Miscibility and transesterification in bisphenol A polycarbonate/poly(ethylene terephthalate) blends

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The microstructure of blends of bisphenol A polycarbonate (PC) and poly(ethylene terephthalate) (PET) was studied by differential scanning calorimetry (d.s.c.), phase contrast microscopy and infra-red spectroscopy. PC and PET were immiscible over the whole composition range studied, for both extruder-mixed and solvent-cast blends. PC/PET is homogenized by transesterification between PC and PET above the melting temperature of PET. Homogeneous transesterification over most of the polymer chains is necessary for homogenization of the blends, because copolymers resulting from transesterification are not efficient as a homogenizer. The immiscibility of the solvent-cast blends is consistent with the phase diagram for the PC/PET/solvent system.

(Keywords: polymer blends; miscibility; bisphenol A polycarbonate; poly(ethylene terephthalate); transesterification)

INTRODUCTION

Recently, there has been considerable scientific and industrial interest in the miscibility of polymers. The spatial structure of polymer mixtures strongly affects their physical properties. Therefore, to create new useful materials by blending polymers, progress in studies on the microstructure of blends and on structure–property relationships is required. Thermodynamical analysis of polymer blends has been done to predict the miscibility and to control the structure of blends. The bisphenol A polycarbonate (PC)/poly(ethylene terephthalate) (PET) system has attracted commercial interest, since both polymers are widely used as high performance plastics. In particular, PC has high impact strength and its solvent resistance is improved by mixing with PET. A number of papers on this system have been published in recent years[1–9].

Nassar *et al.*[1] reported that melt-mixed PC/PET formed homogeneous amorphous phase for compositions with >70 wt% PET and formed inhomogeneous amorphous phase for <70 wt% PET from differential thermal analysis and dynamic mechanical measurement. Murff *et al.*[4] also reported the same kind of results. A carbon–carbon nuclear spin diffusion investigation by Linder *et al.*[5] showed that melt-mixed blends with 75 wt% PET were homogeneously mixed to the order of 4.5–6 Å†. Pilati *et al.*[6] reported that chemical reactions occurred during melt processing of PC/PET with and without Ti catalyst. Godard *et al.*[7] studied the identification and kinetics of these reactions: the main reaction occurring in molten PC/PET was transesterification between PC and PET; other subsequent reactions were degradation, pyrolysis and gel formation, probably due to the instability of the ethylene carbonates produced by the exchange reactions. The copolymer formed by exchange reactions influences the homogeneity of the blends as homogenizer, which complicates the determination of the miscibility of pure homopolymers. Chen *et al.*[8] and Hanrahan *et al.*[9] have shown that PC/PET is immiscible over the whole composition range. Chen *et al.*[8] concluded from differential scanning calorimetry (d.s.c.), dynamic mechanical analysis and infra-red spectroscopy that extruder-mixed blends with a small extent of transesterification had inhomogeneous amorphous phase. Hanrahan *et al.*[9] demonstrated the immiscibility of PC and PET by d.s.c. and dielectric loss spectroscopy for the solvent-cast blends using two kinds of solvent, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and a mixed solvent of phenol and tetrachloroethane in a 40/60 ratio by weight. The contradiction between these conclusions is possibly due to the different degree of transesterification. These experiments were not sufficient to clarify the miscibility or the phase diagrams[10] for the blends, because the temperature range studied was limited and it was not certain whether the system reached the equilibrium state before chemical reaction proceeded seriously. Phase separation or phase resolution should be faster than the reaction in order to determine the physical miscibility of the blends successfully. Therefore, it is required to study exact miscibility for the blends in as wide a temperature range as possible and the effects of chemical reaction on the miscibility in this system.

In this paper, we report on a study of the temporal change in phase structure of the amorphous region and in the crystallinity of the blends during melt processing at 270°C by d.s.c. The miscibility of the blends was checked more exactly by phase-contrast microscopy under variable temperature, and the changes in chemical structure of the blends were studied by Fourier-transform infra-red spectroscopy (*FT*i.r.). The phase diagram for PC/PET/HFIP was determined by measuring the cloud

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† 1 Å $= 10^{-1}$ nm

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points of the solutions. The results are discussed in relation to the phase structure of the solvent-cast blends of PC/PET using HFIP as co-solvent.

