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Miscibility of poly(ethylene terephthalate)/poly(estercarbonate) blend

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Abstract

The miscibility of poly(ethylene terephthalate) (PET) with polyarylate (PAr), polycarbonate (PC), and poly(estercarbonate) (PEC), polyarylate–polycarbonate random copolymer were examined from thermal properties, and morphology. PAr, PC and PEC all showed phase separation behavior in blends with PET. On the other hand, as the carbonate/ester repeating unit ratio increases, the penetration of PEC into PET tends to increase, and the corresponding suppression of crystallization was observed. In SEM study, on the contrary, the apparent morphology was resulted in as if PET and PEC1 are more favorable, which is attributed to the fact that in morphology the control processing condition can be a dominant factor for immiscible blend systems © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Poly(estercarbonate); Miscibility

1. Introduction

For several decades, researches have been focused on the crystalline polymer blends because they have a broad spectrum of properties offered by the crystallization-induced morphology [1]. The morphology determines the physical properties and ultimately the usefulness of polymer blends. The chemical compatibility of the component polymers in the amorphous phase, crystallizability of component polymers, diffusion of the non-crystallizable component and kinetic factors associated with the conditions of processing, have been illustrated as the factors affecting the phase morphology at a given blend of composition [2–9].

To improve the thermal resistance of poly(ethylene terephthalate) (PET), the blends of PET with thermal resistant amorphous polymers, such as bisphenol-A polycarbonate (PC) or polyarylate (PAr) have been investigated by many researchers [10–18]. The study by Nassar et al. [14] about the melt-processed PET/PC blend showed that a homogeneous morphology showing single glass transition temperature (T_g) appeared in the range 70–90 wt% of PET, and the behavior of double T_g in the other ranges. It was also shown that the presence of PC prevents PET from crystallization. Hanrahan et al. [17] obtained similar results with the PET/PC blend system obtained by solution blending. However, Ahn et al. [18], based on their own and other previously provided results, reported that the final morphology of PET/PC could be made diversely from a homogeneous state to a phase-separated state according to the applied processing condition because of the weak interaction between PET and PC, and the possibility of transreaction. These ambiguities seems to be caused by the block or random copolymer created by the transreaction and located at the interfaces to enhance miscibility [10,11], because even for a phase-separated system, it may look like miscible, apparently, in the presence of transreacted products. In addition, the crystallization can give an additional ambiguity on the phase behavior in an amorphous portion, providing higher difficulty in determining the thermodynamic phase behavior.

In this study, in order to see some finer pictures on the phase behavior of PET blends, PAr unit which is known to be immiscible with PET, was incorporated into PC, and these poly(estercarbonate) (PEC) copolymers with the following chemical structure were blended with PET, because the variation of the phase behavior according to the systematic compositional change of ester and carbonate units in PEC, would clarify the phase behavior of PET blend with PC or PAr, and because the PEC itself can be used as a new modifier of PET.

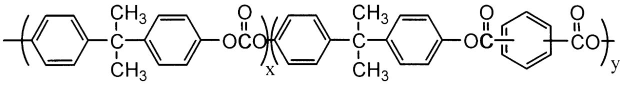

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Table 1
The characteristics of the polymers used

Designation	Carbonate content (mol%)[a]	T_g (°C)	$[\eta]$ (dl/g)	$\bar{M}_w$	Remarks
PET	–	75	0.793	26,000[b]	Tongyang polyester
PAr	–	197	0.359	29,000[c]	Unitika
PEC1	12.3	200	1.003	–	Synthesized
PEC3	29.1	193	0.704	–	Synthesized
PEC7	64.9	172	0.641	51,000[c]	Synthesized
PEC9	90.0	154	0.763	–	Synthesized
PC	100	151	0.225	25,000[c]	Idemitsu

[a] Calculated from the FT-NMR spectra.

[b] Calculated from the intrinsic viscosity and the Mark–Houwink equation, $[\eta] = 12.7 \times 10^{-5}\ \bar{M}_w^{0.86}$ [33].

[c] GPC data calibrated with PS standards.

2. Experimental

2.1. Materials

Bisphenol-A (BPA) for the synthesis of PEC was purchased at 99 + % purity (Aldrich), and used without further purification. Terephthaloyl chloride (TPC, Aldrich) was purified by the Soxhlet extraction with dry *n*-hexane and the pure material was recovered by removal of the hexane by a reduced pressure. Isophthaloyl chloride (IPC, Aldrich) was distilled at a reduced pressure under N_2 flow. All purified acylchloride were kept in a vacuum desiccator. Tetrahydrofuran (THF, Aldrich) was refluxed from sodium metal and distilled before use. Dry dichloromethane (MC, Aldrich) was obtained through refluxing with P_2O_5, followed by distillation. Triethylamine (TEA, Aldrich) was refluxed with ninhydrin for 24 h to get rid of any amine containing active hydrogen, followed by vacuum distillation. The purified TEA was kept with 4 Å molecular sieve. High grade triphosgene (TPh, Aldrich), 4-(dimethylamino) pyridine (DMAP, Tokyo Kasei) and methanol were used without further purification.

