Polym. Bull. (2012) 68:287–298
DOI 10.1007/s00289-011-0630-9

ORIGINAL PAPER

Transesterification effects on miscibility polycarbonate/poly(butylene adipate-*co*-terephthalate) blends

Mi-Ok Jang · Seung-Beom Kim · Byeong-Uk Nam

Received: 18 July 2011 / Revised: 6 September 2011 / Accepted: 10 September 2011 /

Abstract The effects of transesterification on the miscibility of polycarbonate (PC)/poly(butylenes adipate-*co*-terephthalate) (PBAT) blends were investigated. The PC/PBAT blends were prepared with a twin-screw extruder, and then annealed at 260 °C for 5 h to trigger the transesterification reaction. ^{1}H NMR, FT-IR, and WAXD results indicated that transesterification in the annealed PC/PBAT blends took place and led to the formation of a random copolymer structure. Because the copolymer serves as a compatibilizer, the PC/PBAT blends showed improved miscibility, as confirmed by FE-SEM and DMA analyses. The compatible morphology achieved through transesterification ultimately increased the thermal stability of the PC/PBAT blends. We could thus conclude that transesterification in PC/PBAT blends forms a random copolymer which plays an important role as a compatibilizer and consequently improves the miscibility as well as the thermal properties of the blends.

Keywords Polycarbonate (PC) · Poly(butylene adipate-*co*-terephthalate) (PBAT) · PC/PBAT blends · Transesterification

Introduction

Polycarbonate (PC) is an important engineering thermoplastic with high impact strength and heat resistance and a high modulus of elasticity. Owing to its superior properties, PC is widely used in automotive, aerospace, and medical applications as well as in many other fields. However, the chemical resistance of PC has been identified as a major problem in a variety of applications. Thus, many researchers

---

M.-O. Jang · S.-B. Kim · B.-U. Nam (✉)
Department of Applied Chemical Engineering, Korea University of Technology and Education,
Chungnam 330-708, Korea
e-mail: bunam@kut.ac.kr

have attempted to prepare PC blends with other polymers, a route that is considered as an effective way to tailor specific performance properties of desired polymers. In particular, PC blends with various polyesters such as poly(ethylene terephthalate) (PET) [1–5], poly(butylene terephthalate) (PBT) [6–8], poly(trimethylene terephthalate) (PTT) [9–11], and polylactic acid (PLA) [12–14] have garnered heightened attention, because PC/polyester blends in the molten state can react by transesterification, which occurs in accordance with the three reaction mechanisms proposed by Kotliar [15], i.e., alcoholysis, acidolysis, and ester–ester exchange. Transesterification has been recognized as an important factor in the miscibility, crystalline structure, and thermal properties of PC/polyester blends in the past several years.

To produce PC/polyester blends, aliphatic polyesters such as PLA, polybutylene succinate (PBS), and polycarprolactone (PCL) won attention as powerful materials among biodegradable polymers, because they are converted into biomass or carbon dioxide and water by microorganisms in their environment. Although biodegradable aliphatic polyesters show good biodegradability, their thermal and mechanical properties are insufficient to replace conventional polymers with improved properties. In response, aliphatic–aromatic copolyesters have been recently developed by the introduction of an aromatic unit into the main chain of the aliphatic polyester. Aliphatic–aromatic copolyesters have better physical properties and processability as well as improved biodegradability. Figure 1 shows the chemical structure of poly(butylenes adipate-*co*-therephthalate) (PBAT), a representative aliphatic–aromatic copolyester that is prepared by melt polycondensation of 1,4-butanediol, adipic acid, and terephthalic acid. PBAT has improved properties including softness on par with that of LDPE and offers strong potential for use as biodegradable polymer.

In this study, we investigated PC/PBAT blends with the aim of integrating the high toughness and thermal stability of PC with the biodegradability and processability of PBAT. PC/PBAT blends were prepared in a twin-screw extruder and the blends were subsequently annealed at 260 °C for 5 h. We confirmed the occurrence of transesterification after annealing and evaluated the effects of transesterification on the miscibility, crystalline structure, and thermal properties of the PC/PBAT blends.

