Effects of Sub T_g Annealing on the Mechanical Properties of Polycarbonate/Poly(ether ester) Copolymer Blends

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ABSTRACT: To improve the impact strength of polycarbonate (PC) and reduce hardening of PC after sub T_g annealing at 140℃ a thermoplastic elastomer, poly(butylene terephthalate-co-tetramethylene glycol) (PBT-PTMG) was melt mixed with PC. A transesterification inhibitor was added to inhibit reaction between PC and PBT segments during mixing and annealing. Partial miscibility between PC and PBT segments observed for as-molded blends prevents the PBT-PTMG added from fully crystallizing upon cooling, thus acting as an impact modifier of PC. However, the phase separation proceeds as the blends are annealed at 140℃, which is below T_g of PC. This causes increase in the crystallinity of PBT segments, which acts as physical crosslinks, and thus enhances the toughness of PC physically aged.
    KEY WORDS   Polymer Blend / Polycarbonate / Physical Aging / Thermoplastic Elastomer / Impact Modifier / Annealing / Poly(butylene terephthalate-co-tetramethylene glycol) /

Annealing of amorphous polymers under the glass transition temperature (T_g) affects significantly physical properties such as density, modulus and strength, etc.[1,2] Change in physical properties results from the inherent kinetic nature of the glass transition. When a polymer is cooled in a normal process from the melt state, it is in a nonequilibrium state. Therefore, there exists a thermodynamic driving force for conformational rearrangement even though annealing temperature is below T_g and this causes a change in physical properties of polymers. This physical aging brings necessarily the embrittlement of polymers.

Polycarbonate (PC) is one of engineering polymers used in various applications, because of its outstanding properties including optical clarity and toughness. However, it rapidly loses its toughness during physical aging at temperatures just below T_g.[3] To expand the usefulness of PC in a variety of applications, it is important to explore ways to prevent or minimize loss of toughness during sub T_g annealing. Since adding appropriate impact modifiers has been known to be one of effective toughening methods for inherently brittle polymers[4,5] this method may be also effective in toughening PC which loses inherent toughness through physical aging.[6]

Thermoplastic elastomers (TPE) are polymers that exhibit a unique combination of strength, flexibility, and processability due to their phase-separated microstructure.[7] They are composed of two different segments, commonly referred to as soft and hard segments. The soft segments are derived from oligomers having a low T_g and are viscous at service temperatures, imparting flexibility to the polymer. Interactions between the hard segments lead to phase separation in which microdomains formed serve as thermally reversible physical crosslinks. They contribute to the strength and dimensional stability of the polymer. Phase separation may involve hard segment vitrification, crystallization, and/or ionic clustering. Thermoplastic poly(ether ester) elastomers are commercial thermoplastic elastomers usually composed of tetramethyleneterephthalate (PBT) units as hard segments and polyoxytetramethylene (PTMG) units as soft segments. Crystallites of PBT segments are formed on cooling from the melt and act as physical crosslinks. By varying the ratio of hard to soft segments and degree of crystallinity of the hard segments, they show characteristics ranging from soft elastomers to relatively hard elastoplastics. They are used in applications requiring exceptional toughness and flex resistance together with tear and chemical resistance. They are also known to be useful in toughening important engineering polymers such as polyamides[8] and compatibilizing polymer blends.

This study investigates the effectiveness of poly(ether ester) type elastomer as an impact modifier of PC before and after sub T_g annealing. Poly(butylene terephthalate-co-tetramethylene glycol) (PBT-PTMG) elastomer is used. Note that the PBT segments in PBT-PTMG are compatible with PC. The addition of PBT-PTMG is expected to impart high elastic recovery and easy processability to PC and to compensate for the physical aging problem of PC.

EXPERIMENTAL

Polymers used in this study are commercially available and used without further purification. PC is the Calbre 300-15 of Dow Chem. Co. and it has 25000 g mol^{-1} of M_w. Its T_g is 155℃. PBT-PTMG is the KOPEL KP 3344 of Kolon Co., Korea and has two distinct T_gs at $\sim$89 and 44℃, which are corresponding to T_gs of PTMG and PBT segments, respectively. An inhibitor (Mark AX-71), provided by Adeka Argus Chem. Co, was used to prevent transesterification reaction between PC and PBT-PTMG during melt mixing or annealing. The inhibitor is a flake form of organic phosphate complex additive and applicable for PC and PBT.[9]

Blend samples were prepared by melt mixing at 230℃ in the presence of 0.3 wt% transesterification inhibitor

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in an extruder (Toshiba TEM 358), and injection molded using an injection molder (ENGEL ES-330-80). Component polymers were pre-dried at 95℃ for 4 h before mixing. To investigate the effect of sub T_g annealing on the structure and properties of PC/PBT-PTMG blends the injection-molded samples were annealed under nitrogen atmosphere at 140℃ for 1 and 5 h, respectively.