The PET was provided by Tongyang Polyester Co. of Korea. To remove any additives, PET was dissolved in a 50/50 (w/w) mixture of phenol (Ph) and 1,1,2,2-tetrachloroethane (TCE), and precipitated in methanol. Finally, the precipitated PET was washed with hot methanol several times, and dried at 100°C in a vacuum oven for 72 h. PC of Idemitsu and PAr of Unitika were purified by dissolution/precipitation in MC/methanol, and dried at 100°C in a vacuum oven for 72 h.

2.2. Synthesis

The following description is provided for PEC in which the composition of carbonate/ester would be expected to be 1/1 [19].

BPA 22.828 g (0.1 mol), TPC 5.076 g (0.025 mol) and IPC 5.076 g (0.025 mol) were placed into a 1 l three-necked round-bottomed flask equipped with mechanical stirrer, dry ice condenser, addition funnel and ice-bath. Anhydrous THF (100 ml) was added, after which the solids were dissolved slowly to form a light yellowish green solution. A solution of 1.344 g DMAP (0.011 mol, 5.5 mol% of –OH content) in 20 ml THF was added slowly through the addition funnel over decades of minutes. During the addition of DMAP, white bulk precipitates, supposed to be $DMAP^+Cl^-$ salt, were formed. After the addition of DMAP solution, 30.5 ml TEA (0.22 mol, excess amount of –OH content by 10%) diluted with 100 ml THF was added in the same manner. As TEA was added, the white bulk precipitates slowly disappeared and the turbidity of the solution increased.

After the dry ice condenser was charged with acetone and dry ice, TPh in THF solution was added drop-wise through another addition funnel into the reaction flask. The slightly excess amount of TPh was added over a couple of hours and only then the steady increase of viscosity could be found without any change in color or turbidity of solution. After the addition of TPh, the ice-bath was retreated to set the temperature during a chain extension at room temperature. The chain extension was run for 5 h.

THF (200 ml) was added to dilute the mixture and unreacted phosgene was completely removed under a reduced pressure. After solids were filtered off, a clear yellowish solution was obtained. This solution was poured into methanol very slowly and the precipitated white solids were refluxed with hot methanol for several times. The polymer was further purified with successive dissolution/reprecipitation in MC/methanol, and dried at 100°C in a vacuum oven for 72 h.

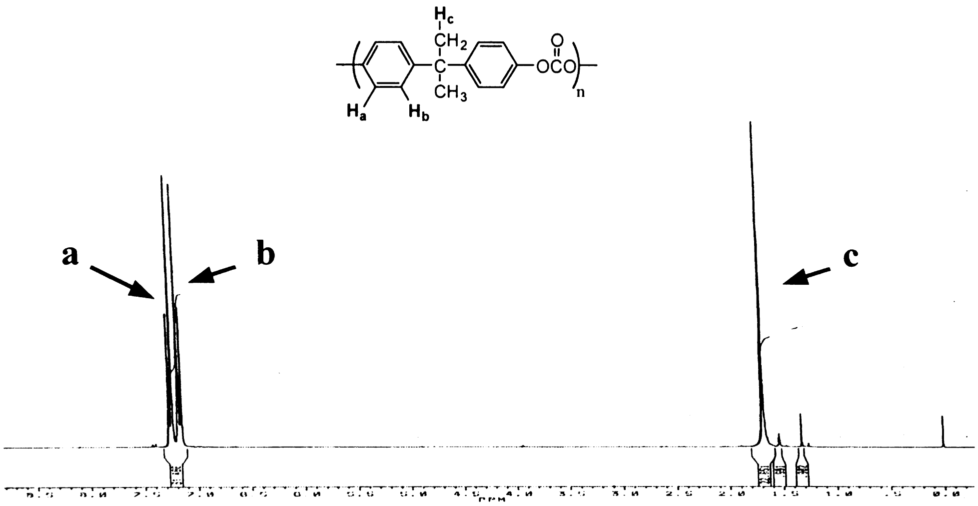
2.3. Characterization

The following procedures were employed to characterize PECs synthesized and PET, and the results are shown in Table 1.

2.3.1. Viscosity

An Ubbelohde viscometer was used at 25.0 ± 0.1°C on a MC solution of PECs, to give an intrinsic viscosity $[\eta]$ (in dl/g). With the same manner, PET was found to have an

