Colloid Polym Sci (2004) 282: 1308–1315
DOI 10.1007/s00396-004-1075-6

ORIGINAL CONTRIBUTION

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Reaction-induced miscibility in blends comprised of bisphenol-A polycarbonate and poly(trimethylene terephthalate)

Received: 26 November 2003
Accepted: 22 December 2003

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Abstract The inherent miscibility and effects of reaction-induced changes on the phase behaviour of blends of poly(trimethylene terephthalate) (PTT) with bisphenol-A polycarbonate (PC) were studied. The as-prepared (solution-cast) blends exhibited two well-spaced and separated glass transition temperatures (T_gs) and a heterogeneous phase-separated morphology, indicating an immiscible system. However, after annealing at high temperature (at 260 °C), the blends' original two T_gs merged into one single T_g, and the annealed blends exhibited a homogeneous morphology, and turned from having a semicrystalline into having an amorphous nature upon extended annealing. The annealing-induced changes of phase behaviour in the blends were analyzed. The homogenization process of the blends upon heating is attributed to chemical transreactions between the PTT and PC chain segments, as evidenced with FT-IR characterization. The IR result showed a new aryl C-O vibration peak at 1,070 cm^{-1} for the annealed blends, which is characteristic of an aromatic polyester structure formed from exchange reactions between PTT and PC. The transreactions between PTT and PC led to a random copolymer comprised of PC/PTT segments, which is believed to serve as a compatibilizer at the beginning stage of transreactions, but at later stage, the random copolymer became the main species of blends and turned to a homogeneous and amorphous phase.

Keywords Polymer blends · Miscibility · Transesterification · Poly(trimethylene terephthalate)

Introduction

The phase behaviour and miscibility in widely studied systems such as poly(ethylene terephthalate) (PET)/polycarbonate (PC) and poly(butylene terephthalate) (PBT)/PC blends have been extensively reported. However, conflicting results have been reported. Murff et al. [1] concluded from measurements of the glass transition temperature (T_g) that partial miscibility (one T_g in PET rich phase) existed in the blends of PET and PC by melt-blending. However, Devaux et al. [2] have pointed out that transesterification could take place in the temperature range used for melt-blending, and the observed T_g changes could be accounted for by copolymer formation rather than miscibility. More recently, Hanrahan et al. [3] attempted solution-cast blending on studying those blend systems to avoid masking of the "inherent" phase behaviour that could have occurred as a result of transesterification. They found that all blends exhibited two separated T_gs, indicating that these two polymers, PET and PC, were inherently immiscible. The same results were published by Heinrichs et al. [4]. Miscibility in

PBT/PC blends has also been examined in a few studies [5, 6, 7], and similar results leading to immiscible PET/PC blends were reported. Transesterification and its effects on the phase morphology in polyester blends have been interesting topics widely studied by several researchers [8, 9, 10, 11, 12, 13, 14, 15, 16].

It has been reported that the phase behaviour of PET/PC [17, 18, 19, 20, 21] and PBT/PC [22, 23] blends could be brought to a significant change (e.g., from apparently immiscible to miscible mixtures) upon annealing at high temperatures. Such changes, however, cannot be over-simplified to an interpretation as physical miscibility behavior because there might have been chemical reactions between the constituent polymers that change not only the physical phase behaviour but also the chemical structure of the polymers. The conventional notion that the transreaction product in PC/polyester blend serves as a "compatibilizer" to enhance "miscibility", leading to a homogeneous mixture must be re-investigated.

In the present report, a study was performed to thoroughly investigate the relationships between the extents of transreactions and apparent changes in miscibility. Focus was placed on clarifying whether the copolymer (transreaction product) was effective to act as a compatibilizer to induce miscibility in a supposedly polyester-compatibilizer-PC blend. Or rather, the homogeneous mixture of polyester/PC upon annealing at high temperatures was a result of transition of the original PC/polyester mixture into a random copolymer. This study used a new polyester, poly(trimethylene terephthalate) (PTT), which differs from the more widely studied PET by one methylene (-CH_2-) group. Microscopy and thermal analysis were performed to characterize the blends before and after heating at high temperatures. Changes in the molecular states of the polymer mixtures upon thermal annealing were investigated using FT-IR analysis.