Thermal properties of blends were measured using a differential scanning calorimeter (DSC), Perkin Elmer DSC-7, at a heating rate of 20℃ min^{-1} from 0℃ to 230℃ after annealing at 140℃ for specified time and then rapid quenching. DSC data of as-molded samples were obtained from second scan at the same heating rate after maintaining the samples at 230℃ for 3 min to destroy thermal history and rapid quenching.

Morphology of blends was investigated using a scanning electron microscope (SEM, JEOL 35 CF) at an accelerating voltage of 20 kV. Samples were fractured in liquid nitrogen and the surface was extracted with tetrahydrofuran (THF) at room temperature for 3 h to remove the PC surface layer.

Infrared (IR) spectra were obtained using a Perkin-Elmer infrared spectrophotometer to examine the formation of block-type copolymers during melt mixing and thus investigate whether Mark AX-71 added acts effectively as a transesterification inhibitor. 50/50 PC/PBT-PTMG blends with and without the inhibitor were subjected to extraction with methylene chloride (CH_2Cl_2) for 10 h in a Soxhlet. PC is completely soluble in CH_2Cl_2 whereas PBT-PTMG is practically insoluble; the weight loss of PBT-PTMG is less than 1 wt% under the dissolving conditions applied. The CH_2Cl_2 soluble fractions were concentrated and cast onto KBr plates. After thorough drying, IR spectra were obtained.

Notched specimens with thickness of 6.4 mm were tested on a TMI impact strength tester. All tests were performed with a pendulum of 27.65 kg cm. At least seven samples of each composition were tested, and average values were used as data. Tensile properties of blends were measured at room temperature using an Instron tester at a crosshead speed of 20 mm min^{-1}. Dumbbell type specimens were used for tensile test. An average value of seven tests was reported.

RESULTS AND DISCUSSIONS

Transesterification reaction takes place in molten mixtures of polycarbonate and polyester. This causes the formation of block-type copolymers and affects the miscibility and final morphology of the blends.[10,11] Thus, the reaction can make the interpretation of experimental results complex and should be prevented during melt mixing or annealing. When PC/PBT-PTMG blends were extracted with CH_2Cl_2, the resultant solutions may contain block-type copolymers as well as neat PC if the transesterification takes place during melt mixing. Figure 1 shows IR spectra of pure PC and CH_2Cl_2 soluble fractions of 50/50 PC/PBT-PTMG blends. For neat PC, the absorption at 1780 cm^{-1} can be assigned to the carbonyl stretching vibration of PC. For the 50/50 blends without the inhibitor (Figure 1C) a new peak at 1720 cm^{-1}, which corresponds to C=O stretching vibrations of PBT segment, is present. The existence of the new
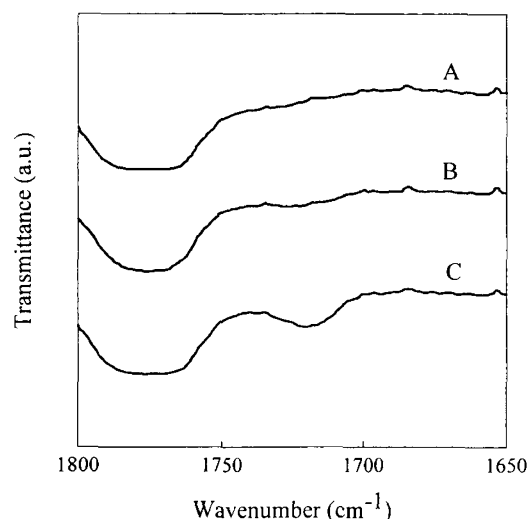

Figure 1. IR spectra of neat PC and 50/50 PC/PBT-PTMG blends: (A) neat PC; (B) blend with an inhibitor; (C) blend without an inhibitor. Mark AX-71 was used as the inhibitor.
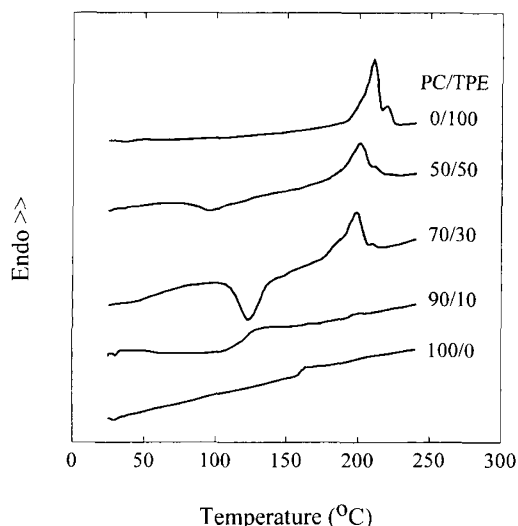