(a) PC



(b) PAr

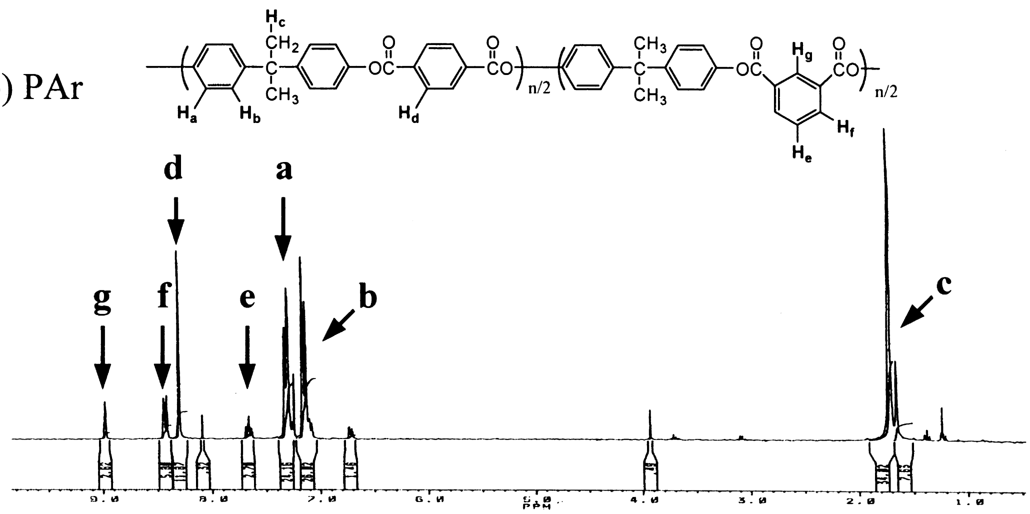


Fig. 1. FT-NMR spectra of: (a) PC; (b) PAr; (c) PEC1; and (d) PEC9.

intrinsic viscosity of 0.793 dl/g in Ph/TCE (50/50) at 25°C. The calculated weight average molecular weight ($\bar{M}_w$), using an intrinsic viscosity was 26,000.

2.3.2. Composition analysis

The composition of PECs synthesized was measured by FT-NMR. NMR spectra were obtained on a Bruker WM-360 FT-NMR spectroscopy at 360 MHz, and deuterated MC as solvent.

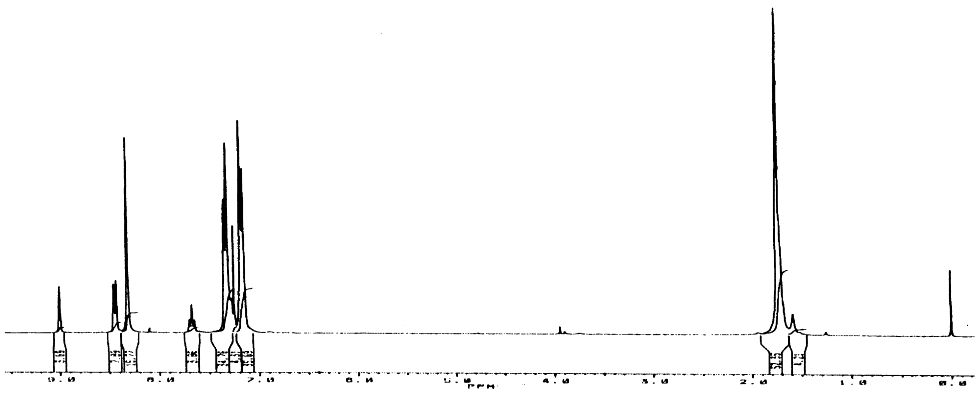
2.4. Blending

Blends of PET/PECs were prepared by the solution/precipitation method. The polymers were weighed in appropriate proportions and dissolved simultaneously in Ph/TCE (50/50) at 40°C to give a solution containing 3 wt% of total polymers. The solution was poured drop-wise into methanol with stirring and the crude precipitate was washed with hot methanol three times, followed by vacuum drying at 80°C for 72 h. All blending ratios are given as weight percent.

2.5. Investigation of phase behaviors

Investigation of thermal behaviors was accomplished with a Perkin–Elmer differential scanning calorimeter, DSC-4. To eliminate a previous thermal history, PET homopolymer and PET/PAr, PET/PC and PET/PECs blends were held at 270°C for 150 s and cooled with a rate of 10°C/min,

(c) PEC1



(d) PEC9

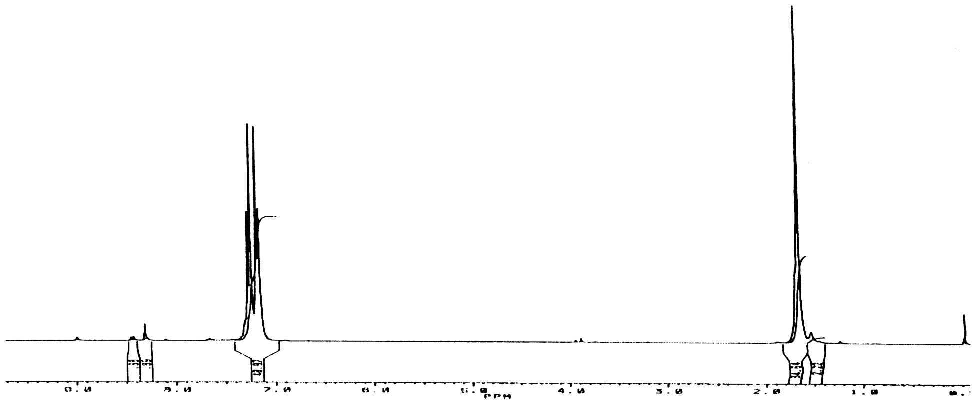


Fig. 1. (*continued*)

followed by heating with a rate of 10°C/min to measure glass transition temperature (T_g) and melting temperature (T_m). Furthermore, to examine melt miscibility, another specimen held at 270°C for 150 s and quenched with liquid N_2 was heated with a rate of 10°C/min. The temperature at half-height of the heat capacity change was taken as T_g. Miscibility was monitored under the criterion that a miscible blend exhibits a single T_g whereas a phase-separated blend shows two separate T_g.

All measured values reported here are based on an average from at least two DSC scans. Pure indium ($T_m^0 = 429.78$ K, $\Delta H_f^0 = 6.80$ kcal/mol) was used as the reference material to correct the values of temperature and heat of fusion.