Materials and methods

Materials and sample preparation Semicrystalline polyester, PTT, was synthesized and supplied by the Industrial Technology Research Institute (ITRI, Taiwan). The T_g and T_m of PTT are 42.8 °C and 228 °C, respectively. The bisphenol-A polycarbonate (PC) used was GE Lexan HF 1130, which has an MW of 23,000 g/mole and a T_g of 142 °C.

To ensure that inherent phase behaviour in the PTT/PC blends was understood first, the blend specimens were prepared by a solution-blending method to avoid any possible effect of thermal heating at elevated temperatures that is inevitable in melt-blending. PTT and PC were first weighed and then dissolved in dichloroacetic acid (4 wt%). After they were fully dissolved, the clear polymer solution was cast into films at 60 °C, then dried in ambient conditions for 24 h. The film samples of the blends were then placed into a vacuum oven at 100 °C for 10 days, to remove the residual solvent.

A study was also conducted to analyze the effects of thermal heating on changes in miscibility and morphology that might be attributed to possible reactions between these two polymers at high temperatures. For this purpose, the PTT/PC blends were thermally annealed at 260 °C for different times (0–180 min) to induce various extents of reactions between the two polymers. The annealed blends were then re-dissolved in the same solvent (dichloroacetic acid), and re-cast to form film samples. For ease of characterization and analysis, the thermally annealed blends were also partitioned into their soluble and insoluble portions by extracting the soluble portion with dichloromethane. The residual insoluble solids in the blends were separated from the dichloromethane-extracted portion in solution, while the soluble solutes in the extracted solution were then precipitated by methanol. For convenience, in the present study, the residual solids and the solutes precipitated from the extracted solution were termed as "insoluble portion" and "soluble portion", respectively.

Apparatus A polarized-light optical microscope (POM) (Nikon Optiphoto-2 POL) with a microscope heating stage (Linkam THMS-600 with TP-92 temperature programmer) was used to examine and confirm the phase structure of polymer blends. POM samples were prepared by casting the polymer solution on glass slides. All observations were performed at the molten state (microscopy hot stage at 250 °C) to avoid crystallites in the blends.

The glass transition (T_g) temperatures, crystallization, and melting temperatures of the blend samples of various compositions were measured with a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-7) equipped with a coolant-circulated intracooler. Measurements of T_g, cold-crystallization, and melting transitions were made at a scan rate of 20 °C/min in the range 0–250 °C. The T_g values were taken as the onset of the glass transition (i.e., change in the specific heat) in the DSC thermograms.

FT-IR spectroscopy (Nicolet Magna-560, USA) was used for investigating the chemical reaction between constituents. Spectra were obtained at 4 cm^{-1} resolution and averages were obtained from at least 64 scans in the standard wavenumber range from 400 to 4,000 cm^{-1}. FT-IR measurements were carried out on thin films cast onto a potassium bromide (KBr) disk. The soluble portion and insoluble portion were first dissolved in dichloroacetic acid and then cast onto KBr. After the residual solvent was removed in the temperature-controlled vacuum oven, the resulting samples were used for the FT-IR experiments.

Results and discussion

Phase separated morphology in PTT/PC blends

Figure 1 shows the DSC thermograms (heating rate of 20 °C/min) of the PTT/PC blends (PTT/PC = 50/50 and 30/70), along with two neat polymers (PTT and PC). Prior to DSC scanning, all specimens were heated to 250 °C (which was about 20 °C higher than the melting point of PTT) for 3 min then rapidly quenched to −10 °C to bring the blend samples to an amorphous state. The DSC traces clearly show that two T_gs (marked on onset positions indicated with arrows) are seen. The square insets in Fig. 1 show the schematic morphology as revealed in the actual POM images for as-cast PTT/PC blends. Except for the two neat polymers that are naturally homogeneous, quite apparent phase domains are observed in the PC/PTT blends, indicating apparent phase immiscibility. Both DSC and POM studies concluded a phase-separated morphology in the as-prepared PTT/PC blend system (prior to annealing at high temperatures). The results of immiscibility for the PC/PTT blends are similar to those of PC/PET blends studied earlier [3, 4].