Experimental

Materials

Polycarbonate (PC) was purchased from SAMYANG CO., Korea. It has a melt flow rate of 30 g/10 min (250 °C, 10 kg). Poly(butylene adipate-*co*-terephthalate)

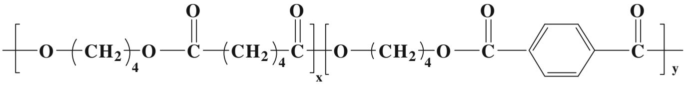


Fig. 1 Chemical structure of poly(butylene adipate-*co*-terephthalate)

(PBAT, $T_g = -30$ °C, $T_m = 110$–120 °C, Ecoflex BX7011) was supplied by BASF. PC and PBAT were dried at 60 °C for 12 h prior to melt blending to minimize hydrolysis degradation.

Preparation of PC/PBAT blends

PC/PBAT blends in different weight ratios were prepared in a twin-screw extruder (Bautek with L/D = 40, 19Φ, co-rotating) at 210–260 °C with a speed of 100 rpm. The weight ratios of the PC/PBAT blends were 100/0, 75/25, 50/50, 25/75, and 0/100, which they were denoted as PC75BPAT25, PC50BPAT50, and PC25PBAT75. Samples for SEM, DMA, and WAXD analyses were compression-molded into 1 mm sheets at 260 °C for 3 min under a pressure of 450 kgf/cm^2 and then dried at 60 °C for 24 h. To confirm transesterification and variation in miscibility, annealing was performed by heating at 260 °C for 5 h in an oven.

Characterizations

The morphology of the PC/PBAT blends was analyzed by field emission-scanning electron microscopy (FE-SEM), using a JSM-7500F (JEOL Ltd., Japan). The samples for the morphology measurements were fractured after immersion in liquid nitrogen. Sputtered with a platinum coating, the fracture surfaces were observed.

The progress of transesterification was determined by ^{1}H NMR, Fourier transform infrared (FT-IR), dynamic mechanical analysis (DMA), and wide angle X-ray diffraction (WAXD) studies. The ^{1}H NMR spectra were obtained with a DRX-300 spectrometer (Bruker) operated at 300 MHz, using $CDCl_3$ as a solvent. The spectra were referenced on residual $CDCl_3$ ($\delta(^1H) = 7.26$ ppm). FT-IR spectra were recorded in attenuated transmitted reflectance (ATR) mode on a FT-IR spectrometer (Perkin-Elmer) at a resolution of 4 cm^{-1} in a frequency range from 4000 to 650 cm^{-1}. DMA was performed on a DMA 8000 (Perkin-Elmer) from −70 to 160 °C at a heating rate of 2 °C/min with a frequency of 1 Hz. WAXD measurement of the blend films was carried out on a Rigaku RTP300 RC with nickel-filtered copper K_α radiation (50 kV and 100 mA). The WAXD profiles were recorded between angles of 6°–40° at a scan rate of 2°/min under ambient conditions. To investigate the thermal stability of the PC/PBAT blends, a thermogravimetric analysis (Perkin-Elmer TGA4000) was conducted from 30 to 800 °C at a heating rate of 20 °C/min.

Results and discussion

PC was melt-blended with PBAT (weight ratio PC/PBAT = 100/0, 75/25, 50/50, 25/75, 0/100) by using a twin-screw extruder. The phase behavior of the PC/PBAT blends was evaluated using a field emission-scanning electron microscope (FE-SEM). Figure 2 shows cross-sectional FE-SEM images of unannealed PC/PBAT blends. It can be seen that domains within the matrix are well dispersed. Sea-island structure is observed in case of PC25PBAT75, however, the size of the dispersed phase, is about 100 nm in overall compositions of the PC/PBAT blends. Therefore, we confirm that PC/PBAT blends show a compatible phase structure having sufficient interfacial adhesion.

It is well known that PC/polyester blends can react by transesterification during melt processing [16–19]. We hence annealed the PC/PBAT blends at 260 °C for 5 h in a vacuum oven. The extents of transesterification are amplified through annealing technique. PC consists of bisphenol A (B), carbonate (C), PBAT consists of butanediol (D), terephthalate (T), and adipic acid (A); the transreaction will yield five components, as seen in Scheme 1.

Scheme 2 shows the chemical structures that are expected to be obtained by the transesterification reaction between PC and PBAT in the PC/PBAT blends. It is seen that the transesterification product can be divided into two types in accordance with the centered unit. Bisphenol A originally bonded to two carbonates in a CBC triad. After transreaction with PBAT, one carbonate unit was replaced by an adipic acid unit in a CBA triad; after a second exchange, both sides of bisphenol A were substituted by an adipic acid unit. In addition, the chain structure in the neighborhood of the terephthalate in the DTD triad is altered. Each side of the terephthalate is substituted by bisphenol A.