EXPERIMENTAL

Sample preparation

The bisphenol A polycarbonate (PC) used was provided by Idemitsu Petrochemical Co. (Idemitsu Polycarbonate N2200; $\bar{M}_n = 14\,400$, $\bar{M}_w = 29\,000$, $\bar{M}_w/\bar{M}_n = 2.02$; tetrahydrofuran as solvent at 40°C). The poly(ethylene terephthalate) (PET) used was obtained from Mitsubishi Rayon Co. (Dianite PA500; $\bar{M}_n = 8100$, $\bar{M}_w = 49\,600$, $\bar{M}_w/\bar{M}_n = 6.11$; HFIP/chloroform 10/90 mixture as solvent at 40°C). The PET sample was produced without Ti catalyst. Ti catalyst remaining in polymer blends seriously accelerates transesterification reaction. The blends without Ti catalyst have a much slower rate of exchange reaction between ester and carbonate groups[6,7]. Therefore, this PET sample was used to avoid the fast transesterification which makes the determination of the miscibility of the blends difficult.

The pre-dried homopolymers were mixed in various compositions by an extruder and were granulated as pellets. The mixtures were dried again in a vacuum oven at 180°C for 1 d to avoid hydrolytic degradation during melt processing. On the other hand, homopolymers with various compositions were dissolved in HFIP and cast at room temperature to make blends without heating. They were dried in a vacuum oven at 60°C for 1 d and at room temperature for a few weeks.

Processing

The extruder-mixed blends were sealed in d.s.c. aluminium pans. Each pan was filled with ≈ 16 mg samples together with $\approx 0.004\,\text{cm}^3$ residual space. The pans with samples were held at 270°C under dry nitrogen atmosphere for various lengths of time in the d.s.c. system (Perkin–Elmer DSC 1B).

Differential scanning calorimetry

Figure 1 shows the thermal program used for d.s.c. measurements. The sealed pans with molten samples were heat treated at 270°C and quenched into liquid nitrogen. They were then heated from room temperature at a rate of $32°\text{C}\,\text{min}^{-1}$ to 200°C under nitrogen atmosphere in the d.s.c. to measure their glass transition temperatures (T_g), quenched again into liquid nitrogen and reheated from room temperature at $32°\text{C}\,\text{min}^{-1}$ to 270°C to measure T_g again. Next, they were crystallized at 200°C from the melt for 1 h and heated at $8°\text{C}\,\text{min}^{-1}$ in order to measure the melting behaviour. They were again crystallized at 230°C from the melt for 1 h and heated at $8°\text{C}\,\text{min}^{-1}$. To examine the temporal changes in T_g, melting point (T_m) and molar heat of fusion for the repeating units (ΔH_f) due to transesterification in the same samples in the molten state, the pans tested as described above were held again at 270°C for a certain time for the melt processing, and the d.s.c. measurement was repeated.

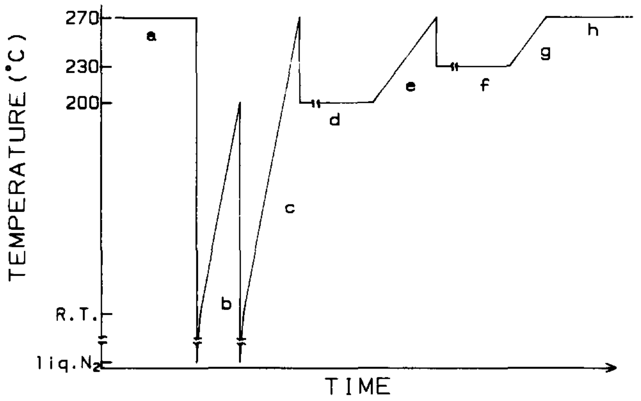


Figure 1 Thermal programme for d.s.c. measurements: (a) melt processing at 270°C; (b) first T_g measurement at $32°\text{C}\,\text{min}^{-1}$; (c) second T_g measurement at $32°\text{C}\,\text{min}^{-1}$; (d) crystallization at 200°C for 1 h; (e) T_m measurement at $8°\text{C}\,\text{min}^{-1}$; (f) crystallization at 230°C for 1 h; (g) T_m measurement at $8°\text{C}\,\text{min}^{-1}$; (h) melt processing at 270°C

The solvent-cast samples were tested by d.s.c. at a heating rate of $64°\text{C}\,\text{min}^{-1}$ to measure T_g.

Phase-contrast microscopy under variable temperature

Phase-contrast microscope observation under variable temperature was carried out for the blends to determine miscibility between homopolymers. Samples sandwiched between two cover-glasses were observed under a phase contrast microscope (Olympus IMT-2) equipped with a temperature controller (Linkam TH-600).

