A) with Poly(1,4-butylene terephthalate)

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Abstract: An immiscible blend of poly(hydroxy ether of bisphenol-A) (phenoxy) and poly(1,4-butylene terephthalate) (PBT) with phase separation was observed in as-blended samples. However, compatibilization of the phenoxy/PBT blends can be promoted through chemical exchange reactions of phenoxy with PBT upon annealing. In contrast to the as-blended samples, the annealed phenoxy/PBT blends had a homogeneous phase with a single T_g that could be enhanced by annealing at 260°C. Infrared (IR) spectroscopy demonstrated that phase homogenization could be promoted by annealing of the phenoxy/PBT blend, where alcoholytic exchange occurred between the dangling hydroxyl group in phenoxy and the carbonyl group in PBT in the heated blends. The alcoholysis reaction changes the aromatic linkages to aliphatic linkages in carbonyl groups, which initially led to the formation of a graft copolymer of phenoxy and PBT with an aliphatic/aliphatic carbonyl link. The progressive alcoholysis reaction resulted in the transformation of the initial homopolymers into block copolymers and finally into random copolymers, which promoted phase compatibilization in blends of phenoxy with PBT. Due to the fact that the amount of copolymers increased upon annealing, crystallization of PBT was inhibited by alcoholytic exchange in the blends.

Keywords: immiscible blend, compatibilization, homogeneous phase, alcoholysis, carbonyl group, copolymers.

1. Introduction

Blending immiscible polymers offers attractive opportunities for developing new materials with useful combinations of properties. Compatibilization and phase homogeneity in blending of immiscible polymers can be enhanced by physical interactions such as van der Waals forces, dipole–dipole interactions, and hydrogen bonding or chemical interactions (reactive compatibilization) such as the formation of covalent bonds between polymers [1–3]. In physical blending, preformed graft or block copolymers are traditionally added to act as compatibilizers. Reactive blending is employed to generate these copolymer compatibilizers *in situ* during melt blending or annealing using functionalized polymers. Generally, reactive blending has several advantages over physical blending, based on the utility and controllability of the polymer processing. In reactive blending, chemical reactions between reactive groups progress during melt blending or heat treatment. Thus, a phase-separated compatibilized blend can be achieved with controllable morphology and interfaces [2–7].

Poly(hydroxy ether of bisphenol-A) (phenoxy) contains ether linkages in the backbone and pendant hydroxyl groups that exhibit outstanding mechanical properties, such as toughness and dimensional stability [3, 5, 8, 9]. In its organic chemistry, oxygen in the hydroxyl group has two lone

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pairs, with negative charges on the *para* and *ortho* positions, which are the activated positions when electron-donating substituents are present [10]. The hydroxyl group in the phenoxy molecule is attached to an aliphatic structure, in which the hydroxyl group is electron-withdrawing and thus strongly activating. The hydroxyl group of phenoxy can interact with proton-accepting functional groups in other polymers in polymer blends. The compatibility of phenoxy and other polymers in polymer blends can be increased by both physical (hydrogen bonding) and chemical (alcoholysis reaction) interactions [8, 9].

If there is a large difference in the electronegativity of functional groups in the components of blends, a strong physical interaction, that is, hydrogen bonding, can enhance their compatibility [11]. The miscibility of polymer blends containing phenoxy typically originates from hydrogen bonding between the hydroxyl group of phenoxy and proton-accepting functional groups of the other polymers, such as polyoxides [12], polyamides [13], polyesters [14,15], poly(methyl methacrylate) [16], poly(ε-caprolactone) (PCL) [17], poly(vinylpyrrolidone) [18], and phenol resin [19]. Coleman et al. [17] studied the strong physical interactions in phenoxy/PCL blends using Fourier-transform infrared (FTIR) spectroscopy. The main conclusion was that the hydrogen-bonded hydroxyl infrared (IR) absorption shifted to lower frequencies as the PCL concentration changed. Such blends exhibit significant shifting of the IR absorption of the hydroxyl group, which is attributed to a pronounced interaction between phenoxy and polymers. This implies that this hydrogen bonding interaction is stronger than the corresponding self-associated hydrogen bonding in neat phenoxy.

Additionally, phenoxy can also form immiscible or partially miscible blends with some aliphatic polyesters (e.g., poly(ethylene succinate) [20], poly(butylene acid) (PBA) [5], and poly(3-hydroxybutyrate) (PHB) [21]) and aromatic polyesters (e.g., poly(ethylene terephthalate) (PET) [22], poly(trimethylene terephthalate) (PTT) [23], poly(butylene succinate-*co*-butylene adipate) [P(BS-*co*-BT)] [3], and poly(ethylene 2,6-naphthalenedicarboxylate) [24]). However, the chemical interactions that occur following high-temperature annealing enhance miscibility. Such blends exhibit a significant positive deviation from the linear relationship between T_g and composition, which is attributed to a pronounced interaction between phenoxy and polymers. Furthermore, reactions in polymer blends are widely used both to improve their properties, such as compatibility, and to synthesize new polymeric materials with desired properties. In the molecular structure of polyesters, the carbonyl group is polar (the electronegativity of oxygen is larger than that of carbon; therefore, the carbonyl group has a large dipole moment); thus, the carbonyl carbon atom is partially positively charged and hence can act as an electrophile. Therefore, these molecules easily undergo nucleophilic substitution reactions [25]. Therefore, the pendant hydroxyl groups of phenoxy can participate in a specific chemical reaction, that is, alcoholysis, with polyesters. During reactive blending, the interfacial chemical reactions form copolymers *in situ*, which suppresses coalescence and reduces interfacial tension. As a result of this, a stable and fine morphology is attained with enhanced interfacial adhesion between the phases. Additionally, compatibilization can introduce reactive molecules that are capable of forming the desired copolymers *in situ* and directly during blending or annealing of the reactive polymer blends [2–5].

Our study aims to contribute to an understanding of how to control the compatibilization of phenoxy and poly(1,4-butylene terephthalate) (PBT). Blends of different compositions were produced and melt-annealed, resulting in chemical interaction–induced evolution of phase compatibilization in blends of phenoxy with PBT. Analyses were performed in order to investigate the chemical interactions, the influence of the annealing procedure on the degree of chemical interaction, and the influence of the chemical interactions on the crystallization behavior. Changes in the thermal behavior, morphology, and molecular structures of blends with various compositions were investigated and discussed in relation to the chemical interactions.