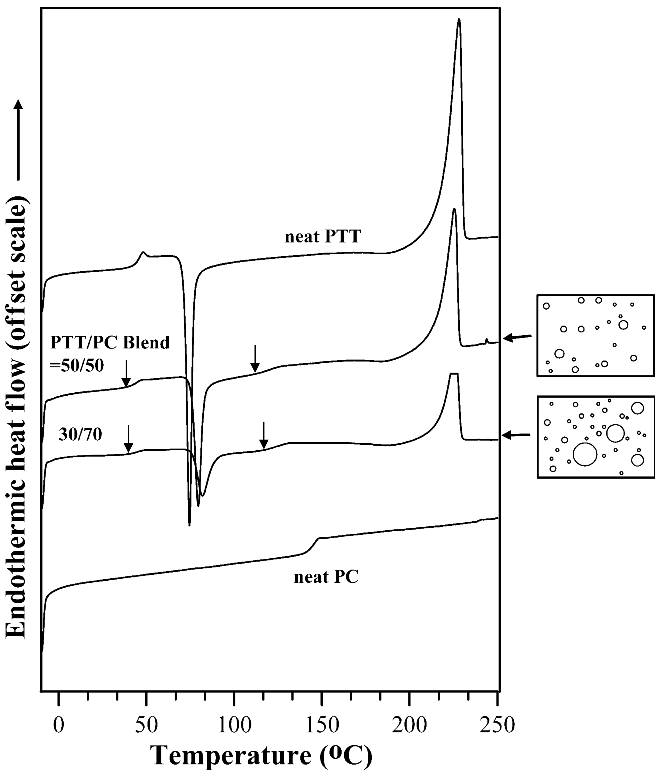


Fig. 1 differential scanning calorimeter (DSC) traces of the poly(trimethylene terephthalate) (*PTT*)/polycarbonate (*PC*) blends of two different compositions (50/50, 30/70) in comparison with two neat polymers (PTT, PC). *Insets* show the schemes of polarized-light optical microscope (POM) morphology of the blends

PTT/PC blends annealing

PTT/PC blends were annealed at 260 °C for different times. Microscopy and thermal analysis were then performed to characterize the blends after heating treatments. Figure 2 shows the DSC thermograms of the PTT/PC = 50/50 blend annealed at 260 °C for increasingly longer times (from 0 to 180 min). After annealing at 260 °C for more than 15 min, the original two T_gs in the blends merged to a single and sharp T_g. In addition, the cold-crystallization temperature (T_{cc}) of the heated blends gradually increases while the melting temperature (T_m) decreases with increase of the annealing time imposed on the blends. Eventually, at extended annealing times (e.g., 120 min or longer), both T_{cc} and T_m of the blends disappear, indicating transition into an amorphous state. The insets in Fig. 2 show the schematic features of the actual POM images for the PTT/PC = 50/50 sample that had been annealed at 260 °C. Upon progressively longer annealing, the original phase-sepa-

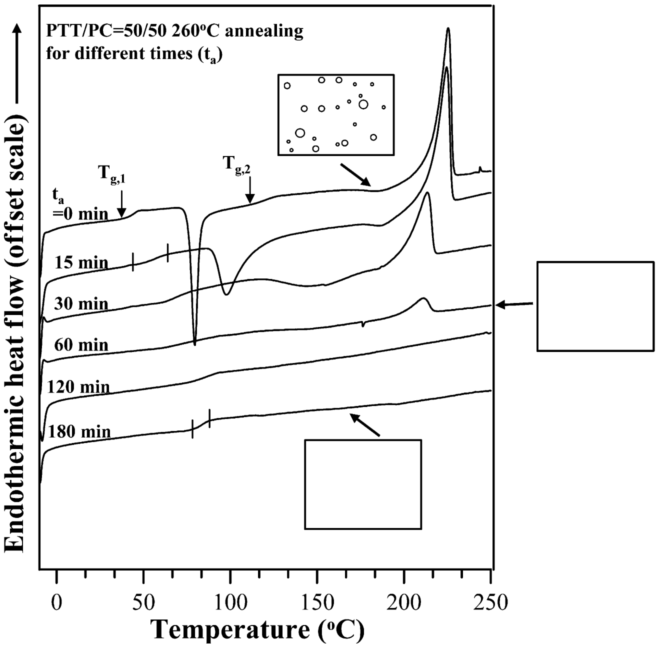


Fig. 2 DSC traces of PTT/PC = 50/50 blends annealed at 260 °C for increasingly longer times (0 to 180 min). Insets show the schemes of POM morphology evolution upon annealing. T_g Glass transition temperature

rated domains eventually disappear, and the morphology in the annealed PTT/PC blends turns homogeneous. Similarly, Fig. 3 shows the DSC thermograms of PTT/PC (30/70) blend samples annealed at 260 °C for increasingly longer times (from 0 to 180 min). Similar homogenization of the blend upon annealing at high temperatures was evidenced.