Figure 2. DSC thermograms of as-molded PC/PBT-PTMG blends.

peak indicates that transesterification has occurred during melt mixing and the two polymers are chemically linked. On the other hand, for the 50/50 blend with the inhibitor (Figure 1B) a peak at 1720 cm^{-1} is not observed, indicating that the inhibitor added in this study is effective in preventing the transesterification reaction between PC and PBT segments during melt mixing. Since the transesterification rate increases with annealing temperature,[10] the transesterification during sub T_g annealing is negligible and does not affect change in physical and morphological properties. The effect of annealing at melt state, above melting temperature of PBT, on the compatibility of PBT/PC blends is well reviewed in another article.[12]

Measuring T_g of polymers is essential for assessing blend miscibility.[13] Usually, miscible blends show single and composition-dependent T_gs, whereas for immiscible blends multiple transitions are observed. Figure 2 shows the DSC thermograms of as-molded samples at 0 to 230
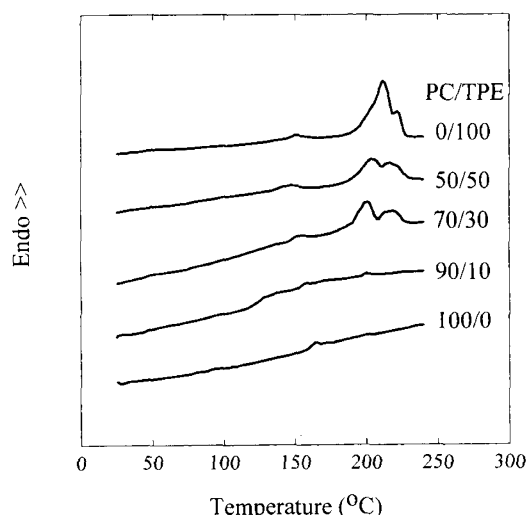
Figure 3. DSC thermograms of PC/PBT-PTMG blends, annealed at 140℃ for 5 h.

Figure 4. Scanning electron micrographs of 70/30 PC/PBT-PTMG blends: (A) as-molded; (B) 1 h, and (C) 5 h annealed at 140 ℃, respectively.

℃. T_g of PTMG segments is not observed in the thermograms because it is about −90℃. Miscibility between PC and PBT segments in PBT-PTMG may be inferred from the following results. First, as-molded 90/10 blend has a single T_g at 121℃ between T_gs of PC and PBT segment. Second, above 30 wt% of PC cold crystallization temperatures of PBT segments are observed, indicating that PC prevents significantly melt crystallization of PBT segments during rapid quenching in the DSC cell. The results clearly show that there is a certain amount of miscibility between PC and PBT segments under the mixing conditions in this study. Partial miscibility of PC and PBT has been reported by several research groups[14,15] and the results here are consistent with them. Miscibility between PC and PBT segments prevents PBT segments from fully crystallizing during sample preparation and as a result PBT-PTMG copolymer does not effectively act as an impact modifier of PC at the as-molded state.