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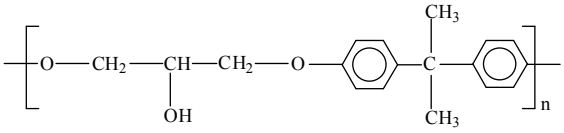
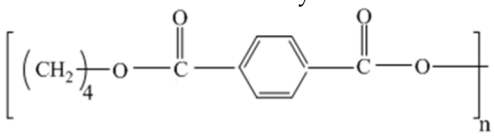
2. Experimental

2.1. Materials and Methods

Poly(hydroxy ether of bisphenol-A) (known as phenoxy) was purchased from Scientific Polymer Products (New York, USA), with M_n = 23,000 g/mol, M_w = 80,000 g/mol, and T_g = 90°C. Poly(1,4-butylene terephthalate) (PBT) is a research-grade resin with no additives, which was obtained from Chang Chun Corp. (Hsinchu, Taiwan). The aryl polyester, PBT, is semicrystalline, with a glass transition temperature (T_g) of 35°C, an average molecular weight (M_n) of 25,000 g/mol, and an apparent melting temperature (T_m) of 225°C. The chemical structures of the repeating units of PBT and phenoxy are as follows:



Phenoxy



PBT

In order to ensure that the inherent phase behavior of the physical blends was initially understood, blend specimens were prepared by solution blending to avoid thermal heating effects at elevated temperatures, which are inevitable in melt blending. Blends of phenoxy with PBT were prepared by solution blending/casting using hexafluoroisopropanol (HFIP, $C_3H_2OF_6$) as a good mutual solvent. The two constituent polymers at a concentration of 0.04 g mL^{-1} in solution were mixed in the desired proportions, stirred thoroughly, and cast onto glass dishes at 50°C. The solvent was evaporated at 50°C for 24 h, and then samples were degassed for one week in a vacuum oven at 80°C to remove the residual solvent prior to characterization. Blend compositions of phenoxy/PBT were fixed at 10/90, 30/70, 50/50, 70/30, and 90/10. These samples are designated as "as-blended." As-blended materials were further held at 260°C for different periods of time (0–180 min) to evaluate the effects of heat annealing. These latter samples are designated as "heat-annealed." The different blend compositions were then exposed to a temperature of 260°C for various periods of time. The soluble portions of the reacted samples were extracted with HFIP, and the residual solids and extracted solution were kept separately for FTIR analysis.

2.2. Characterization

2.2.1. Differential Scanning Calorimetry. The thermal behavior of the blends, such as glass transition temperatures (T_g), melting temperatures (T_m), and nonisothermal crystallization, was characterized using a differential scanning calorimeter (DSC) (PerkinElmer PYRIS I) equipped with an intracooler under purging with nitrogen. All samples were pressed into flat films with a mass of 3–5 mg to ensure good thermal conduction and temperature distribution. The samples underwent the following thermal cycles. Samples were heated rapidly from 0°C to 260°C, held at this temperature for various annealing times (t_a), and then cooled at a rate of 10°C/min to 0°C. The annealing times of phenoxy/PBT blends that were heated at 260°C were 2, 4, and 6 min. The blends underwent various numbers of cycles (n). The overall annealing time, $\Sigma t_a(260°C) = n \cdot t_a(260°C) \equiv \Sigma t_a$, was varied from 2 min (n = 1) to 42 min (n = 7).

2.2.2. Scanning Electron Microscopy. To further confirm the phase structure of the polymer mixtures, the morphology of the fracture surfaces of the blends was examined using a scanning electron microscope (SEM) (Hitachi, Model 4800).

2.2.3. FTIR Spectroscopy. FTIR spectroscopy (PerkinElmer Spectrum 100) was used to investigate the molecular interactions between the constituents. Spectra were obtained at a resolution of 4 cm^{-1}, and averages were obtained from at least 64 scans in the standard wavenumber range 400–4000 cm^{-1}. Two

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spectroscopic techniques were used. Thin films for FTIR studies were obtained by casting phenoxy/PBT solutions onto potassium bromide (KBr) disks at 50°C and then removing them in vacuum at 80°C. In order to evaluate chemical reactions at a high temperature, samples were subjected to designated thermal treatments (isothermal 260°C for 3 h). The samples cast on KBr pellets were heated, cooled to ambient temperature, and examined using FTIR spectroscopy. Another method for preparing the FTIR sample was a powder grinding/mixing and pellet-forming (pressed-disk) technique. The blend sample (about 2 mg) was intimately mixed with approximately 300 mg of dry, powdered KBr. Uniform mixing of the blend sample with KBr was conducted by thoroughly grinding in a smooth agate mortar. The blend KBr mixture was then pressed with a special die under a pressure of 800 kgf/cm^2 into a transparent disk.

3. Results and Discussion

3.1. Phase Morphology Analysis

Figure 1 shows DSC thermograms of as-blended phenoxy/PBT with various compositions. Thermal analysis of phenoxy/PBT blends determined two glass transition temperatures between the T_g values of the components; the T_g values approach each other but do not coincide. Phenoxy and PBT are immiscible or partially miscible, and two glass transition regions were observed, designated as $T_{g,phenoxy}$, associated with phenoxy-rich regions, and $T_{g,PBT}$, associated with PBT-rich regions. The T_g values of PBT in the phenoxy/PBT blends increase slightly and linearly with the phenoxy weight fraction in the figure; in contrast, the T_g values of phenoxy in the phenoxy/PBT blends fall as the phenoxy weight fraction in the figure decreases. Similar studies on the thermal analysis of polymer blends have shown that the T_g values of immiscible systems approach each other but do not coincide for poly(butylene succinate-*co*-butylene terephthalate) [P(BS-*co*-BT)]/phenoxy [3], polycarbonate/poly(methyl methacrylate) [26–28], poly(pentamethylene terephthalate)/poly(ether imide) [29], poly(hexamethylene terephthalate)/poly(ether imide) [29], and polycarbonate/polystyrene [27] blends. The crystallization behaviors, with respect to glass transition, at PBT contents exceeding 10%, are indicated by crystalline melting, and crystalline melting temperatures are also shown in Fig. 1. In the crystalline polymer, the basic units of crystalline polymer morphology include crystalline lamellae consisting of arrays of folded chains. The melting temperature increases with the degree of perfection of the crystal structure and depends on the thickness of the chain-folded crystalline lamellae [30, 31]. Calorimetric scans of blends with PBT contents exceeding 10 wt.% exhibit endothermic melting of PBT. T_m declined slightly as the phenoxy content increased, as observed in Fig. 1. With small amounts of phenoxy present, thin crystalline lamellae were found to be located between thicker lamellae, forming spherulites in the phenoxy/PBT blends. This also demonstrates partial miscibility in the phenoxy/PBT blends.