Furthermore, at extended annealing, the blends seemed to reach a final state. The T_{cc}s and T_ms of the blends eventually disappeared and the T_g stayed at a constant for the samples annealed at 260 °C for 120 min or longer. Figure 4 describes the changes of T_g and T_g breadth with increasing annealing time at 260 °C for the PTT/PC = 30/70 sample. Upon annealing at high temperatures, the initial two T_gs eventually merge into a single and sharp T_g, which indicates that the blends are transformed from an originally immiscible state to a homogeneous one.

The effect of annealing at high temperatures on the PTT/PC blends was also examined by analyzing through a T_g versus composition plot in Fig. 5. In addition, the T_gs data in this plot were obtained from the blends that were annealed at 260 °C for 60 and 180 min, in other words, single T_g blends. These T_gs data were further fitted into two quantitative models (Fox or Gordon-Taylor equations). Apparently, Fig. 5 shows that the classic Fox equation for the binary blend systems [24]: $1/T_g = (w_1/T_{g1} + w_2/T_{g2})$ might deviate from the observed T_g-composition relationship. As the Fox model shows some deviation from the experimental data, alternative models might be more desirable. Thus, the Gordon-Taylor equation [25] was used for describing this system with an additional parameter, k:

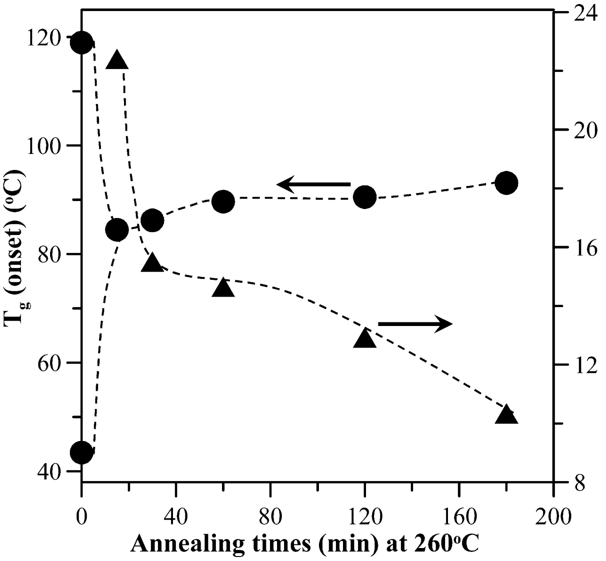


Fig. 4 T_g (onset values) and T_g breadth vs. annealing times at 260 °C of PTT/PC = 30/70 blend

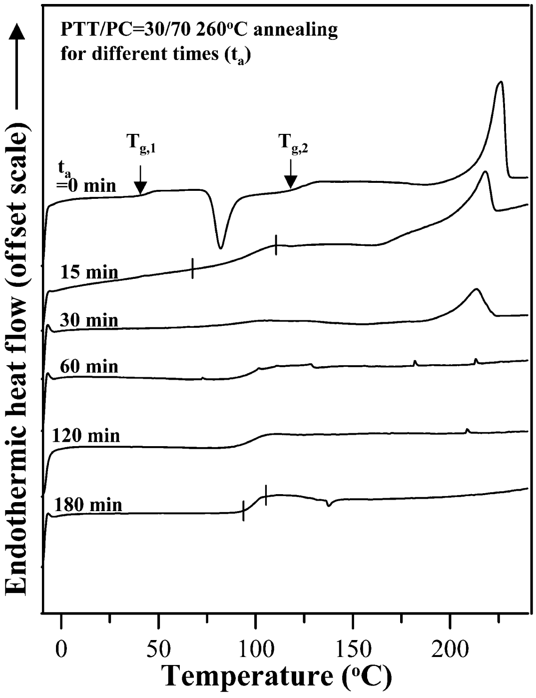


Fig. 3 DSC traces of PTT/PC = 30/70 blend annealed at 260 °C for times from 0 to 180 min