Figure 3 shows the effect of sub T_g annealing on the thermal properties of PC/PBT-PTMG blends, annealed at 140℃ for 5 h. For 90/10 blend two distinct T_gs are observed at the temperatures of 123 and 151℃. This indicates that 90/10 blend, which was miscible at as-molded state, is phase-separated into two distinct phases. However, it is noteworthy that partial miscibility is maintained for the blend because T_g at 123℃ is still observed. When the content of PC is above 30 wt%, two significant changes in the thermograms are observed after sub T_g annealing. First, T_g of PC is observed around 150℃. Second, cold crystallization exotherms are not observed upon heating, indicating that crystallites of PBT segments are well developed during annealing. Crystallinity of PBT segments in the blends, measured from the area of melt endotherms, significantly increases with annealing compared to that of as-molded samples. The results mentioned above indicate the phase separation of PC and PBT segments during sub T_g annealing and thus after annealing PC cannot restrict crystallization of PBT segments no longer. As a result, the PBT domains are well developed by phase separation and thus number of
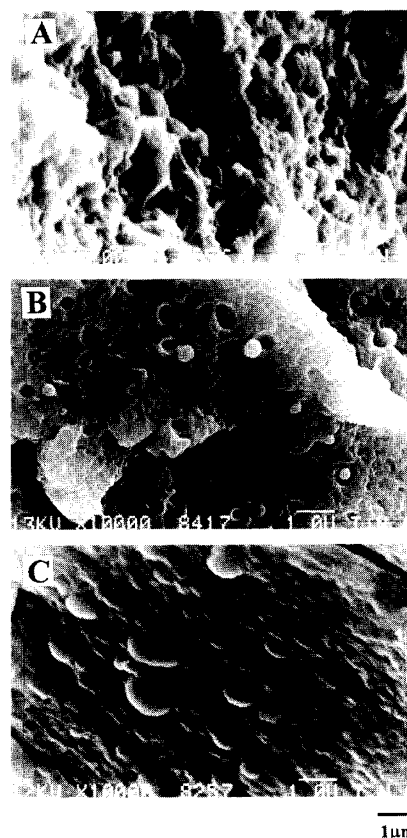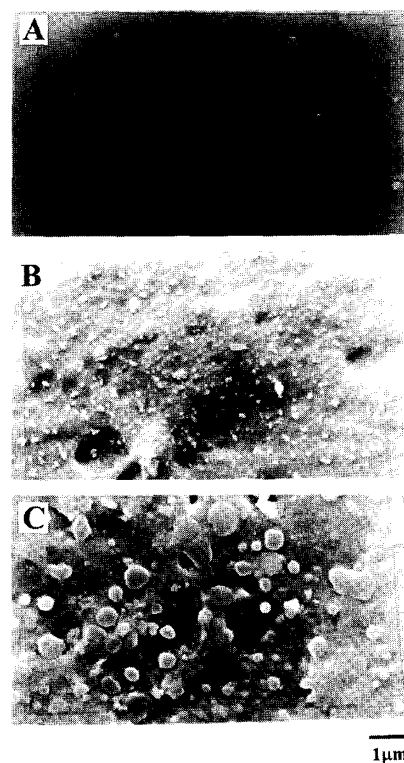

Figure 5. Scanning electron micrographs of 50/50 PC/PTE blends: (A) as-molded; (B) 1 h, and (C) 5 h annealed at 140℃, respectively.

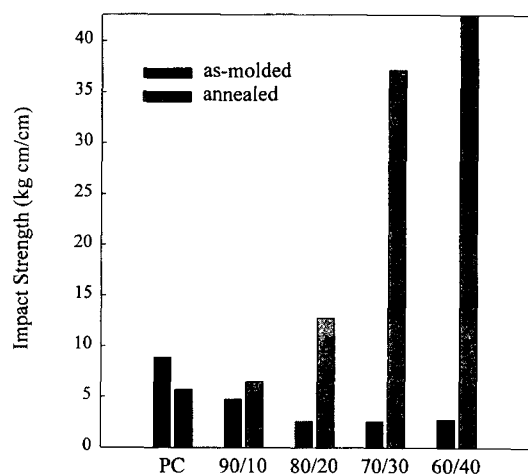**Figure 6.** Impact strength of PC/TPE blends: (■) as-molded; (■) annealed at 140°C for 5 h.

Figure 7. Modulus (A) and strain at break (B) of PC/TPE blends: (■) as-molded; (■) annealed at 140°C for 5 h.

physical crosslinks, which contribute to recover the elastic property of PBT-PTMG, increases after annealing. This is confirmed in the section on mechanical properties.

The phase separation during sub T_g annealing indicates that the partial miscibility between PC and PBT observed in as-molded samples is not driven by a thermodynamic force. The miscibility may be induced by shear force during mixing.[16,17] Okamoto and Inoue reported that blends of PC and PBT, prepared at 290°C using a melt mixing, have lower critical solution temperature (LCST) of about 198°C; only below 198°C the blends are homogeneous. They attributed the reason why the blends show miscibility at the molecular level even though the processing temperature is higher than the LCST to the elevation of LCST under shear. In this study we annealed blend samples at 140°C, much lower than LCST of PC/PBT blends reported by Okamoto and Inoue, but observed the phase separation. Although the presence of PTMG segments affects the phase behavior of PC/PBT blends, the discrepancy between the two results is significant. Further experiments may be required to explain the phase behavior of PC/PBT-PTMG blends under shear.