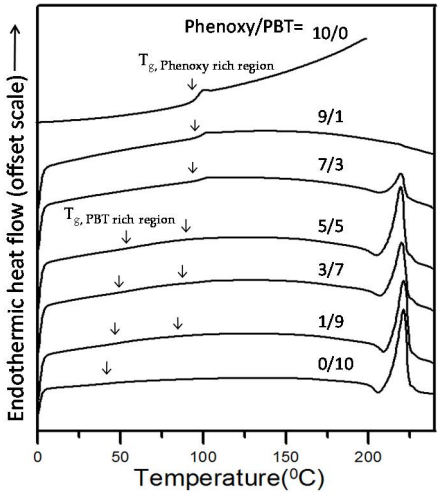

Figure 1. DSC traces for quenched phenoxy/PBT blends

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The above T_g results demonstrate that the phenoxy/PBT blends exhibited two T_g values on a second DSC scanning after quenching from above 240°C. The phase separation could be detected by thermal analysis, and the heterogeneous phenoxy/PBT blends were thermodynamically immiscible [3, 5]. Additionally, the fracture surfaces of the phenoxy/PBT blends with two T_g values were examined using SEM. Figure 2 [micrographs (a)–(e)] shows the cross sections of the same blends with various compositions. The micrographs show particulate domains (5–10 μm) scattered across the fracture surfaces (cross sections) of the blends for all compositions. From left to right, the micrographs show that the PBT component (the aggregated particle domains) forms a continuous phase, with phenoxy forming a discrete phase, for the PBT-rich blends. Similarly, the phenoxy component forms a continuous phase, with the PBT component forming a discrete phase (the dispersed particulate domains), for the phenoxy-rich blends. SEM results demonstrated that the two T_g values of the phenoxy/PBT blends might be explained by the phase-separated morphology, which was observed in the as-blended phenoxy/PBT blends.

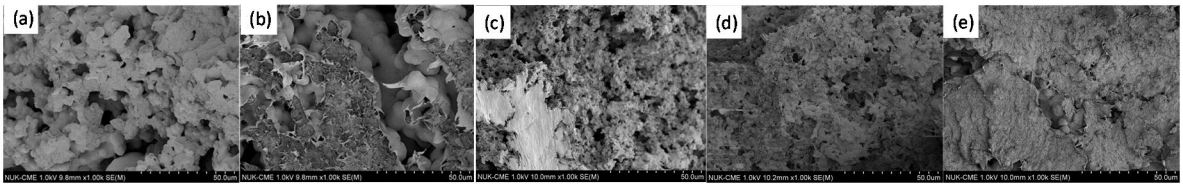

Figure 2. SEM images of phenoxy/PBT blends (1,000x): (a) phenoxy/PBT = 1/9, (b) phenoxy/PBT = 3/7, (c) phenoxy/PBT = 5/5, (d) phenoxy/PBT = 7/3, and (e) phenoxy/PBT = 9/1

In order to observe the effect of temperature on the phase morphology, the as-blended phenoxy/PBT blends were annealed at 260°C for various periods of time and then examined using optical microscopy (OM). Figure 3 shows optical micrographs [(a)–(e)] of the phenoxy/PBT blends with five compositions after being heated at 260°C for various periods of time. Before annealing, the as-blended phenoxy/PBT blends of various compositions, including phenoxy-rich (dark domains) and PBT-rich (white domains) ones, exhibited phase separation. For the immiscible compositions, the phase domain sizes depended on the composition and decreased as the PBT weight fractions increased, as shown in the micrographs. According to the micrographs, in the immiscible blend, the size of the phase domain decreased, and this eventually disappeared as the annealing time increased. After annealing at 260°C for 30 min, the blend's morphology became homogeneous, suggesting that the specific interaction between phenoxy and PBT can improve miscibility in the phenoxy/PBT blend at the annealing temperature.

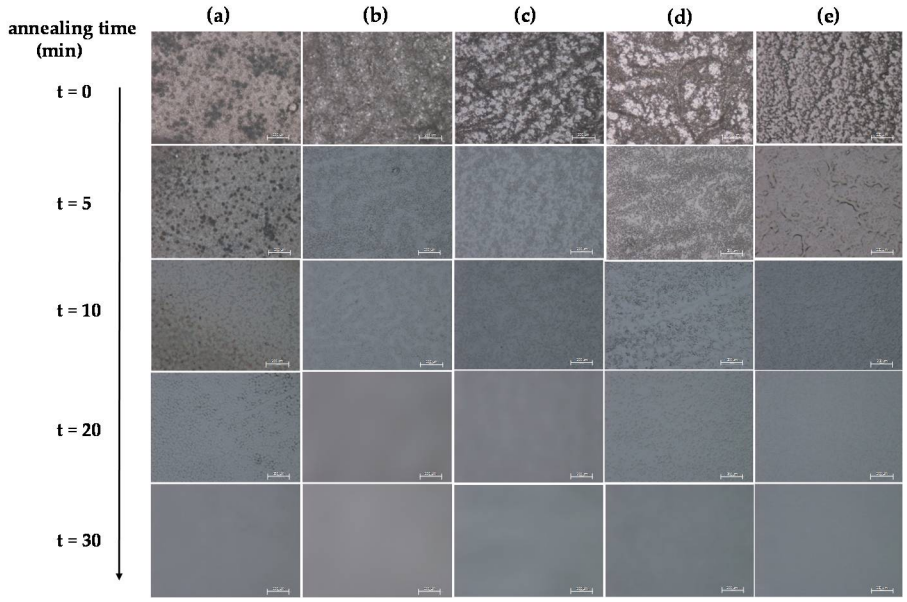

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Figure 3. Optical micrographs of the phenoxy/PBT blends of various compositions annealed at 260°C for various periods of time: (a) 9/1, (b) 7/3, (c) 5/5, (d) 3/7, and (e) 1/9

Figure 4 shows DSC thermograms of the phenoxy/PBT blends of various compositions annealed at 260°C for 180 min. The two T_g values for phenoxy and PBT were 95°C and 36°C, respectively, during the early stage of annealing, before converging to a single T_g later in the annealing process. In the thermal analysis of polymer blends, a single T_g-based value was applied to identify the miscibility or compatibilization of the phenoxy/PBT blends during DSC experiments [2, 3, 32]. Figure 4 shows only a single, composition-dependent T_g for each blend, suggesting that phenoxy can mix with PBT homogeneously to form a miscible blend. As shown in Fig. 3, an optical microscope was used to examine the phenoxy/PBT blends, and the blends of various compositions annealed at 260°C for 30 min were found to be plain and transparent with no discernible phase domains/boundaries. When the annealing time was above 30 min, the phases of all the phenoxy/PBT blends, as revealed by OM, were domain-free and transparent. OM examinations also showed a single-phase morphology for the heated blends of phenoxy with PBT. DSC and OM indicated that the blends were all miscible, with close mixing of the two polymeric segments of BT and the hydroxy ether of bisphenol-A in the heated blends.