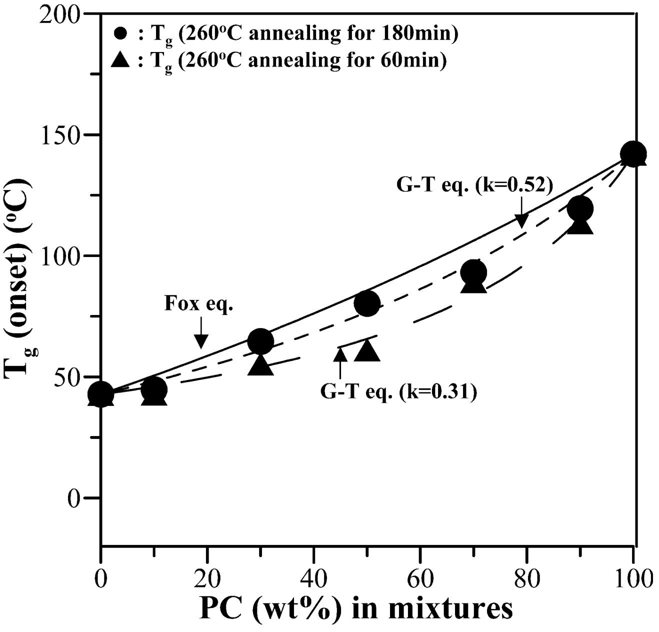


Fig. 5 T_g (onset values) as a function of composition for the heated PTT/PC blends. The plot also shows comparisons with the Fox equation (*solid curve*) and Gordon-Taylor model (*two dashed curves*), respectively

$$T_g = \left(w_1 T_{g1} + k w_2 T_{g2}\right) / (w_1 + w_2) \quad (1)$$

where 1 and 2 were the lower-T_g component (PTT) and higher-T_g component (PC), respectively. The fitting parameter (k) has been suggested to correlate with the interactions between the constituent polymers in miscible blends. Generally speaking, a larger k value means a stronger interaction between the polymers. In this case, $k = 0.52$ was obtained for the blends annealed at 260 °C for a long time ($t = 180$ min), but a smaller k value (0.31) was obtained for the samples annealed at 260 °C for a shorter time ($t = 60$ min).

For purely physical blends without possibility of chemical reactions, a larger k would normally mean greater interactions between the polymers. However, in this system, which has been proven to possess the capability of transreactions, the difference of the values of k in the blends heated for different times must be interpreted in different ways. This phenomenon of increasing k in the heated blends should mean that the morphology of the heated blends is gradually homogenized to a more uniform state upon annealing at longer times. Some earlier studies claimed that the annealing process would enhance the miscibility in the polyester/PC blends [14, 15, 16, 17, 18, 19, 20, 21]. However, this notion must be more properly refined. As PTT and PC can undergo transreactions at elevated temperatures, they cannot be regarded as physical blends after annealing. Instead, the homogenization might very well be a result of going from the state of two homopolymers that are originally physically mixed to a state of a randomly distributed copolymer.

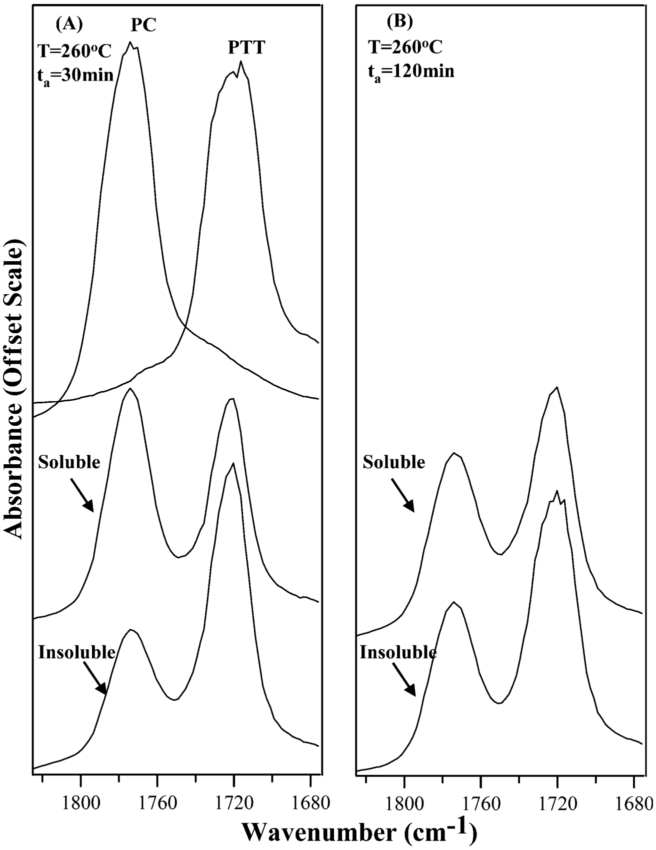


Fig. 6A, B IR spectra showing the C = O stretching bands for the soluble-portion vs. insoluble portion of PTT/PC = 50/50 blend heated (at 260 °C) for different times. **A** 30 min. **B** 120 min