In order to examine the morphology of blend mixtures, we used scanning electron microscopy, for which two kinds of specimens were provided as follows. Identical two specimens were held at 270°C for 150 s. The one was quenched with liquid N_2, while the other was rapidly cooled to a given temperature, and held with varying time. All the specimens were fractured in liquid N_2, and the fractured surface was gold-coated with a thickness of 0.3 μm. The instrument used was Jeol JSM-35CF and the accelerating voltage was 15 kV.

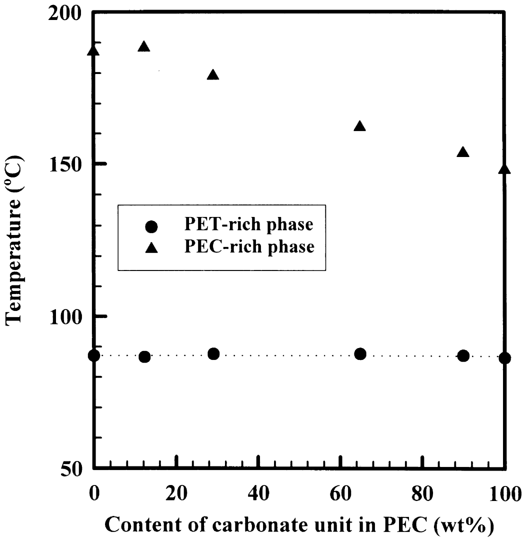


Fig. 2. The glass transition temperatures of PET/PECs (50/50) blends.

3. Results and discussion

3.1. Synthesis of PECs

As addressed in Section 2, synthesis of random copolymers containing carbonate and ester unit based on BPA was conducted through successive two step reactions, in which the first step was to make hydroxyl-terminated oligoarylate, of which the molecular weight is controlled by the mole ratio of acylchloride to BPA. The second step is the chain extension of oligoarylate with phosgene obtained from the decomposition of TPh. As shown in Table 1, all PECs were found to have high intrinsic viscosity and T_g between those of PC and PAr, showing that high molecular weight was successfully obtained.

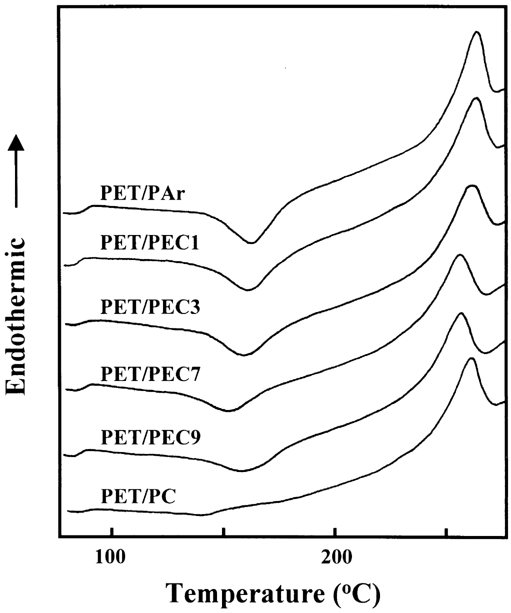


Fig. 3. The DSC thermograms of PET and PET/PECs (50/50) blends quenched from the melt state.

The composition of PECs synthesized was examined on FT-NMR. Compared with PC, PAr has additional proton peaks in the aromatic region, such as the singlet at 8.32 ppm for terephthalate units, and the singlet at 9.00 ppm, the doublet at 8.46–8.43 ppm and the triplet at 7.68 ppm for isophthalate units, as found in Fig. 1, which shows that the integration ratio of peaks corresponding to terephthalate and isophthalate units over those corresponding to BPA phenylene units changes with composition. Therefore, the composition of PECs can be calculated through the comparison of the peak areas representing phenyl protons in BPA and tere/isophthalate units, and the results in Table 1 were obtained.

3.2. Amorphous phase behaviors

Glass transition temperatures of PET/PEC blends with a composition of 50/50 by weight, which were 10°C/min-cooled from melt, are presented in Fig. 2. All of these blends exhibit two separate T_gs at temperatures around T_g of constituent polymers, irrespective of the carbonate/ester composition in the PEC copolymer. This reveals the immiscibility between PET and PECs, as expected from the previously reported miscibility results of PET/PC and PET/PAr blends [10–18]. Recently, an interesting result, that the crystallization can induce a phase-separated morphology on melt-miscible polymer blend such as PVDF/PMMA [6–9], PBT/PAr [20–23] or PCL/PVC [24,25] has been reported. Due to the possibility of the crystallization-induced phase separation and ambiguous results concerning partial miscibility of PET/PC blend, we scrutinized the miscibility of PET/PEC blend at melt state. For the determination of melt-miscibility, samples quenched with liquid N_2 from melt were used to obtain a heating scan (Fig. 3). While T_g of PEC cannot be observed due to masking by the cold crystallization peak of PET, a distinct glass transition behavior of the amorphous PET phase can be observed at nearly the same temperature as in the PET homopolymer, indicating that PET/PECs blends are immiscible even at melt state.