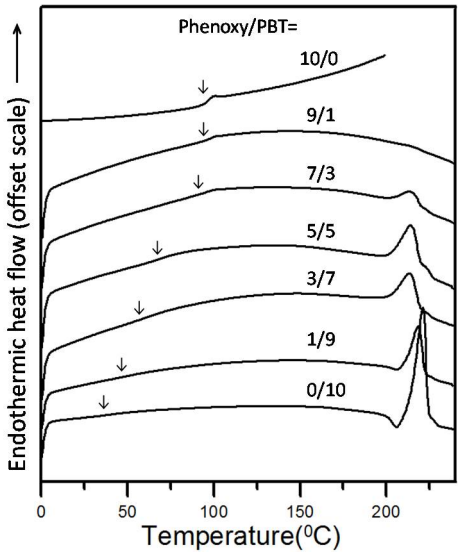

Figure 4. DSC traces of the phenoxy/PBT blends of various compositions annealed at 260°C for 180 min: (a) 1/9, (b) 3/7, (c) 5/5, (d) 7/3, and (e) 9/1

The effect of high-temperature annealing on the phenoxy/PBT blends was also examined by analyzing the T_g versus composition plot shown in Fig. 5. Additionally, the inset blocks show the corresponding SEM morphology of the heated blends. The T_g data in this plot were obtained from the phenoxy/PBT blends that were postannealed at 260°C for 180 min, where the blends were homogenized into one phase, that is, formed single T_g blends. The morphology and the T_g–composition relationship clearly show that the annealed/heated phenoxy/PBT blends are single-phase. This suggests that the miscibility observed in the heated blends was no longer caused by an entropic contribution, and the interactions between the two components were of the van der Waals type or, at most, aided by specific interactions between the polar groups in the phenoxy and PBT molecules. However, the T_g–composition curve is S-shaped. This S shape can be considered to positively deviate from the linear relationship between 0 and 50 wt.% phenoxy and negatively deviate from linearity within the 50–100 wt.% phenoxy composition range. This nonuniform shifting resulted in the observed sigmoidal T_g–composition curves. Kwei [33] proposed a relationship to describe the S-shaped T_g–composition curve:

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$$T_g = \frac{w_1 T_{g1} + w_2 k T_{g2}}{w_1 + k w_2} + q w_1 w_2 . \quad (1)$$

In this equation, ω_i is the weight fraction of component i and $T_{g,i}$ is its glass transition temperature, k represents the ratio of the thermal expansion coefficients or specific heat of phenoxy and PBT, and q is an empirical parameter that is related to the interchain interaction strength. Figure 5 shows the fitting of the T_g data to this relationship. The values were found to be 1.5 and −10 for k and q (at 260°C for 180 min), respectively. The negative q value for the blends suggests stronger interactions between the components after annealing [3]. The above modeling equation for a well-mixed or homogeneous state can be used to describe the T_g–composition relationship in phenoxy/PBT blends, indicating the formation of a miscible state with no inhomogeneous domain or phase separation. If the T_g elevation in the blends is due to intermolecular links through chemical reactions between the phenoxy and PBT, the maximum extent of reactions will occur in blends of phenoxy with PBT contents between 0 and 50 wt.%, as judged by the maximum increase in T_g within this composition range. Clearly, the extents of chemical reactions between phenoxy and PBT were affected by not only the treatment temperature but also the blend compositions.

These results all suggest that chemical reactions are induced by heat treatment of the phenoxy/PBT blend. An earlier study noted that favorable interchange reactions may proceed via the hydroxyl group and carbonyl groups in phenoxy and aliphatic/aromatic polyester blends [34–36]. The carbonyl groups of polyester possess a negative charge on the oxygen and a positive charge on the carbon of the C=O bond. The carbonyl carbon atom becomes electrophilic and thus reacts with nucleophiles in the group. Electrophilic compounds (Lewis bases) that attack the electron-poor (δ+) end of this bond are nucleophiles. Phenoxy, with the pendant hydroxyl group (electron-pair donor) in the repeating unit, enables interaction with the carbonyl group of PBT (proton-accepting functional group) in the polymer blends upon heating. Chemical interactions were observed between phenoxy and PBT upon annealing, which enhanced the miscibility and increased the T_g values of the phenoxy/PBT blends. Consequently, FTIR spectroscopy was used to probe the species that might participate in reactions.

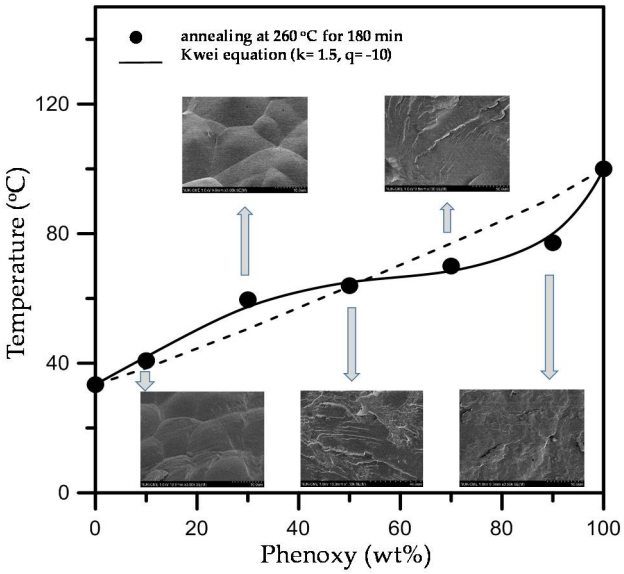

Figure 5. Plots of glass transition temperatures with SEM morphology versus compositions after isothermal treatment at 260°C for 180 min. The curve show fitting of the data to Gordon–Taylor equation

3.2. Chemical Interactions in the Reactive Blend

Figure 6 [diagrams (a)–(c)] shows the carbonyl absorption peaks in the IR spectra of the solution-cast phenoxy/PBT blends with 10, 50, and 90 wt.% of PBT, respectively, after heating at 260°C for