Chemical reactions between PTT and PC

Chemical reactions between the PTT and PC chain segments of the PTT/PC blends might be likely upon annealing at high temperatures. PC/PTT blends were heated to induce transreactions of various extents. The heated blends then contained PTT, PC, and certain fractions of an exchanged random copolymer of PTT-PC segments. The solvent-extracted portion should contain mostly the amorphous random copolymer (product of the transreactions) and PC homopolymer (that are readily soluble in dichloromethane), while the insoluble portion contained mainly the un-exchanged PTT homopolymer that is insoluble in dichloromethane. For ease of analysis, the heated blends were dichloromethane-solvent-extracted into soluble and insoluble portions. The extracted soluble portion and insoluble portion were characterized with FT-IR analysis. Figure 6 shows the C = O stretching bands for the soluble portion and insoluble portion of the blends heated at 260 °C for different times: (A) 30 min, and (B) 120 min. The C = O stretching bands of the carbonyl group in neat PC and PTT were observed at 1,780 and 1,720 cm^{-1}, respectively. Interestingly, the absorption peak at 1,720 cm^{-1}, characteristic of the C = O stretching of PTT chain segment, was found in the spectra of the soluble portion and its intensity increased with the annealing time imposed on the samples. In addition, the absorption peak of the PC C = O stretching at 1,780 cm^{-1} was revealed in the IR spectra of the insoluble portion and the intensity also increased with annealing time. The same phenomenon in the PBT/PC blends has also been reported [22]. The 1,720 cm^{-1} peak (in the soluble portion spectra) might be attributed to the C = O stretching of PTT chain fragment linked on the reaction-caused copolymer backbone in the soluble portion, and the 1,780 cm^{-1} absorption peak (in the insoluble portion spectra) was believed to be associated with the C = O stretching of the PC segments in the copolymer in the insoluble portion. In other words, the chemical reaction occurred upon annealing at high temperatures and chain segments of PTT and PC exchanged with each other, especially between the ester structures of two homopolymers.

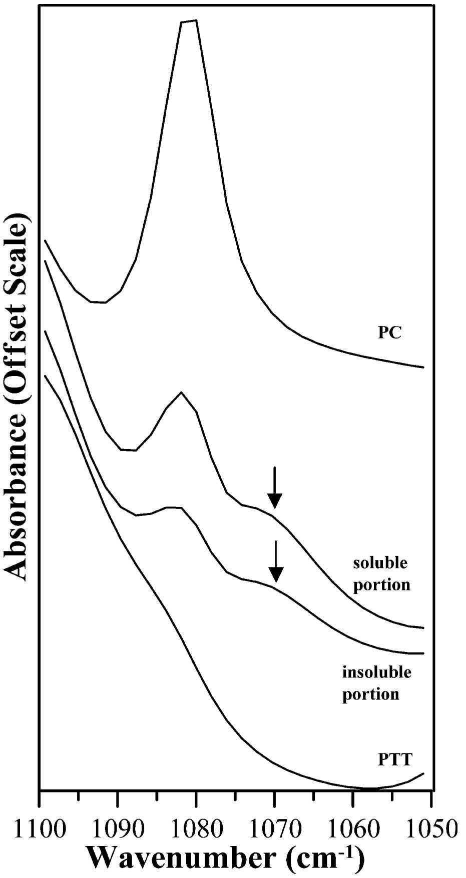
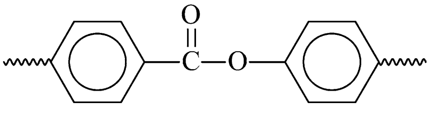


Fig. 7 FT-IR spectra (C-O from 1,050 to 1,100 cm^{-1}) for the soluble portion vs. the insoluble portion of PTT/PC = 50/50 blend annealed at 260 °C for 120 min