To scrutinize the effect of blend composition on the miscibility of PET/PEC blends, mixing with weight ratios of 90/10, 70/30, 50/50, 30/70, and 10/90 was conducted for the two copolymers, PEC1 and PEC9. Fig. 4 shows T_gs of PET/PEC1 and PET/PEC9 blends. Double T_g behavior can be observed at both blends, representing that immiscibility is retained, when the blend composition is varied. Detailed investigation, however, showed that there are differences in the T_g shift with a content of carbonate unit in PEC. The number of separate glass transitions and their variation with composition depends upon the penetration ability of the amorphous polymer into regions occupied by the semicrystalline polymer [23]. Following the phase separation analysis by Rellick et al. [26], we separate the phase component contributing to each T_g in Fig. 4 by assuming that each T_g

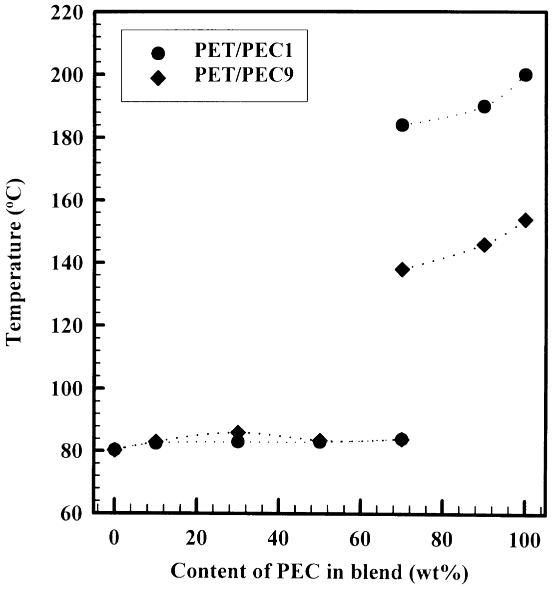


Fig. 4. The glass transition temperature change of PET/PEC1 and PET/PEC9 blends as a function of blend composition. The data were obtained with specimens 10°C/min cooled from the melt state.

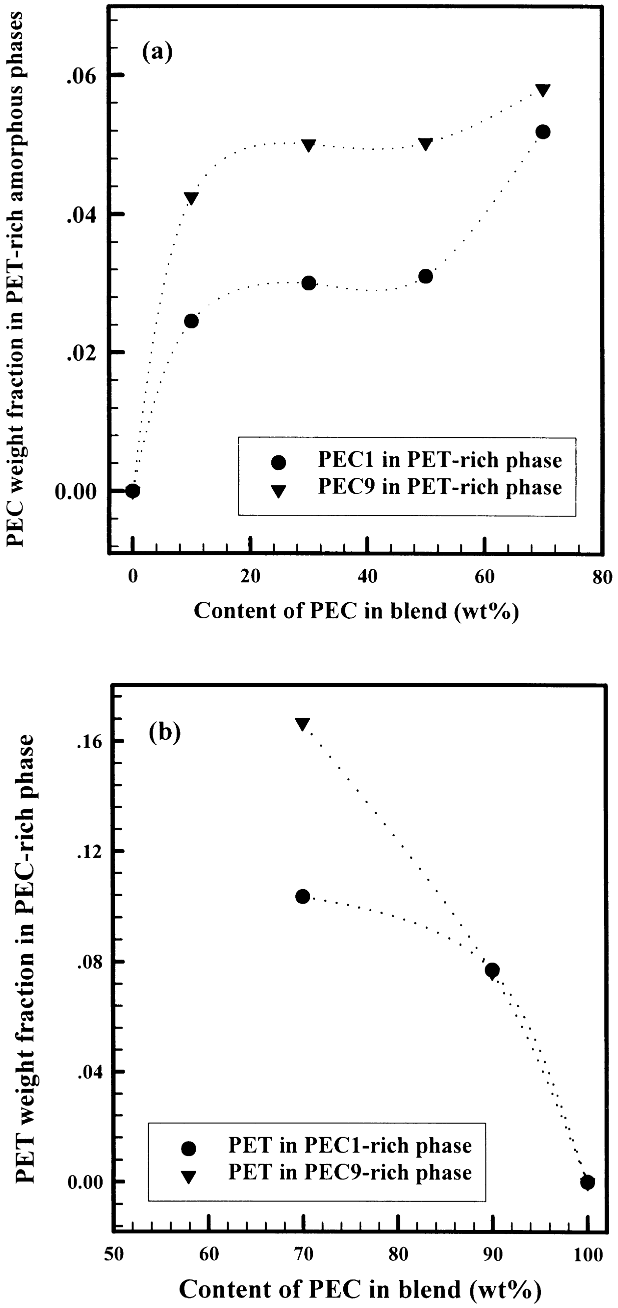


Fig. 5. Amorphous phase compositions as a function of blend composition, which show (a) amount of PEC entrapped in PET-rich amorphous phases, and (b) that of amorphous PET in PEC-rich phases. The data were calculated by the Fox equation for specimens with T_gs in Fig. 4.

follows the Fox equation [27], and the results are described in Fig. 5. Compared with PEC1, higher amount of PEC9 appeared penetrating into the amorphous PET phase. When PET is the minor component, its amount in the PEC9 phases was found to be higher than that in the PEC1 phases. That is, phase separation of PET/PEC9 was developed much lesser than that of PET/PEC1. It has been previously reported by Kim et al. [13] that PC and PET blend has a heterogeneous morphology with a limited compatibility, whereas PAr and PET blend has been known to be as an immiscible system to date. Combining our DSC results and discussions reported up to now, it is affordable to tell that although miscibility cannot be established, the carbonate units allow PET/PEC blends to become compatible to some extent.