We performed ^{1}H NMR spectroscopy to determine the transesterification reaction after annealing for 5 h, as shown in Scheme 2. First, we show the NMR

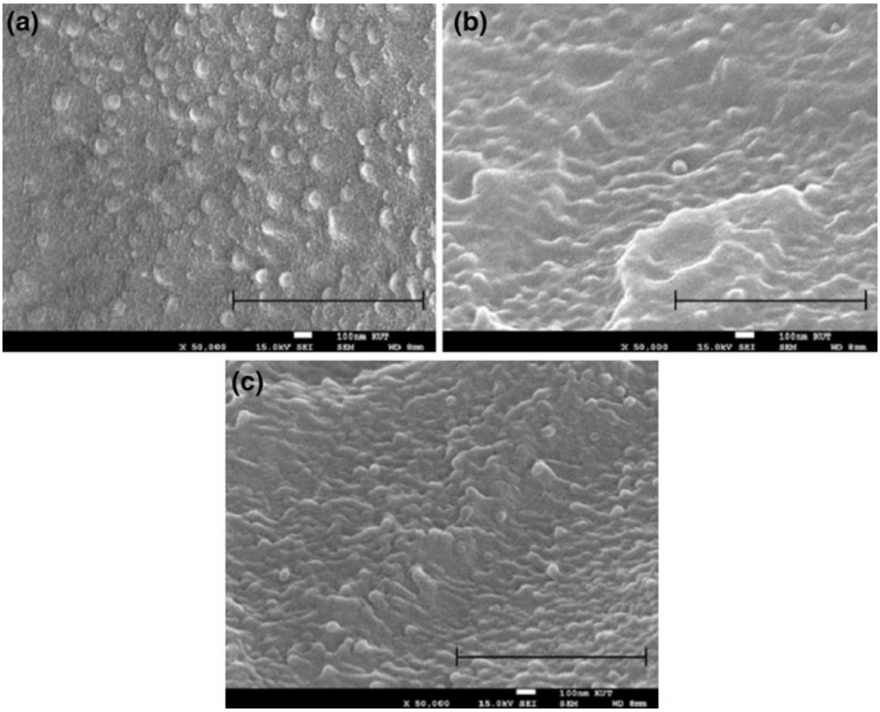
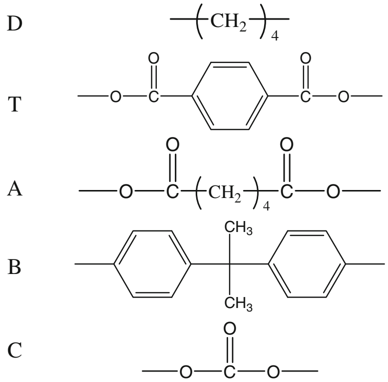
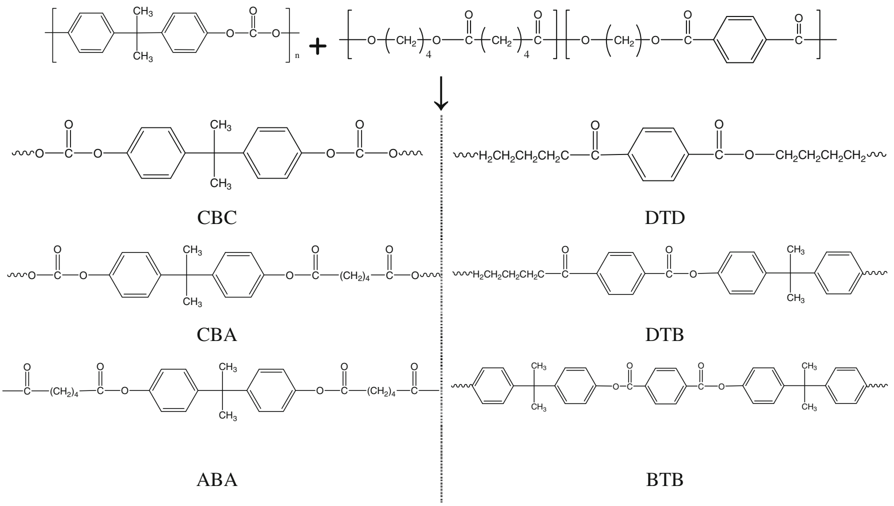


Fig. 2 Cross-sectional FE-SEM images of unannealed PC/PBAT blends (*scale bar* 1 μm); **a** PC25PBAT75, **b** PC50PBAT50, **c** PC75PBAT25