In addition, samples for phase-contrast microscopy and i.r. spectroscopy were heat treated in the d.s.c. system as described above. The microscope observations of the melt-processed samples were performed at temperatures from 250 to 300°C at a heating rate of $10°\text{C}\,\text{min}^{-1}$.

Fourier-transform infra-red spectroscopy

Sample films were cast from HFIP solution for Fourier-transform infra-red (*FT*i.r.) spectroscopy. Interferograms were averaged 64 times in the *FT*i.r. spectrometer (Bruker 113V). I.r. spectra were obtained from 400 to $4000\,\text{cm}^{-1}$ with a resolution of $1\,\text{cm}^{-1}$.

Determination of the phase diagram of PC/PET/HFIP

PC/PET/HFIP solutions with various compositions were prepared in vials and cloud points were observed both at room temperature (25°C) and in a hot water bath (60°C). For the 9/1, 8/2, 5/5, 2/8 and 1/9 (by weight) PC/PET solutions, the cloud points were measured by changing the concentration of solution with a resolution of 0.1 wt% HFIP.

RESULTS AND DISCUSSION

Temporal change in thermal properties of molten PC/PET

Figure 2 shows typical d.s.c. thermograms for PC/PET = 5/5 by weight melt-processed for 15 min at 270°C. Thermogram (a) was obtained for the sample quenched from 270°C and (b) for the sample quenched from 200°C after the first heating. They have two types of thermal transition behaviour. The lower temperature transition is assigned to a glass transition of PET-rich phase, and the higher to a glass transition of PC-rich phase. We define T_g as indicated by the arrows in the thermograms. For the homopolymers, we obtained $T_{g,\text{PC}} = 153°\text{C}$ and $T_{g,\text{PET}} = 79°\text{C}$ by d.s.c. measurement with a heating rate of $32°\text{C}\,\text{min}^{-1}$. The first thermogram exhibits an exothermic peak near 160°C, which is considered to be a crystallization behaviour of PET. Since such crystallization peaks interfere with the detection of the higher glass transition behaviour, the different types of heat scan are necessary. For the first heat scan there is

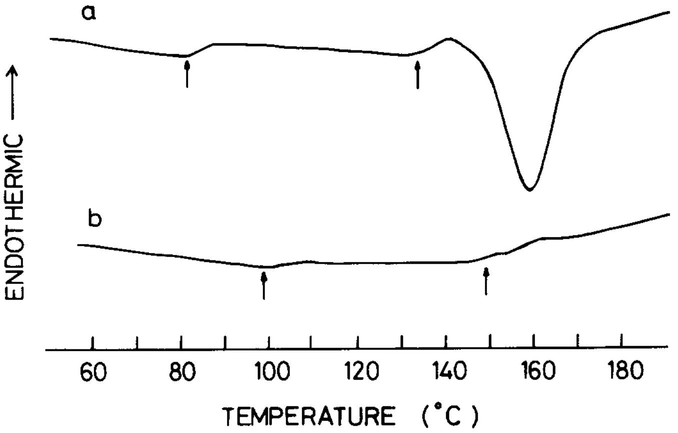


Figure 2 D.s.c. thermograms for PC/PET = 5/5 (by weight) heat treated at 270°C for 15 min: (a) first heat, quenched from melt; (b) second heat, quenched from 200°C

no crystalline phase in the samples, and we can detect mainly the lower T_g. For the second scan there is some crystalline phase formed during the first heat scan, and we can detect mainly the higher T_g without interference from crystallization behaviour. The difference in the T_gs of the blends between the first and the second heat scan is not negligible, while PET homopolymer with different crystallinity shows no significant difference in T_g. The shift of T_gs due to crystallization in the blends can be explained by the change in composition in both PC-rich and PET-rich amorphous phase.

The temporal changes in T_g during melt processing for various compositions are shown in *Figure 3*. At the beginning of the processing there are two T_gs, reflecting inhomogeneous amorphous phase for all compositions. However, a single T_g is observed after sufficient time of melt processing. Although there is some scatter in the observed T_gs, melt processing certainly makes the blends homogeneous. The final, single T_g was almost the same for the first and the second heat scan. The initial T_gs in the second heat scan and the final T_g are plotted against composition in *Figure 4*.