It has been known that the degree of interaction between constituents in blends of semicrystalline polymers affects their crystallinity and equilibrium melting points. Hence, in order to verify our speculation concerning for a compatibility variation with the PEC composition, a careful DSC study was conducted to estimate crystallinity and $T_{\mathrm{m}}^{0}$for PET, and PET/PEC1 and PET/PEC9 blends.

Fig. 6 shows that melting enthalpy of PET in blends is much lower than that of PET homopolymer, and enthalpy drop increases as some of the ester unit in PAr is replaced by a carbonate unit to get PEC. Crystallinity drop is highly dependent on an interaction between blend constituents, and the corresponding melting enthalpy decrease in blend is more evident when two polymers are more favorable. This variation in the melting enthalpy strongly supports the change in compatibility between PET and PEC, when the relative composition of ester/carbonate units in PEC varies.

Within the instrument capacity to cool the samples, it was determined that isothermal crystallization could be well carried out for PET homopolymer and PET/PEC1 (90/10) at temperatures ranging from 200 to 220°C. For PET/PEC9 (90/10), however, it was not impractical to apply the same T_c range, at which PET crystallizes sluggishly, and hence another T_c range from 175 to 195°C was chosen, in which PET/PEC9 blend showed a crystallization rate comparable to that of PET/PEC1.

The typical melting behaviors of PET, PET/PEC1 (90/10)

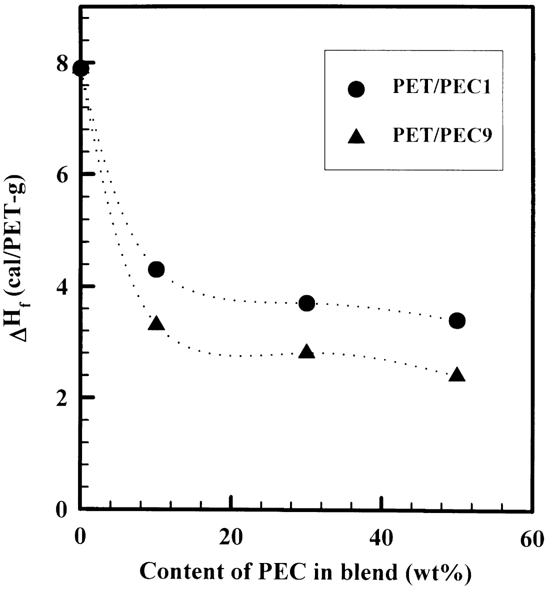


Fig. 6. The change of melting enthalpy of PET crystalline phase as a function of the blend composition. The data obtained with specimens cooled with a rate of 10°C/min were normalized with PET weight.

and PET/PEC9 (90/10) crystallized for 10 h over a range of T_c are given in Fig. 7. As shown in Fig. 7, isothermally crystallized PET can exhibit up to three melting endotherms. One of these is generally small and located ca. 5–10°C above the crystallization temperature. The origin of these melting endotherms is not well established, but the best explanation to date appears to be that they are associated with the melting of crystals formed in the interlamellar regions that are constrained by the pre-existing lamellae [28]. Melting, recrystallization, remelting are frequently observed when heating a semicrystalline polymer in the DSC [29,30]. From the heating rate experiments suggested by Runt et al.[22], the peak temperature of the second melting endotherm at 10°C/min was chosen to represent the melting point of the as-crystallized material. For semicrystalline polyesters such as PBT, it has been reported that the determination of experimental melting points is a function of the crystallization time through at least 10 h [22]. However, the accurate investigation on the crystallization behavior itself is not our concern, and melting endotherms derived from the 5 and 10 h experiments were the same with an experimental error. Therefore, we assumed that the isothermal crystallization is perfectly completed for 10 h. T_m^0 was determined using the Hoffman–Weeks approach [31], i.e. extrapolation of a plot of T_m vs. T_c to $T_m = T_c$. In Fig. 8, the melting points of PET are given as solid circles, which were extrapolated to a value of $T_m^0 = 288.0$°C. With the same manner, it was obtained that T_m^0 is 282.5°C for PET/PEC1 (90/10), and 268.2°C for PET/PEC9 (90/10). The reported value of T_m^0 for the PET homopolymer is somewhat lower, which has been determined to be 280°C [32]. This inconsistency seems to result mainly from the inaccurate reading of melting point. As stated before, during heating in DSC, melting, recrystallization and remelting occur successively, and melting thermogram is obtained as a superimposed form of each thermal behavior. Thus, precise reading of melting point on such a thermogram is impossible. Nonetheless, T_m^0 drop of PET/PEC9 blend was found to be so significant, compared with that of PET/PEC1 blend, enough to compensate the uncertainty in melting point measurement. As well as for a larger loss of melting enthalpy in PET/PEC9 blend, this larger drop of equilibrium melting point is attributed to the higher compatibility of PET/PEC9 than that of the PET/PEC1 blend.