Scheme 1 Components in transreaction between PC and PBAT





Scheme 2 Expected chemical structures of transesterification products of PC and PBAT

spectra of homopolymers in Fig. 3. According to the literature [20–23], PC has two distinct peaks, at $\delta = 7.29$ and $\delta = 1.67$, corresponding to the aromatic protons and methylene protons of bisphenol A, respectively. The PBAT homopolymer show several peaks, at $\delta = 8.1$, $\delta = 7.4$ $\delta = 4.43$–4.0, $\delta = 2.34$, and $\delta = 1.6$–1.97, which are assigned to aromatic protons of terephthalate and methylene protons of $–CH_2OCO–$, $–OCCH_2–$, and $–(CH_2)_2–$, respectively.

Figure 4 shows the ^{1}H NMR spectroscopy results before and after annealing the PC/polyester blends. Under the unannealed state, as shown in Fig. 4a, the spectra of the PC/polyester blends correspond with the respective spectra of the constituent components. After annealing the PC/polyester blends at 260 °C for 5 h, several new peaks were observed at $\delta = 8.4$–8.1, $\delta = 7.0$, and 6.7 as a result of transesterification, as seen in Fig. 4b [23]. These changes to the spectra upon annealing provide further information about the structural changes and progress of transesterification.

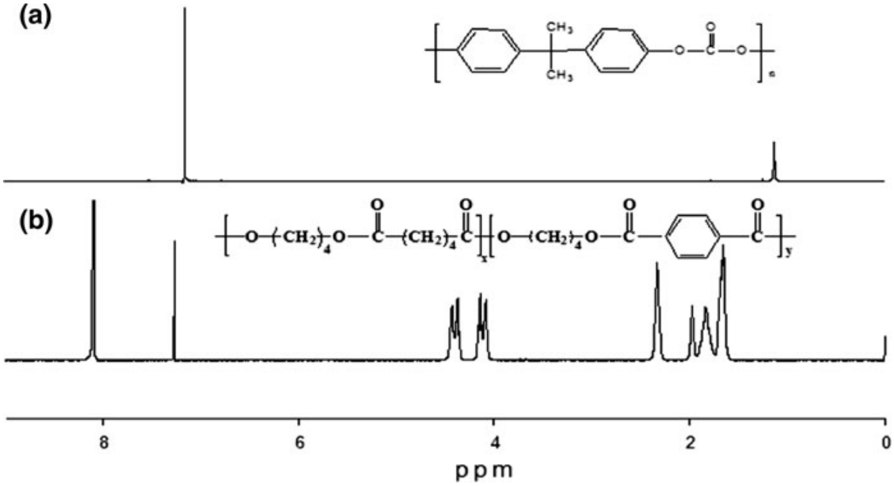


Fig. 3 ^{1}H NMR spectra of a PC (**a**) and PBAT (**b**)

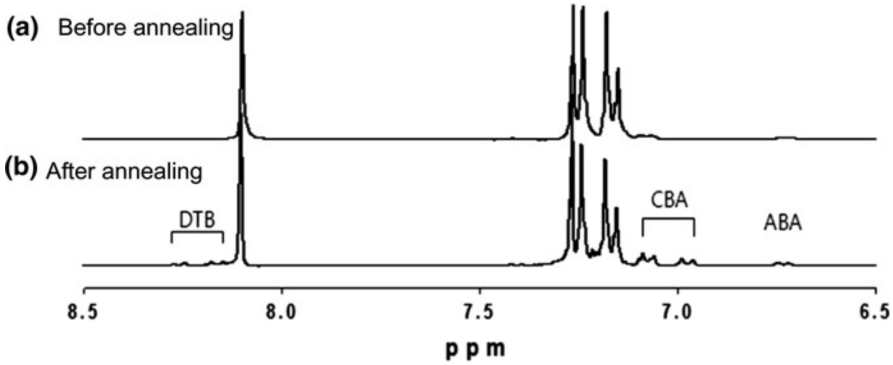


Fig. 4 ^{1}H NMR spectra of a PC/PBAT blends before and after annealing at 260 °C

The new peaks in the region of $\delta = 8.4$–8.1 are assigned to aromatic protons of terephthalate in a DTD or DTB triad, and the structural changes of the bisphenol A unit coincide with those of terephthalate. The peaks at $\delta = 7.0$ and 6.7 are attributed to the aromatic protons of bisphenol A substituted by an adipic acid unit. Therefore, it is confirmed that transesterification occurred during annealing of the PC/polyester blends.