Phase separation is obvious when the morphology of the blends is observed using a scanning electron microscopy. Figures 4 and 5 show the morphology changes of 70/30 and 50/50 PC/PBT-PTMG blends with annealing time at 140°C. As-molded samples show continuous miscible phase whereas annealed blends exhibit the dispersed domains, which are crystalline PBT-PTMG phases as we infer from the blend composition. The size of dispersed phase increases with annealing time. Since the annealing temperature is 140°C, below T_g of PC, the phase growth seems not to be due to typical coarsening processes such as coalescence. The thermal-induced phase separation during sub T_g annealing was confirmed from the observation that the interdomain spacing and absolute intensity measured from small angle X-ray scattering (SAXS) experiments is increased with annealing time (not shown here).[18]

How effective the sub T_g annealing on the impact strength of PC/TPE blends is shown in Figure 6. For as-
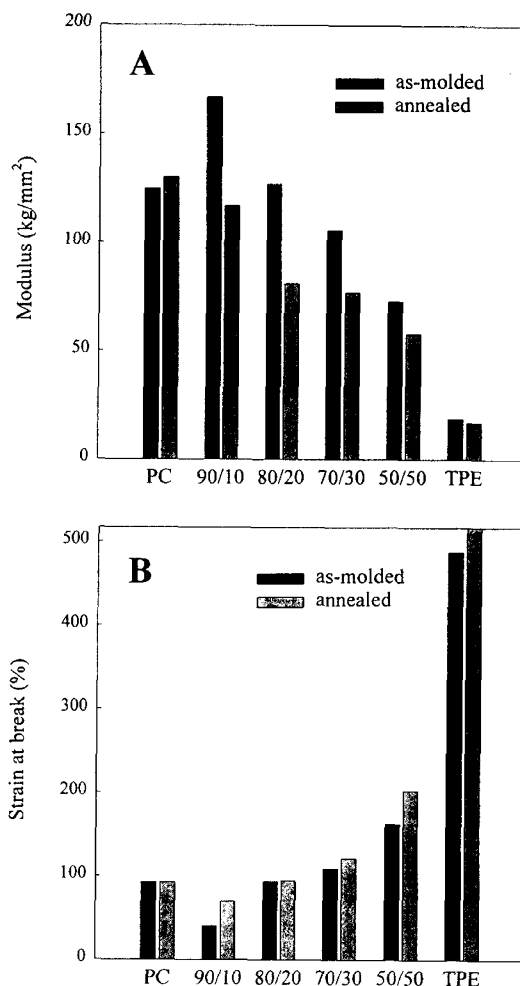
molded samples the toughness of PC decreases on adding PBT-PTMG. This may be because the crystalline phase, which acts as physical crosslinks, is not fully developed in the matrix of PC due to the miscibility of PC and PBT segments. However, after 5 h annealing at 140°C the toughness of the samples significantly increases compared to those of as-molded samples. The impact strength of PC slightly decreases due to physical aging after sub T_g annealing. It is clear that the increase in the impact strength after annealing is closely related to the crystalline domain of PBT developed during annealing.

Stress–strain measurement was done to ascertain the effects of sub T_g annealing on the tensile properties of PC/PBT-PTMG blends. The results are shown in Figure 7. Since the elastic property of PBT-PTMG is recovered as the phase separation proceeds with annealing, the modulus of the blends (Figure 7A) decreases and elongation at break (Figure 7B) increases after annealing. The change in tensile properties reflects the recovery of TPE property after sub T_g annealing, because pure TPE has lower modulus and higher elongation at break than pure PC. However, the change in tensile properties is not dramatic compared to that in the impact strength shown in Figure 6. Impact and tensile tests indicate that only when crystallites of PBT segments in the PBT-PTMG polymers are formed through the sub T_g annealing, they

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act as effective impact modifiers. Thus, sub T_g annealing is effective for toughening PC/PBT-PTMG blends.

SUMMARY

How sub T_g annealing affects the structure and properties of PC/PBT-PTMG blends was investigated in this study. As-molded blends prepared by melt mixing show miscibility between PC and PBT segments in the PBT-PTMG. Impact strength of the blends was thus very poor. The phase separation proceeds as the blends are annealed at the temperature below T_g of PC, causing the development of the crystalline structure of PBT segments which acts as a physical crosslinks and thus enhances the toughness of PC. Miscibility between matrix and the component acting as physical crosslinks in TPE prevents the TPE from being an effective impact modifier of the matrix. To recover the elastic properties of TPE in the blends, they should form a crystalline domain *via* an appropriate treatment such as sub T_g annealing.

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