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various periods of time. In each diagram, the carbonyl-stretching peak shifts to gradually higher frequencies as the heating time increases. For example, in diagram (a), the carbonyl absorption peak for the phenoxy/PBT blend (10 wt.% PBT) is seen to shift to a higher wavenumber by up to 11 cm^{-1} for the blend sample heated for 180 min at 260℃. Diagram (b) shows a similar phenomenon for the carbonyl peak of the blend with 50 wt.% PBT. The shifts remain significant but are slightly reduced compared to the blend with 10 wt.% after heating for the same time at 260℃. Note that the heating-induced shift in the carbonyl absorbance becomes gradually less apparent for the phenoxy/PBT blends with increased PBT contents of 50 and 90 wt.%. Diagram (c) shows that the phenoxy/PBT blend with 90 wt.% PBT exhibits a peak shift of a mere 5 cm^{-1} after heating for 180 min at 260℃. This suggests that the chemical interaction was limited to a lesser extent when the PBT content was high in the blends and phenoxy became the limiting species.

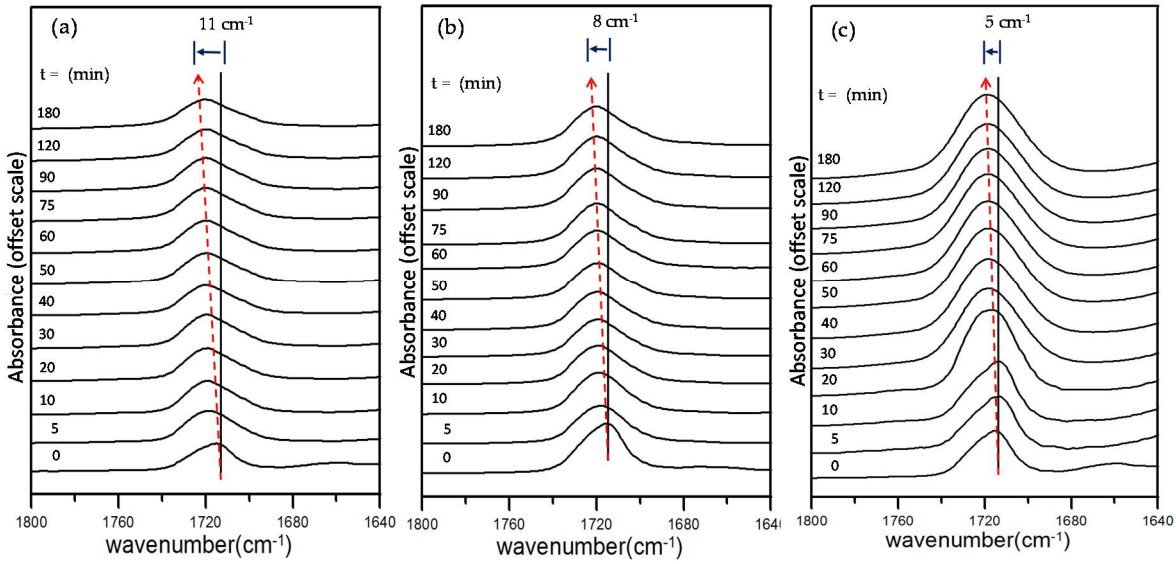

Figure 6. FTIR spectra in the carbonyl-stretching region of phenoxy/PBT blends after heating at 260℃ for various periods of time as indicated: phenoxy/PBT = (a) 9/1, (b) 5/5, and (c) 1/9

One of our earlier studies demonstrated that an exchange reaction occurs between copolyesters and phenoxy. Phenoxy, with a pendant hydroxyl group in the repeating unit, enables interaction with the carbonyl group of copolyesters in the polymer blends. These chemical interactions result in the replacement of covalent bonds in the polymers, changing the linkages adjacent to the carbonyl group of polyesters. Polymers with various linkages adjacent to the carbonyl group exhibit a shift in the carbonyl IR absorption. Carbonyl absorption bands at 1,733, 1,724, and 1,713 cm^{-1} were attributed to C=O stretching of aromatic-(CO)-O-aromatic, aliphatic-(CO)-O-aliphatic, and aromatic-(CO)-O-aliphatic structures, respectively [5]. In the phenoxy/PBT blend, the carbonyl group in the original unreacted PBT chain is linked to aromatic and aliphatic linkages (aromatic-(CO)-O-aliphatic); however, exchange reactions change the linkages (two aliphatic) adjacent to the carbonyl group (aliphatic-(CO)-O-aliphatic).

Figure 7 shows carbonyl-stretching bands that were obtained from the phenoxy/PBT (5/5) blend annealed at 260°C for 180 min. The figure shows the carbonyl absorbance shifts in the IR spectra of the heated blends (curve c) and leached solid (curve d), along with the spectra of the as-blended sample and extracted solute, which are shown on the same diagram as curves a and b, respectively. In curve b, the carbonyl absorbance band of the heated extracted solute is similar to that of the as-blended sample, which suggests that the linkages adjacent to the carbonyl group of PBT (aromatic-(CO)-O-aliphatic) are the same for the as-blended sample and the extracted solute. In curve c, not only is the absorption peak of the carbonyl group at 1,713 cm^{-1}, but also a new carbonyl absorbance band at 1,724 aliphatic-(CO)-O-aliphatic cm^{-1} is observed. These suggested that two types of linkages adjacent to the carbonyl group (and aliphatic-(CO)-O-aromatic structures) are found in the heated blends. In curve d, the carbonyl absorbance band shifts to a higher frequency for the leached solid

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samples, which suggests that extensive aliphatic linkages adjacent to the carbonyl group (aliphatic-(CO)-O-aliphatic) are formed in the leached solid samples. However, the leached solid sample primarily contains species of the exchange reaction, polymer segments with aliphatic-(CO)-O-aliphatic and aliphatic-(CO)-O-aromatic structures. In the heat-annealed phenoxy/PBT blends, extensive exchange reactions produced a cross-linked network that formed residual solids in HFIP.