Figure 7 represents the FT-IR spectra (1,050 to 1,100 cm^{-1}) for the soluble portion in comparison with the insoluble portion extracted from the PTT/PC = 50/50 blend annealed at 260 °C for 120 min. A new peak at 1,070 cm^{-1} is seen in both the soluble and insoluble portions. From the literature [22], the 1,070 cm^{-1} peak is also present in PBT/PC blends annealed at high temperatures. The 1,070 cm^{-1} peak is characteristic of a fully aromatic ester structure (i.e., COO linked to two phenyl groups on each side) that is a result of transreactions between PC and polyester, as in Structure [22]:



This 1,070 cm^{-1} IR absorption band is believed to be a C-O vibration in the fully aromatic ester structure.

From observation and analysis of the FT-IR spectra, a possible mechanism about transesterifications between PTT and PC can be proposed in Scheme 1.

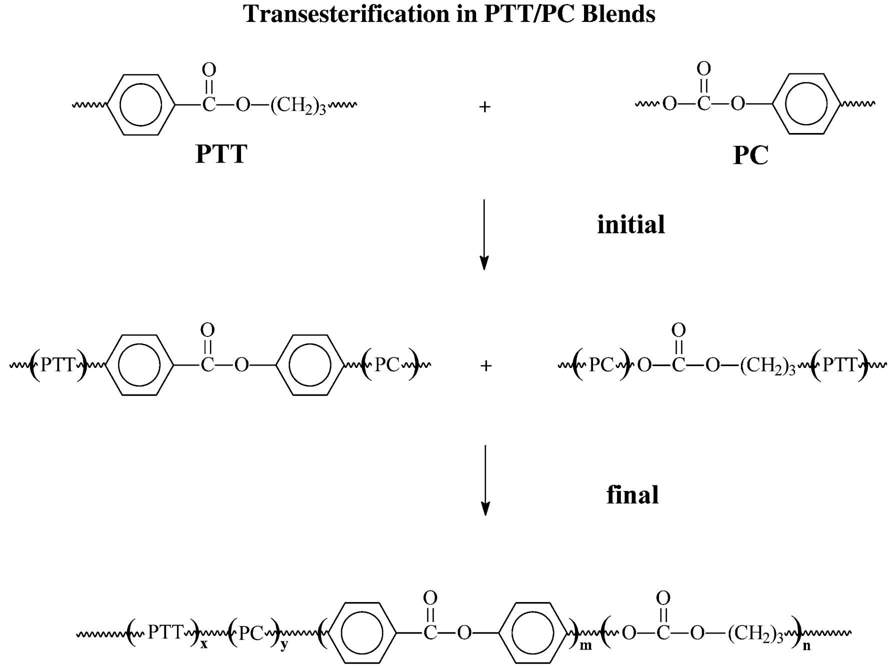
This mechanism shows that the carbonyl groups of PTT are exchanged with the carbonate groups in PC upon annealing at high temperatures, and the exchange leads to formation of possibly a new copolymer that is comprised of randomly spaced segments detached from the PC and PTT chains.

Earlier studies [18, 19, 20, 21] have claimed that the PC-polyester copolymer might act as the compatibilizer in the blend to improve the miscibility between the different polyester and PC chains. This interpretation might be partially valid. However, it must be pointed out that the “compatibilization effect” alone cannot be the main effect leading to a homogeneous morphology at extended annealing. It is known that two immiscible polymers can probably be compatibilized to exhibit better mechanical properties, but it is generally impossible to compatibilize two originally immiscible polymers into a homogeneous and thermodynamically miscible blend system simply by introducing a compatibilizer. The homogenization from an immiscible into a homogeneous phase in the annealed PC/PTT blends must be exemplified in more convincing ways. It is believed that transesterification reactions in the PTT/PC blends upon annealing indeed occurred, and the random copolymer formed from this exchange reactions might act as a compatibilizer in the earlier stages of reactions; however, in the later stages of transreaction, the randomly linked copolymer becomes the main species of product. In other words, PC and PTT chains are no longer the original homopolymers, but instead, random copolymers comprised of the exchanged PTT-PC segments. Owing to the increased exchange reactions between these two chains, T_{cc} initially increases and T_m decreases. For specimens subjected to even longer annealing times, no T_{cc} or T_m were observed and a single T_g was seen, indicating that they eventually were turned into a totally amorphous state through an extensive exchange reaction.