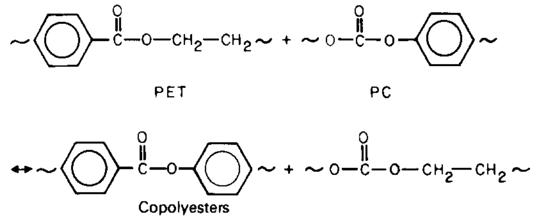
Figure 5 shows a typical thermogram of the melting behaviour for the blends. The melting temperature T_m is shown by an arrow. The value of ΔH_f is calculated from the area of the endothermic peaks. The temporal changes in T_m and ΔH_f during melt processing for various compositions are shown in *Figure 6*. For compositions with ≤ 50 wt% PET, T_m and ΔH_f decreased with processing time before the T_gs became single, and the blends exhibited no crystallization after complete homogenization. For compositions with ≥ 80 wt% PET, the decrease in crystallinity occurred after the T_gs became single. However, the time required for complete homogenization was not determined clearly since it is difficult to detect the glass transition of PC-rich phase in blends with a small PC fraction. The initial, distinct increase in crystallinity fro 10 wt% PET blend is due to further phase separation from the extruder-mixed state, which implies that the system is immiscible at the temperature of the melt processing. The similar tendency for the other compositions is probably also due to phase separation.

Temporal change in phase structure of molten PC/PET

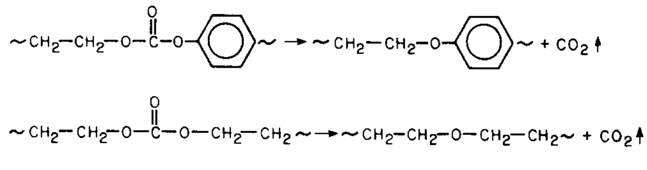
The miscibility of the blends is confirmed by phase-contrast microscope images observed under isothermal condition. *Figure 7* shows a set of examples of phase-contrast microscope images. The growth in the size of the phases demonstrates that the system is immiscible[11]. Our observations for blends with various compositions under the phase-contrast microscope can be summarized as follows.

In almost the entire composition range from 2 wt% PET to 98 wt% PET, PC/PET was immiscible in the temperature range 250–300°C, where the growth of phase separation pattern was recognized. The average molecular weights for the polymers are comparable with those in other studies[1,2,4,5]. Above 250°C, the phase boundaries disappeared from the blends by homogenization from the phase-separated state. Then bubbles appeared in the blends because of chemical reaction. The homogenization occurred more rapidly as the temperature was increased. The homogenization of the thermodynamically immiscible blend must be due to chemical reaction. In this case, the chemical reaction should be transesterification. In fact, transesterifiaction in PC/PET without Ti catalyst has been reported[6], and immiscible polyester blends have been shown to be homogenized by transesterification during melt processing[12,13]. Chemical reactions occurring in molten PC/PET were supposed to be[7]:

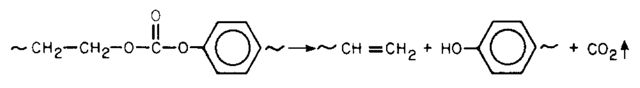
(1) transesterification between ester and carbonate groups:



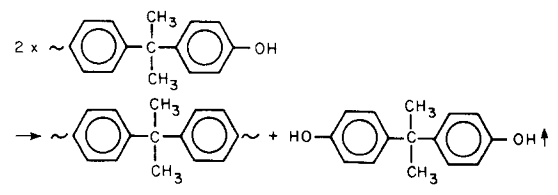
(2) ethylene carbonate degradation with CO_2 release and formation of ether groups:



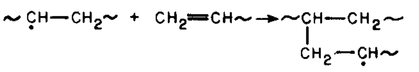
(3) ethylene carbonate degradation with CO_2 release and formation of phenol and vinyl chain ends:



(4) phenol chain end reaction:



(5) gel formation of vinyl chain ends during pyrolysis of PET:



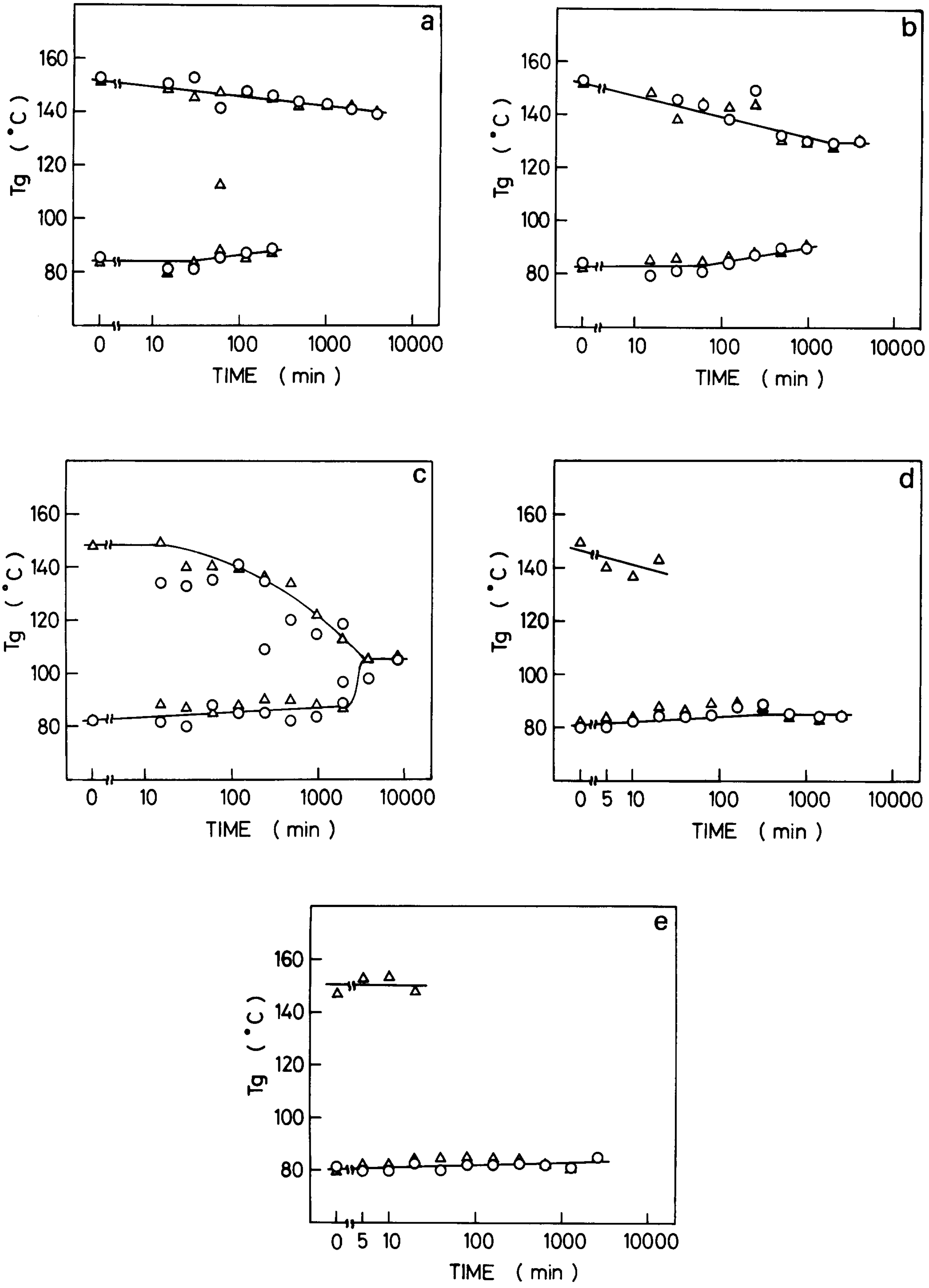


Figure 3 Temporal changes of T_gs during melt processing at 270°C: ○, first heat; △, second heat. (a) PC/PET=9/1; (b) PC/PET=8/2; (c) PC/PET=5/5; (d) PC/PET=2/8; (e) PC/PET=1/9 (by weight)

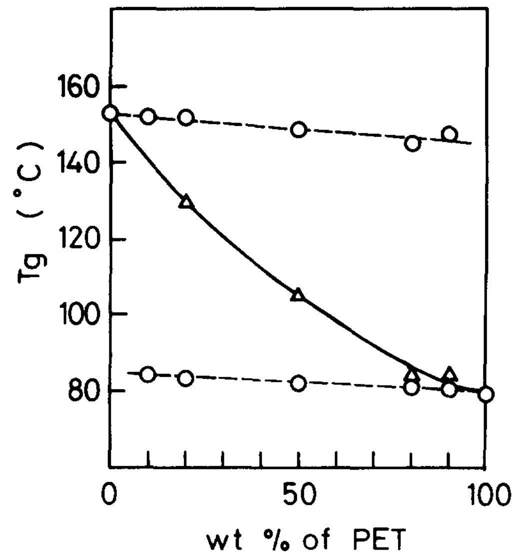


Figure 4 T_gs for various PC/PET compositions before and after melt processing at 270°C: ○, before melt processing; △, after 3840 min for PC/PET = 9/1 and PC/PET = 8/2, after 8220 min for PC/PET = 5/5, and after 2560 min for PC/PET = 2/8 and PC/PET = 1/9