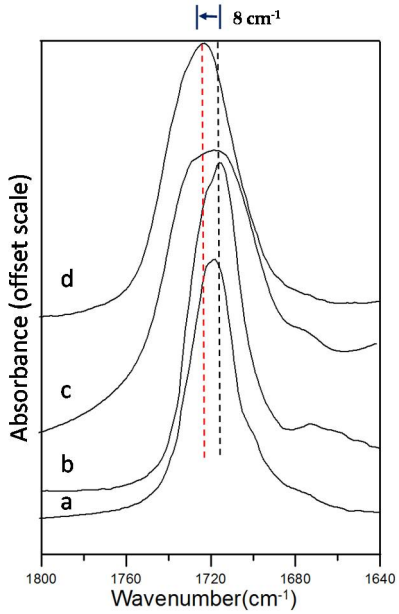

Figure 7. FTIR spectra of phenoxy/PBT (5/5) in the carbonyl-stretching region for blends annealed at 260°C for 180 min. Spectrum (a) is as-blended, (b) is the extracted solution, (c) is the heat-annealed sample, and (d) is the leached solid sample

The pendant hydroxyl group in phenoxy exhibits proton-donor characteristics when it interacts with carbonyl groups in PBT, which contains proton acceptors. Therefore, alcoholytic exchange can increase the compatibility of phenoxy with PBT in polymer blends upon annealing. Scheme 1 shows the mechanisms of the chemical interactions between the hydroxyl groups in phenoxy and the carbonyl groups in PBT. Polyesters react with a source of hydroxyl groups in the phenoxy in a phenoxy/PBT blend because –OH is a strongly activating group, Lewis base, or nucleophile, which attacks the δ^+ end of the –O–C=O bond [25]. Clearly, in the heated blends, one product is fragmented PBT terminated with –OH, which originated from breakage of the carbonyl in joining with the proton in phenoxy. This can be viewed as alcoholysis. As proposed in the mechanisms, the reactions of the hydroxyl group of the phenoxy with an aliphatic/aromatic linked carbonyl group of PBT initially led to the formation of a graft copolymer of phenoxy and PBT with an aliphatic/aliphatic carbonate link. Further reactions produced a complex mixture of polymer chain structures with an increasingly wider distribution of aromatic/aliphatic and aliphatic/aliphatic carbonate links. The degrees of reactions and the structures formed in the blends depended on the initial blend compositions and reaction conditions (i.e., heating temperatures and periods of time). Additionally, the progressive alcoholysis reaction results in the transformation of initial homopolymers into block copolymers and finally into random copolymers. The formed copolymers influence the compatibility of phenoxy and PBT. Finally, with extended heating, a highly linked structure was formed, which helped ensure blend miscibility. Note that the extensive alcoholysis reaction in the phenoxy/PBT blend formed a cross-linked network that was insoluble in the solvent and remained as a residual solid. Additionally, the interlinked network elevated the glass transition temperatures of the blends upon heating.

Thus, the blends containing optimal PBT contents exhibited higher degrees of reactions, resulting in a structure with more aliphatic/aliphatic carbonyl chain links. Additionally, the exchange reaction between the hydroxyl group in phenoxy and the carbonyl group in PBT converted the original aromatic/aliphatic linked carbonate in the linear PBT chains into aliphatic/aliphatic carbonyl

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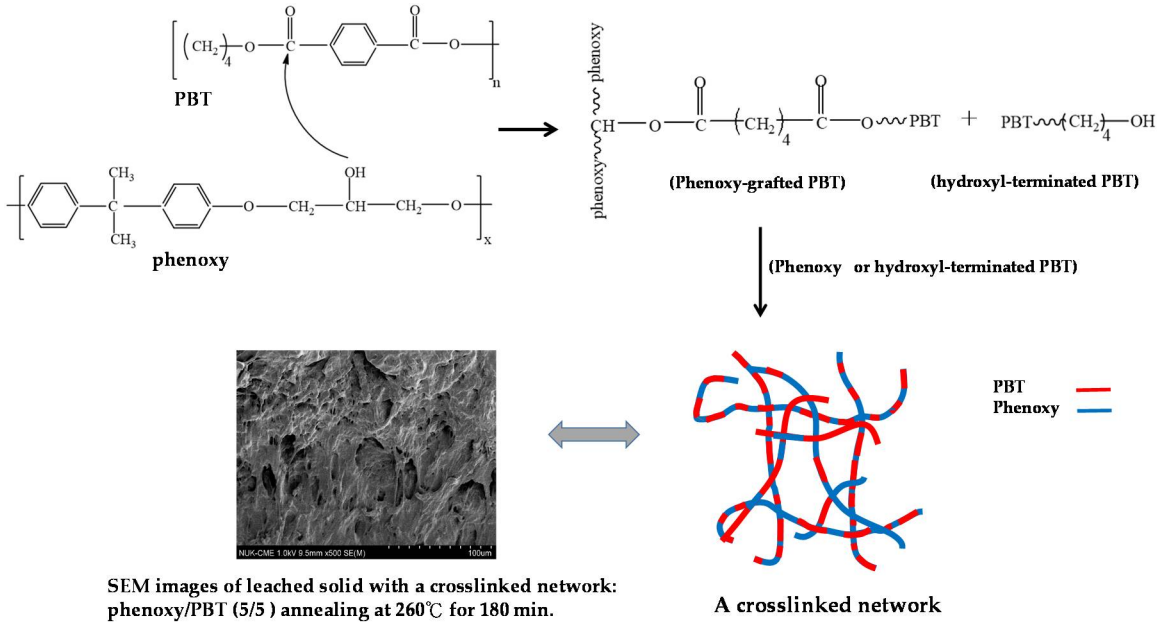
ester links between phenoxy and PBT. Meanwhile, the exchange reaction transforms the originally linear PBT chains into grafted PBT segments on the phenoxy, which can still undergo cross-linking reactions or homopolymerization since additional hydroxyl groups remain available. The change from aromatic/aliphatic to aliphatic/aliphatic carbonyl links resulted in the absorption peak of the carbonyl group being shifted downward by as much as 6–11 cm^{-1}, depending on the heating times and blend compositions. These FTIR results further supported the proposed reaction mechanisms.