We estimate the degree of randomness of the copolyester formed by transesterification from the ^{1}H NMR values of bisphenol A. The relative fractions (f) of centered bisphenol A unit, which is calculated from the intensity of three kinds of signals in the ^{1}H NMR spectrum, are listed in Table 1 ($f_{\mathrm{CBC}} + f_{\mathrm{CBA}} + f_{\mathrm{ABA}} = 100$). The changes of the integral values for PC/polyester blends with different compositions before and after annealing are included in Table 1. The fractions of C–B and B–A linkages were calculated via the following equation.

Table 1 Changes of sequence distribution and calculated degree of randomness in PC/PBAT blends before and after annealing

Time (h)	f_{CBC} (%)	f_{CBA} (%)	f_{ABA} (%)	f_{CB} (%)	f_{BA} (%)	Randomness
PC/PBAT = 25/75, $F_{\mathrm{C}} = F_{\mathrm{B}} = 0.52$, and $F_{\mathrm{A}} = 0.48$						
0	100	0	0	100	0	0
5	68.1	26.5	5.4	81.35	18.65	0.36
PC/PBAT = 50/50, $F_{\mathrm{C}} = F_{\mathrm{B}} = 0.77$, and $F_{\mathrm{A}} = 0.23$						
0	100	0	0	100	0	0
5	81.6	15.2	3.2	89.2	10.8	0.14
PC/PBAT = 75/25, $F_{\mathrm{C}} = F_{\mathrm{B}} = 0.91$, and $F_{\mathrm{A}} = 0.09$						
0	100	0	0	100	0	0
5	98.7	0	1.3	98.7	1.3	0.014

$$f_{\mathrm{CB}} = f_{\mathrm{CBC}} + 0.5 f_{\mathrm{CBA}}, f_{\mathrm{BA}} = f_{\mathrm{ABA}} + 0.5 f_{\mathrm{CBA}}$$

These parameters represent the probability of a C unit locating next to a B unit and an A unit next to a B unit. After transesterification with PBAT, bisphenol A originally bonded carbonate in CBC triad can be located in CBA and ABA triad. The degree of randomness, which means the distribution unit in the copolymer, is defined from mole fraction, e.g., $F_{\mathrm{BA}} = f_{\mathrm{BA}} \cdot F_{\mathrm{B}}$, according to the following equation

$$\text{Randomness } (B) = F_{\mathrm{BA}}/(F_{\mathrm{B}} \cdot F_{\mathrm{A}})$$

With $F_{\mathrm{C}}(=F_{\mathrm{B}})$ and F_{A} are mole fraction of carbonate unit (C), bisphenol A (B), and adipic acid (A).

If $B = 0$, it is a mixture of homopolymers, whereas $B = 1$ corresponds to a random distribution. From the value of randomness seen in Table 1, we could confirm that the degree of randomness was enhanced as the content of PBAT was increased in the PC/PBAT blends, ultimately causing higher transesterification in the PC/PBAT blends.

The FT-IR spectra of PC and the PC50PBAT50 blend before and after annealing are shown in Fig. 5. After annealing the PC50PBAT50 blend, a new small band was observed at 1070 cm^{-1}. This small band is assigned to C–O–C stretching vibration in the ester linkage of the fully aromatic ester structure, which is newly generated by the transesterification reaction (as seen for DTB or BTB in Scheme 2). These spectra are further evidence of the transesterification reaction. From the results of ^{1}H NMR and FT-IR, we can further confirm that transesterification between PC and PBAT occurs after annealing at 260 °C for 5 h.

Miscible blends generally show a single glass transition temperature between those of the homopolymers. We measured the glass transition temperature using DMA equipment to determine the influence of annealing on the miscibility of the PC/PBAT blends. Figure 6 shows the temperature dependence of tan δ for unannealed and annealed PC/PBAT blends with different compositions. As shown in Fig. 6, for the PC/PBAT blends before annealing, two separated tan δ peaks of PC and PBAT were observed and shifted toward each other. Interestingly, after annealing the PC/PBAT blends at 260 °C for 5 h, we could see only a single tan δ