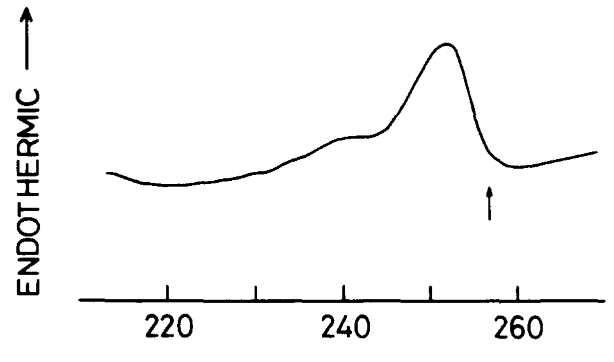
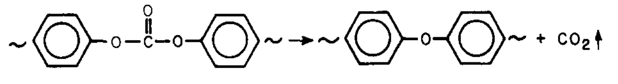


Figure 5 D.s.c. thermogram for PC/PET = 2/8 (by weight) crystallized at 200°C for 1 h before melt processing

(6) PC degradation:



The main reaction is transesterification (1). Unstable ethylene carbonates formed by reaction (1) are efficiently decomposed with CO_2 release in reactions (2) and (3), and the residual amount of ethylene carbonate is low. The bubbles observed in the microscope images under isothermal condition are ascribed to CO_2 gas produced in reactions (2) and (3). The decrease in molecular weight resulting from reaction (3) is compensated by reactions (4) and (5). This is consistent with the absence of a drastic decrease in T_gs for the polymers during melt processing in our d.s.c. measurements. PC degradation (6) is much slower than ethylene carbonate degradation.

In molten PC/PET, growth of phase domains occurs at the beginning of the melt processing. Inside both the domains, the probability of encounter of PC and PET molecules is small. Therefore, the transesterification reaction proceeds less effectively in the phase-separated state. The effective transesterifying process is accelerated by the formation of copolymers, which improves the miscibility between PC and PET. That is, homogenization kinetics is controlled by interdiffusion of reacted polymers through the interface. When the copolymer formation reaches a certain level, the blends homogenize by themselves. In the homogeneous region, the reaction proceeds most effectively.

In general, crystallinity in copolymers or in miscible blends is much less than that in homopolymers[14,15]. Our d.s.c. experiments are consistent with this tendency. Some scatter in T_g, T_m and ΔH_f data is probably due to the differences in domain sizes and interphase amounts caused by the rather complicated heating–cooling programme.

Phase structures were also investigated by phase-contrast microscopy under variable temperature for the samples melt-processed in the d.s.c. system. We examined the homogeneity of the samples, and the results are given in *Table 1*. We think that the miscibility in equilibrium can be checked more exactly by microscope observation than by T_g measurement using d.s.c. for the following reasons: first, glass transition behaviour for a small amount of components is very hard to detect with d.s.c. and, second, the d.s.c. measurements in this study were carried out in

Table 1 Homogeneity of PC/PET examined by temperature controlled phase-contrast microscopy

PC/PET (by weight)	Processing time (min)	Homogeneity[a] (250–290°C)
9/1	0	×
	60	×
	120	×
	240	×
	480	○
	960	○
8/2	0	×
	120	×
	240	×
	480	×
	960	× (250–280°C)
	1900	○
	3900	○
5/5	0	×
	120	×
	240	× (250–280°C)
	480	× (250–280°C)
	960	△
	1900	○
	3900	○
2/8	0	×
	5	×
	10	×
	20	×
	40	×
	80	× (250–280°C)
	160	× (250–270°C)
	320	× (250–270°C)
	640	○
1/9	0	×
	5	×
	10	×
	20	×
	40	×
	80	○
	160	○
	320	○