Scheme 1. Mechanisms of the chemical interactions between phenoxy and PBT

The carbonyl-stretching band clearly shifted to the high-frequency side of the PBT carbonyl band, which strongly resembles that observed for the heated phenoxy/PBT blends, and it would be reasonable to assign this band to the aliphatic/aliphatic carbonyl chain links of PBT. If we curve-resolve the spectrum showing the carbonyl-stretching band of the phenoxy/PBT (9/1) blend annealed at various periods of time into two components (aliphatic/aromatic and aliphatic/aliphatic linked carbonyl group), we will obtain the result shown in Fig. 8. The shift in the carbonyl IR absorption of the annealed phenoxy/PBT blend was investigated using the commercial software "PeakFit 4.12" (Systat Software Inc.) in order to observe the composition of the aromatic-(CO)-O-aliphatic and aliphatic-(CO)-O-aliphatic species in the PBT sequence. In the annealed phenoxy/PBT blend, the carbonyl-stretching band was fitted to the carbonyl absorption bands at 1,713 and 1,724 cm^{-1}, attributed to C=O stretching of the aliphatic-(CO)-O-aliphatic and aromatic-(CO)-O-aliphatic structures, respectively. Assuming that the absorption coefficients of the two carbonyl bands attributed to aliphatic/aliphatic and aromatic/aliphatic carbonyl groups are similar in magnitude, we can calculate the fraction of each in the phenoxy/PBT blend as a function of the annealing time at 260°C. Figure 9 shows the mole fractions of the aromatic/aliphatic (1,713 cm^{-1}) and aliphatic/aliphatic (1,724 cm^{-1}) linked carbonyl groups in the phenoxy/PBT (9/1) blend annealed at 260°C for various periods of time. As the alcoholysis reaction in the phenoxy/PBT blend progressed, the aliphatic/aliphatic linked carbonyl groups increased with the annealing time; conversely, the aromatic/aliphatic linked carbonyl groups decreased as the annealing time increased. The original aromatic/aliphatic linked carbonate in the linear PBT chains formed aliphatic/aliphatic carbonyl ester links between phenoxy and PBT for the phenoxy/PBT blend annealed at 260°C for 180 min. Having established spectroscopically that no further reaction occurs at 260°C in the blend and recognizing that errors may be introduced by assuming identical absorption coefficients, we believe that we observed the effect of incomplete scrambling due to cross-linking and gelation. Indeed, phenoxy-rich blends were observed to gel after 180 min at 260°C and were no longer completely soluble.

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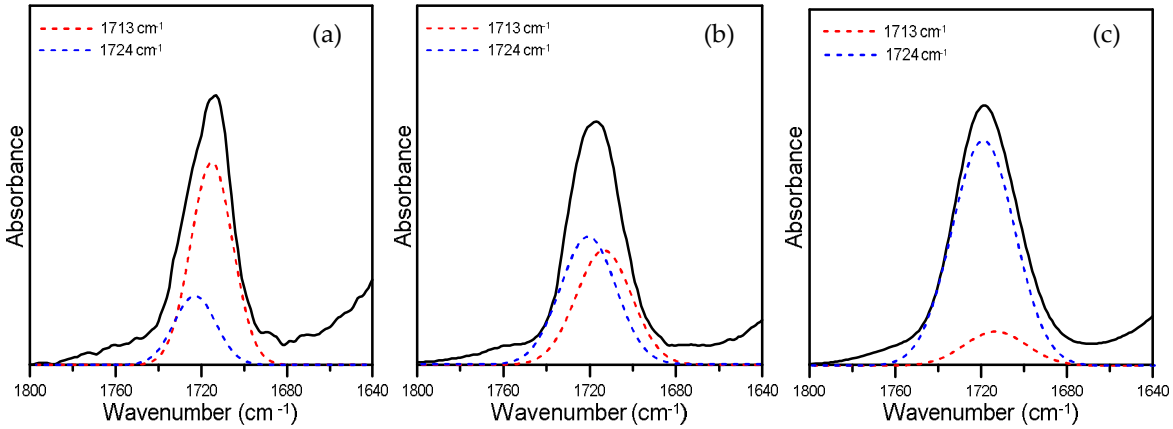

Figure 8. Deconvoluted IR absorbance peaks in the carbonyl-stretching region for phenoxy/PBT (9/1) after isothermal treatment at 260°C for various periods of time: (a) 5 min, (b) 20 min, and (c) 90 min.

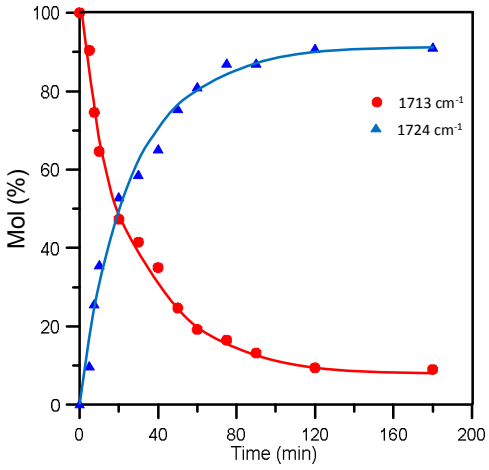

Figure 9. Mole fraction of specimens as a function of heating time for phenoxy/PBT (9/1) at 260°C

3.3. Effect of Chemical Interactions on the Crystallization Behavior

In the reactive blends, the progressive exchange reaction results in the transformation of the initial homopolymers into block copolymers and finally into random copolymers. The formed copolymers influence the compatibility of the blends. Additionally, the transesterification also influences the crystallization behavior of semicrystalline polymers in the blends. The transition to block or random copolymers decreases the crystallinity because of the dissimilarity of the copolymer chemical units [36–38]. In this work, the effect of the progressive exchange reaction on the crystallization behavior of PBT was investigated for the heated phenoxy/PBT blends. Due to the fact that PBT-rich blends have crystalline characteristics, the nonisothermal crystallization of phenoxy/PBT = 1/9 blends was used to study this effect. Figure 10 shows DSC thermograms of the nonisothermal crystallization behavior of phenoxy/PBT = 1/9 samples that underwent seven cycles of annealing between 0°C and 260°C. In Figs. 10(a), 10(b), and 10(c), the heating rate was 10°C/min and the annealing times (t_a) at 260°C were 2, 4, and 6 min, respectively. In these figures, both the exothermic heat of crystallization (ΔH_c) and the crystallization temperature (T_c) of PBT decreased as the annealing time increased and/or the number of cycles of annealing to 260°C increased. This suggests that the alcoholysis reaction between phenoxy and PBT takes place not only in the melted sample but also in the amorphous phase of the sample under thermal annealing below the melting temperature. Increasing the annealing time and the number of cycles of annealing increases the alcoholytic exchange between phenoxy and PBT, and therefore copolymers are observed in the blends.