3.3. Morphology

In the previous section, it was shown through the analysis of thermal behaviors of crystalline and amorphous phases that PET has no miscibility with PEC irrespective of the copolymer composition, and the carbonate content of PEC can increase the degree of mixing with PET to a certain extent. In this section, we attempt to scrutinize morphological features

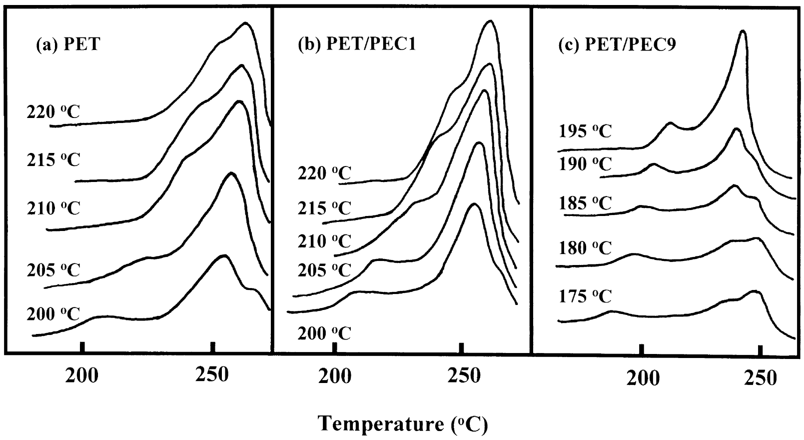


Fig. 7. The melting thermograms of PET, PET/PEC1 (90/10) and PET/PEC9 (90/10) blends crystallized at a given T_c. All thermograms were normalized with PET weight.

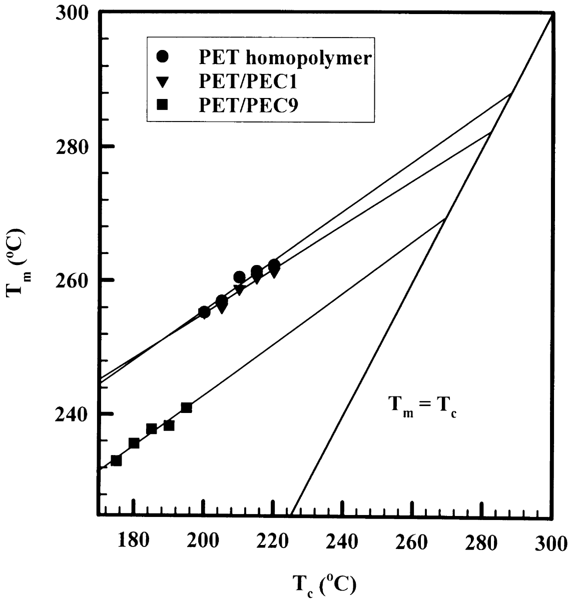
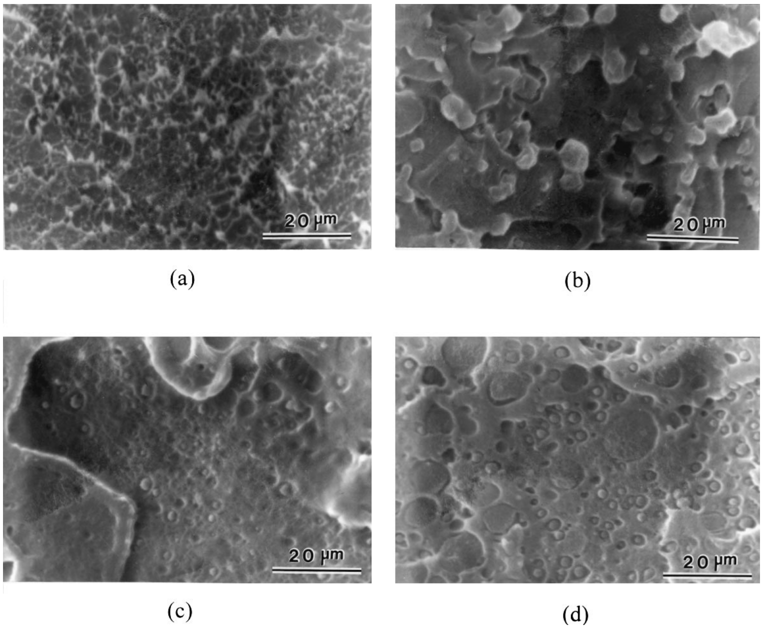


Fig. 8. Hoffman–Weeks plot for determination of equilibrium melting temperatures of the PET homopolymer, and PET/PEC1 (90/10) and PET/PEC9 (90/10) blends.

for the PET/PEC1 and the PET/PEC9 blends with varying blend composition.