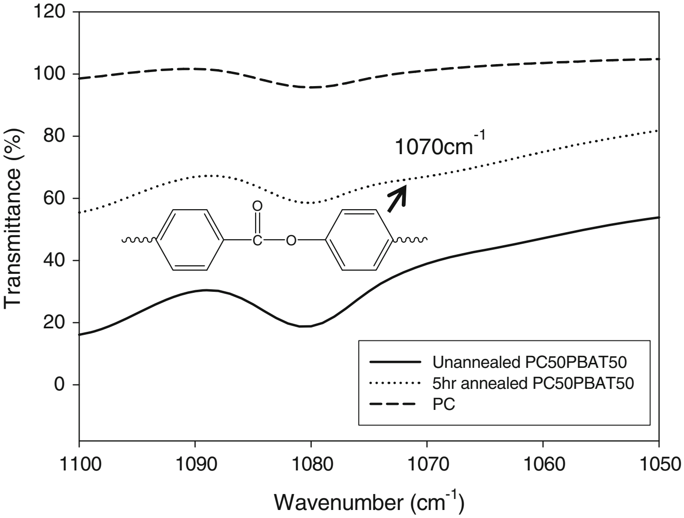


Fig. 5 FT-IR spectra of PC and PC50PBAT50 blend before and after annealing

peak in the overall composition. It is well known that tan *δ* peaks correspond to the glass transition temperatures of the component polymers. From the tan *δ* peak results in Fig. 6, we present the glass transition temperature (T_g) of PC, PABT, and PC/PBAT blends in Fig. 7. The glass transition temperature of PBAT and PC are known to be −20 and 150 °C, respectively. In the case of the unannealed blends, there is a slight shift of T_g to higher or lower values as a function of composition. It appears that the unannealed PC/PBAT blends are a partially compatible blend system. After annealing, the two clearly separated T_g values approach each other and become significantly similar. A single T_g is observed between the T_g of the homopolymer in the case of a specific composition. This indicates that the partially miscible PC/PBAT blends are converted into a compatible blend system. In other words, it can be concluded that transesterification between PC and PBAT produces a random copolyester, and thus this strongly influences the miscibility of PC/PBAT blends by acting as a compatibilizer.

To confirm whether the crystal structure of the PC/PBAT blends was influenced by annealing, WAXD measurement was performed. Figures 8 and 9 show the crystal structures of PC/PBAT blends with different compositions before and after annealing. The PBAT shows five main diffraction peaks at (011), (010), (111), (100), and (111) plan corresponding to the diffraction patterns of the PBT homopolymer [21]. On the other hand, PC displays a smooth and broad peak. These results indicate that PBAT has a crystalline structure, whereas PC has an amorphous structure. For unannealed blends, as seen in Fig. 8, PC/PBAT blends with PC content up to 50 wt% maintain a semi-crystalline structure. After annealing the PC/PBAT blends, however, the intensity of the diffraction peak decreases compared to the unannealed blends. Notably, we can verify that the structure of the PC50PBAT50 blend is altered from a crystalline structure to an amorphous structure by annealing.

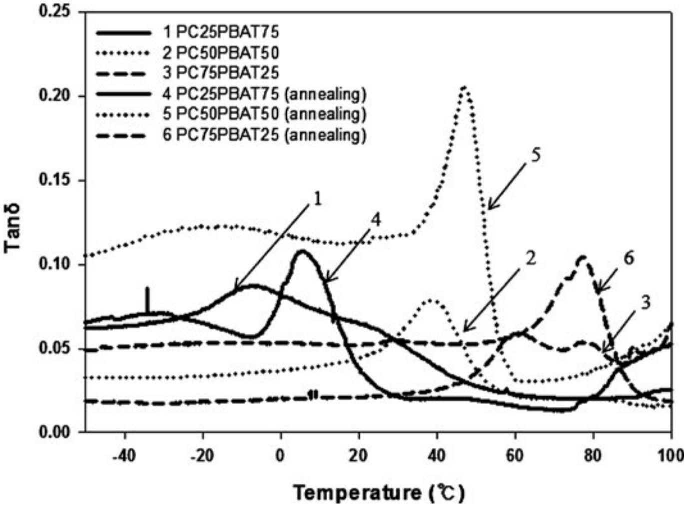


Fig. 6 Influence of annealing on temperature dependence of tan δ for PC/PBAT blends