Evidence of irreversibility

A physical state is readily reversible, while a chemically changed state is not. The POM graphs (for brevity, not shown here) showed that for the as-prepared PTT/PC = 50/50 (solution-casting), it exhibited apparently phase-separated domains, while the same blend that had been heated (for 30 min, 60 min, 120 min, respectively), re-dissolved and cast into films were apparently free of any phase domains, suggesting that the heated blends readily underwent a homogenization process. Figure 8 demonstrates the DSC results of the heated blends (heated for different times) that had been re-dissolved and re-cast from solutions. Interestingly, the re-dissolved and re-cast blends show only one T_g. Furthermore, with increasing annealing time, the T_{cc} shifts to a higher

Scheme 1 Transesterification in PTT/PC blends



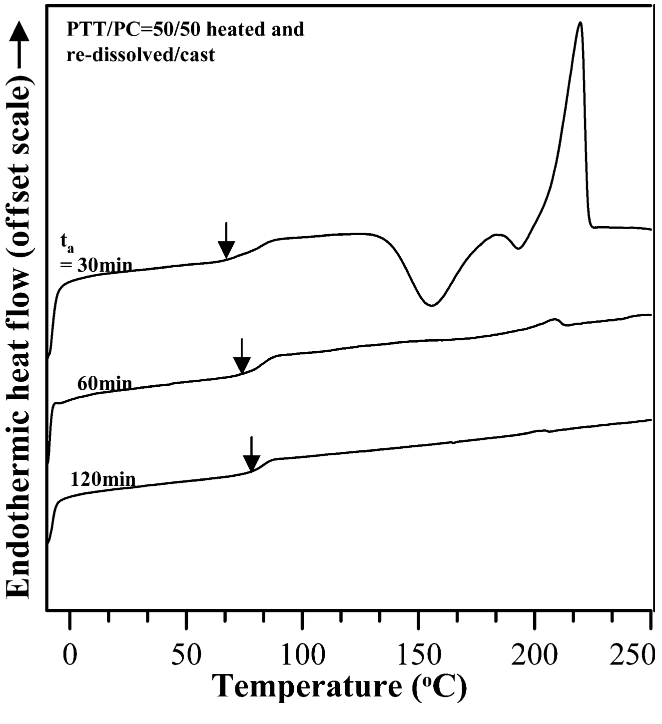


Fig. 8 DSC traces of a re-dissolved/re-cast PTT/PC = 50/50 blend that had been heated at 260 °C for different times

temperature and the T_m shifts to a lower temperature. There are no traces of T_{cc} and T_m for the blend heated (at 260 °C) for 120 min. The POM and DSC results show that a single T_g is apparent and the morphology of the heated PC/PTT blends after the re-dissolving/re-cast process were homogeneous and differed from the original phase-separated morphology of the as-prepared PC/PTT blends. In other words, the changes upon annealing of the blend were irreversible.

To conclude, this study has demonstrated that the PTT/PC blends were inherently immiscible in the amorphous state. The blends revealed two T_gs and heterogeneous phase morphology. With annealing at high temperature, the original two phases were converted to one single phase. According to the experimental results (POM and DSC) of re-dissolved samples, the main factor of the change of miscibility in the blend (after annealing at high temperatures) was attributed to the chemical reaction between PTT and PC. In addition, from the measurement of FT-IR spectroscopy of both soluble and insoluble samples after annealing, a new absorption peak was seen at 1,070 cm^{-1} and was characteristic of a new aromatic polyester structure.

FT-IR spectra revealed the occurrence of a transesterification reaction between PTT and PC chain segments, and this exchange reaction produced the new copolymer, which acted as the compatibilizer in the PTT/PC blends in the earlier stage of the reaction. After annealing at high temperature for a longer time, in other words, at a later stage of reaction, the random copolymer became the main species of product. However, it must be pointed out that the "compatibilization effect" alone cannot be the main effect leading to a homogeneous morphology at extended annealing. It is believed that transesterification reactions in the PTT/PC blends upon annealing indeed occurred, and the random copolymer formed from these exchange reactions might act as a compatibilizer in the earlier stages of reactions; however, in the later stages of transreaction, the random copolymer become the main species of product, exhibiting a homogeneous phase.

Acknowledgement The support of this work by Taiwan's National Science Council (# NSC 91 2216 E 006 021) is gratefully acknowledged.

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