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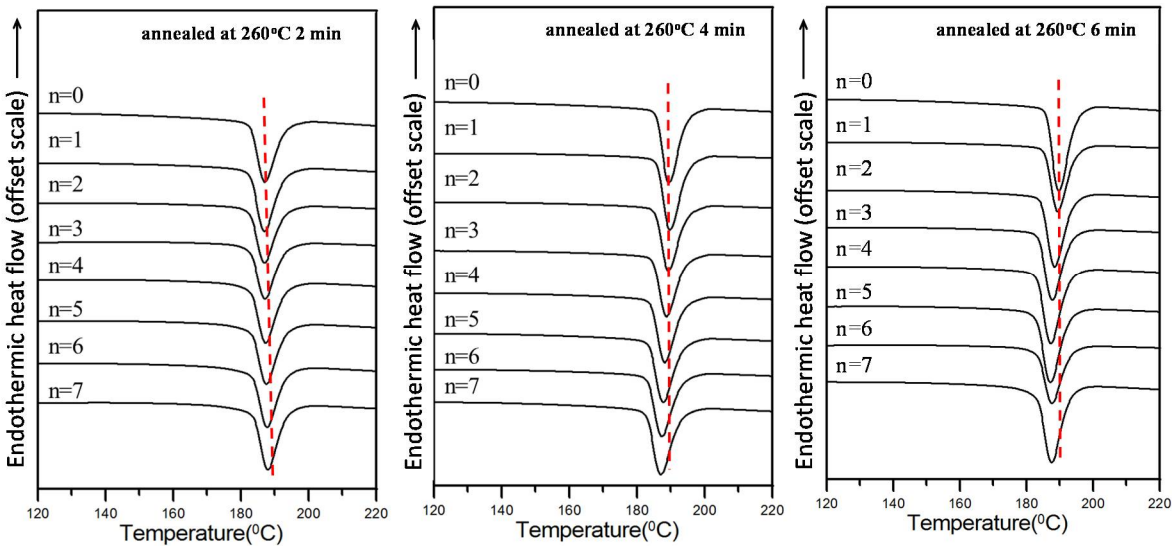

Figure 10. DSC thermograms of the crystallization behavior of phenoxy/PBT = 1/9 samples after cycles of annealing at 260°C for various periods of time followed by cooling: (a) 2 min, (b) 4 min, and (c) 6 min.

The effect of the total annealing time on the alcoholysis reaction was investigated using the change in the nonisothermal crystallization temperature (T_c). Figure 11 shows T_c as a function of the total annealing time for the phenoxy/PBT = 1/9 sample. In this experiment, the annealing time t_a varied from 0 to 6 min. T_c decreased faster when n was higher for a given total annealing time. These results suggest that the alcoholysis reaction intensified as the total annealing time increased, resulting in a stepwise increase in the copolymer content. In the blends, the digression of T_c upon annealing increased with the annealing time, owing to the inhibition of crystallization by the shortening of PBT segments with aromatic-(CO)-O-aliphatic carbonyl groups in the copolymers. In the crystalline polymer, the basic units of the crystalline polymer morphology include crystalline lamellae consisting of arrays of folded chains [37, 38]. The decrease in the degree of crystallization of PBT as the total annealing time (Σt_a) increased reveals the reduction of regular crystalline lamellae in PBT. The behavior that was expected as a consequence of the copolymers increased upon annealing because of the inhibition of crystallization by alcoholytic exchange.

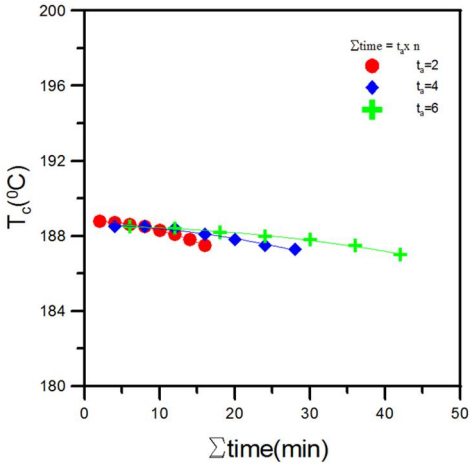

Figure 11. T_c as a function of the total annealing time for the phenoxy/PBT = 1/9 sample

4. Conclusions

As-blended phenoxy/PBT blends exhibited immiscible phases with two distinct T_g values, and the initially phase-separated blends could eventually merge into a homogeneous phase with a single T_g

on annealing at 260°C for 180 min. The presence of hydroxyl and carbonyl groups in the constituent polymers does not guarantee hydrogen bonding, which would induce miscibility. However, chemical exchange reactions upon annealing probably caused phase homogenization in phenoxy/PBT blends. The results of this study demonstrate that heat annealing can induce phase homogenization in phenoxy/PBT blends, which exhibit chemical interaction–induced miscibility. FTIR analysis reveals heat-induced shifting of the carbonyl-stretching band due to changes in the linkages adjacent to the carbonyl group of PBT. In this work, the pendant hydroxyl group in phenoxy exhibited proton-donor characteristics when it interacted with carbonyl groups in PBT that contain proton acceptors. In the phenoxy/PBT blend, the carbonyl group in the original unreacted PBT chain is linked to aromatic and aliphatic linkages (aromatic-(CO)-O-aliphatic); however, alcoholysis changed the linkages adjacent to the carbonyl group (aliphatic-(CO)-O-aliphatic). The reactions of the hydroxyl group of phenoxy with an aliphatic/aromatic linked carbonyl group of PBT initially led to the formation of a graft copolymer of phenoxy and PBT with an aliphatic/aliphatic carbonyl link. Further reaction produced a complex mixture of polymer chain structures with an increasingly wider distribution of aromatic/aliphatic and aliphatic/aliphatic carbonate links. Additionally, the progressive alcoholysis reaction changed the initial homopolymers into block copolymers and finally into random copolymers. The formed copolymers influenced the compatibility of phenoxy and PBT. Therefore, alcoholytic exchange can increase the compatibility of phenoxy with PBT in polymer blends upon annealing. The chemical interactions in the phenoxy/PBT blends affected not only the compatibility of the blends but also the crystallization behavior of the semicrystalline polymer in the blends. In the reactive amorphous/semicrystalline polymer blends, arrays of folded chains in the crystalline lamellae of PBT were interrupted by the copolymers formed in the exchange reaction. These reduced the ordering of the polymer chain, subsequently reducing the degree of crystallization of PBT in the blends.

Acknowledgments: The authors would like to thank the Ministry of Science and Technology of the Republic of China, Taiwan, for financially supporting this research under Contract No. MOST 105-2221-E-390-005.

Author Contributions: The study was designed by Chean-Cheng Su. The data collection was performed by Hsiang-Ching Wang. The data analysis was performed by Chean-Cheng Su, Jing-Liu and Cheng-Fu Yang. The overall planning was directed by Chean-Cheng Su.

Conflicts of Interest: The authors declare no conflict of interest.

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