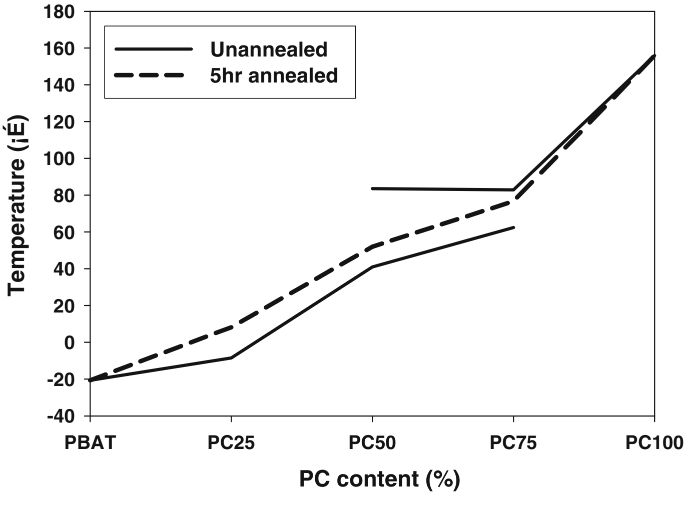


Fig. 7 Influence of transesterification on T_g behaviors of PC/PBAT blends

Therefore, it is thought that the random copolyesters produced by transesterification induce a random distribution in PC/PBAT blends, suppressing the crystallization of PBAT in the PC/PBAT blends as a result.

The thermal stability of the PC/PBAT blends before and after annealing was investigated by a thermogravimetric analysis (TGA). As seen in Fig. 10, the TGA curves of the PC/PBAT blends exhibit distinct thermal weight losses. Although the thermogravimetric reduction is not directly proportional to the weight fraction of the PC/PBAT blends, the thermal stability of the blends depends on their PC content.

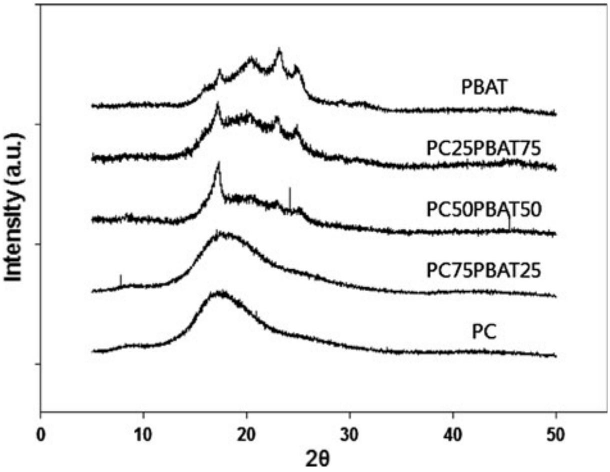


Fig. 8 WAXD patterns for the unannealed PC/PBAT blends with different compositions

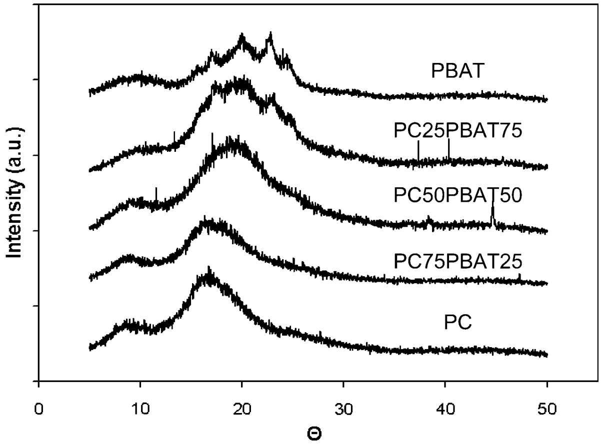


Fig. 9 WAXD patterns for the annealed PC/PBAT blends with different compositions

As the content of PC is increased, the thermal stability also gradually increases. The blends with higher PBAT content exhibit the lowest initial decomposition temperature, which is due to the low thermal properties of PBAT. When PC/PBAT blends are annealed, the decomposition temperature of the blends rises compared to the case of the same composition in unannealed blends. According to Gel Permeation Chromatography (GPC) results, the number average molecular weight (M_n) of PC50PBAT50 declined from 15,633 to 10,263 g/mol. Even though the molecular weight of blends decreases after annealing, the thermal stability of blends is enhanced. It is thought that the copolyester formed by transesterification serves as a compatibilizer, thereby improving the compatibility between the components. This is in good agreement with the DMA results. Thus, the enhanced miscibility of