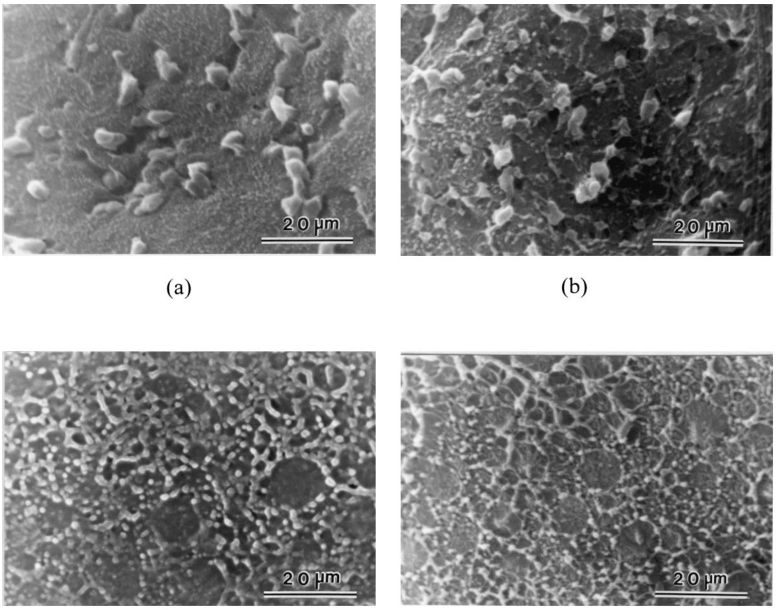
Fig. 9 shows scanning electron micrographs of PET/PEC1 and PET/PEC9 blends. These micrographs were obtained at the cryogenically fractured surfaces of specimens prepared by quenching from the melt state. As expected from the dual T_g behavior, the morphology exhibiting heterogeneous state was observed for all specimens. However, in the case of PET/PEC1, sea–island morphology appears to be poorly developed, whereas for the PET/PEC9 blend, spherical domain structures are well developed and regularly dispersed, and the interface between the dispersed PEC9 domain and the continuous PET phase looks clear. In a sense, these results can be interpreted that PET and PEC1 are more favorable to each other than PET and PEC9. Especially, in the case of PET/PEC1 (90/10), the apparent morphology looks as if PET and PEC1 are miscible. In fact, as observed in the previous section, PEC1 does not have higher compatibility with PET, and thus, the morphologies shown in Fig. 9 were considered to be the results of competition between thermodynamic repulsion and kinetic entrapping. The interaction energy between PET and PECs is not so significant, irrespective of the carbonate/ester composition in PEC, and therefore, processing conditions such as blending method, thermal treatment history, etc are supposed to be of importance in determining the phase morphology. PEC1 is lesser mobile than PEC9 in the temperature range in which the crystallization of PET, and phase separation occurs, as characterized by their T_gs. The lower mobility of PEC1 builds up a potential barrier to suppress rejection of PEC1 molecules from the PET phase, resulting in an ambiguous phase separation when quenched.

To verify this speculation, annealing experiments were attempted, providing an appropriate condition to allow polymeric chains to escape from the kinetically entrapped state. Fig. 10 shows scanning electron micrographs of PET/PEC1 (70/30) and PET/PEC9 (70/30) blends. These micrographs were obtained at the cryogenically fractured surfaces of specimens prepared by annealing for 10 or 60 min after



(a) (b) (c) (d)

Fig. 9. Scanning electron micrographs of cryogenically fractured surfaces of PET/PEC1 and PET/PEC9 blends: (a) PET/PEC1 (90/10); (b) PET/PEC1 (70/30); (c) PET/PEC9 (90/10); and (d) PET/PEC9 (70/30).



(a) (b)

(c) (d)

Fig. 10. Scanning electron micrographs of annealed specimens of PET/PEC1 and PET/PEC9 (70/30) blends: (a) PET/PEC1 annealed at 210°C for 10 min; (b) PET/PEC1 annealed at 210°C for 60 min; (c) PET/PEC9 annealed at 190°C for 10 min; and (d) PET/PEC9 annealed at 190°C for 60 min.

quenching from the melt state. The temperatures, where the crystallization rate was found to be comparable through the isothermal crystallization experiments at several T_c, were chosen as annealing temperatures, 210°C for the PET/PEC1 blend and 190°C for the PET/PEC9 blend.

In Fig. 10, we can see that the dispersion of minor PEC phase is much finer in the PEC9 blend than in the PEC1 blend. This also supports the better compatibility of PET with PEC9 than with PEC1, as discussed in previous sections. The deformation of the dispersed PEC phase during the fracturing process is more evident when the dispersed PET phase has a higher crystallinity by longer annealing. This may be due to an enhanced tenacity of the dispersed PET phase at higher crystallinity.

4. Conclusion

We have examined thermal behaviors and morphology to study PET/PECs blends prepared with a full composition range. In all blends, we observed two glass transitions: the upper T_g is close to that of the PEC copolymer, while the lower T_g appears around that of the PET homopolymer, exhibiting immiscibility. From the phase separation analysis using T_g shift with a blend composition, it was observed that as the content of carbonate repeating units in PEC increases, the penetration of PEC into PET tends to increase. Furthermore, in measuring the equilibrium melting temperature and the melting enthalpy, it was found that the crystallization of PET is notably suppressed, and that these changes in PET/PECs blend are dependent on the carbonate content in PEC. Consequently, through experiments of blends with PC–PAr copolymer, it was verified that PET/PAr blend is completely immiscible, while PET/PC blend has a little better compatibility.

However, in the SEM study of specimens quenched from melt state, it was observed that the phase separation in PET/PEC1 is severely restricted, which exhibits that in the morphology control processing conditions such as thermal treatment history can be dominant factors for the immiscible blend systems.

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