[a] ○, homogeneous; ×, inhomogeneous; △, ambiguous

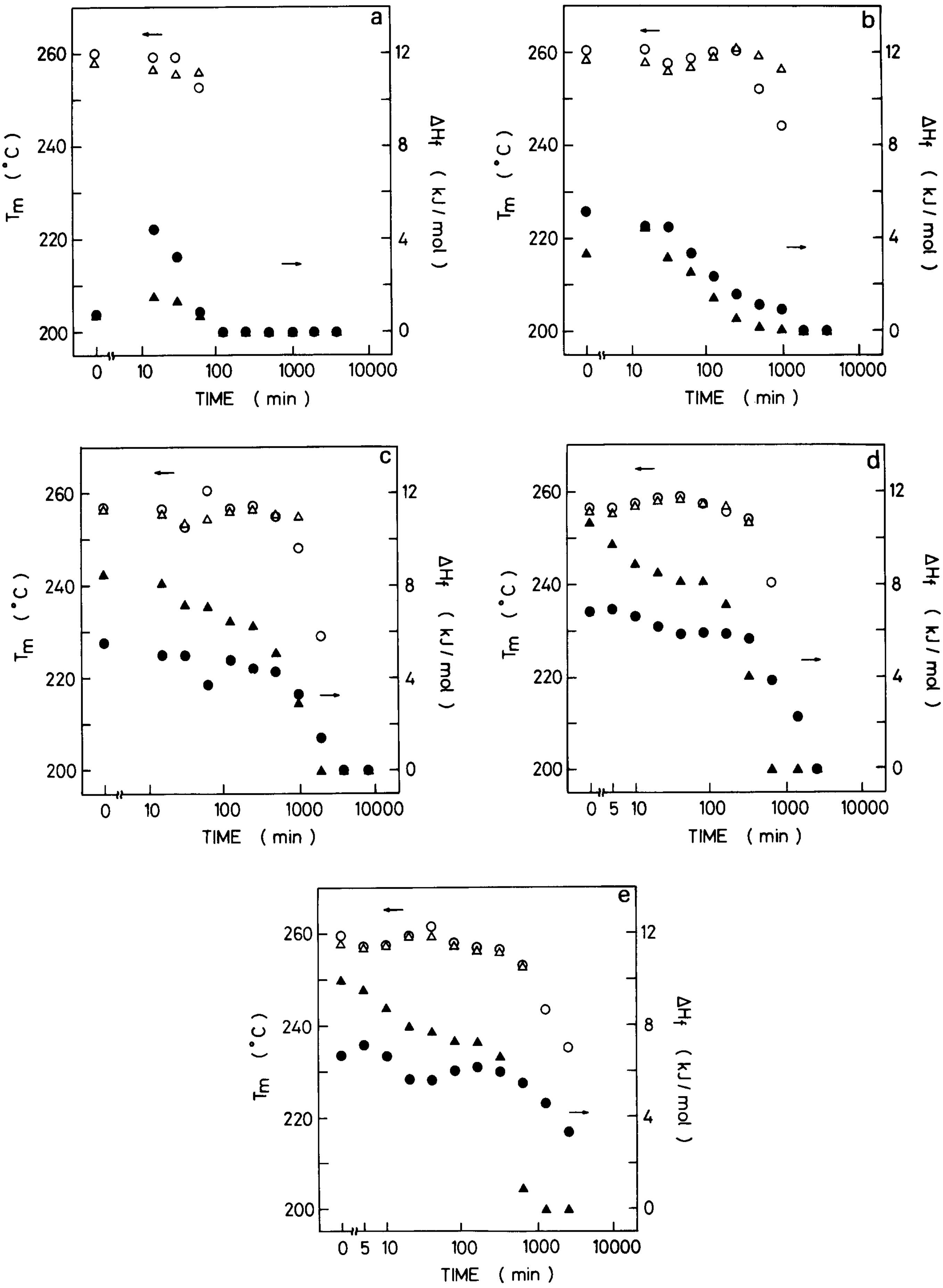


Figure 6 Temporal changes of T_m and ΔH_f during melt processing at 270°C: ○, T_m crystallized at 200°C for 1 h; △, T_m crystallized at 230°C for 1 h; ●, ΔH_f crystallized at 200°C for 1 h; ▲, ΔH_f crystallized at 230°C for 1 h. (a) PC/PET = 9/1; (b) PC/PET = 8/2; (c) PC/PET = 5/5; (d) PC/PET = 2/8; (e) PC/PET = 1/9 (by weight)