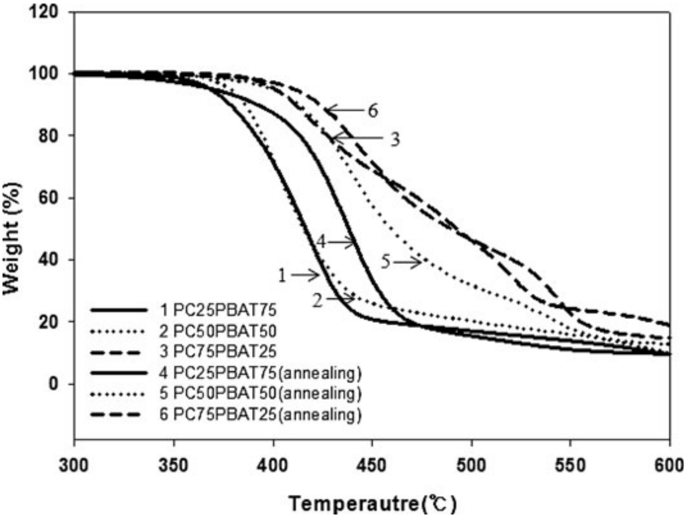


Fig. 10 Influence of transesterification on thermograms of PC/PBAT blends

the blends consequently causes higher thermal stability. In particular, the compatibilization effect of the copolyester on the blends is greater in the case of a large amount of PBAT. Therefore, it is reasonable to conclude that the miscibility by transesterification is associated with the composition of the blends and also results in improvement of the thermal stability.

Conclusions

The effect of transesterification on the PC/PBAT blends was thoroughly investigated with FE-SEM, ^{1}H NMR, FT-IR, DMA, WAXD, and TGA. The phase morphology of the PC/PBAT blends showed a compatible structure in terms of overall composition, as determined by FE-SEM. ^{1}H NMR and FT-IR analyses verified that the transesterification reaction by annealing occurred between PC and PBAT in the PC/PBAT blends, forming a random copolymer. Because the copolymer acts as a compatibilizer after annealing, the PC/PBAT blends have a perfectly miscible phase and are transformed from a crystalline phase into an amorphous structure, as revealed by DMA and WAXD results. We also confirmed that the thermal stability of the PC/PBAT blends is enhanced by the better miscibility of the blends. From these results, we conclude that transesterification in PC/PBAT blends plays an important role in improving their miscibility and thermal properties.

Acknowledgments This study was supported by a grant from the cooperative R&D Program funded by the Korea Research Council Industrial Science and Technology & the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

References

1. Nassar TR, Paul DR, Barlow JW (1979) J Appl Polym Sci 23:85
2. Muff SR, Barlow JW, Paul DR (1984) J Appl Polym Sci 29:3231
3. Hanrahan BD, Angeli SR, Runt J (1986) Polym Bull 15:455
4. Suzuki T, Tanaka H, Nishi T (1989) Polymer 30:1287
5. Wang LH, Huang Z, Hong T (1990) J Macromol Sci Phys B 29:155
6. Hobbs SY, Dekkers MEJ, Watkins VH (1987) J Polym Bull 17:1436
7. Hopfe I, Pompe G, Eichhom K (1997) Polymer 38:2321
8. Elisabete M, Saraiva S (2007) Polym Test 26:378
9. Chiu F-C, Ting M-H (2007) Polym Test 26:338
10. Huang D-H, Woo EM, Lee L-T (2006) Colloid Polym Sci 284:843
11. Indose A, Alain B, Yves G, Sabu T (2010) Ind Eng Chem Res 49:3873
12. Oh TS, Ryou JH, Chun YS, Kim WN (1997) Polym Eng Sci 37:838
13. Guo M, Brittain WJ (1998) J Macromol 31:7166
14. Kazuhiro H, Shotaro N, Takashi I (2010) Polymer 51:3934
15. Kotliar AM (1981) J Polym Sci Macromol Rev 16:367
16. Devaux J, Godard P, Mercier J (1982) J Polym Sci 20:1875
17. Devaux J, Godard P, Mercier J (1982) J Polym Sci 20:1881
18. Devaux J, Godard P, Mercier J (1982) J Polym Sci 20:1895
19. Devaux J, Godard P, Mercier J (1982) J Polym Sci 20:1901
20. Pham QT, Petiaud R, Waton H (1984) Proton and carbon NMR spectra of polymer. Wiley-Interscience, New York
21. Puglisi C, Samperi F (1998) J Macromol 31:650
22. Devaux J, Godard P, Mercier JP (1982) J Polym Sci Polym Phys Ed 20:1881
23. Gan Z, Kuwabara K, Yamamoto M, Abe H, Doi Y (2004) Polym Degrad Stabil 83:298