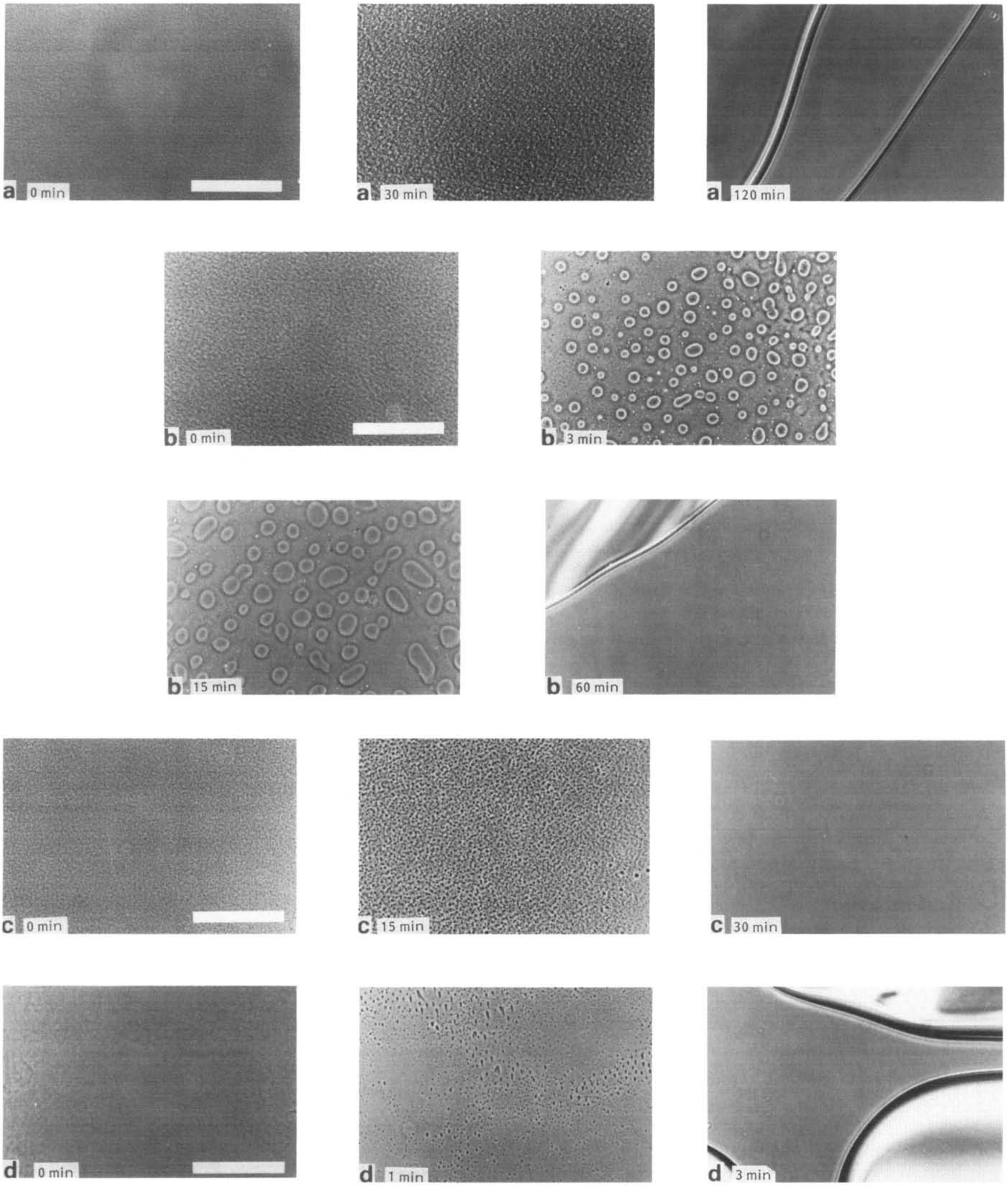


Figure 7 Images observed under phase-contrast microscope. White bars indicate 200 μm. (a) PC/PET = 8/2 (by weight). temperature = 250°C; (b) PC/PET = 5/5, temperature = 250°C; (c) PC/PET = 2/8, temperature = 250°C; (d) PC/PET = 1/9, temperature = 300°C. The outsides of the boundaries are bubbles for (a) 120 min, (b) 60 min and (c) 3 min

non-equilibrium state during phase resolution from large-size phase structure. Therefore, the results shown in *Table 1* are different from those of T_g measurements in *Figure 3*. However, homogenization in PET-rich samples was apparently faster than in PC-rich samples. The conclusion by Nassar *et al.*[1] and Murff *et al.*[4] that PET-rich blends were miscible and the others were not is considered to be due to ignorance of homogenizing rates for different compositions.

Temporal change in chemical structure of molten PC/PET

Figure 8 shows infra-red spectra for solvent-cast films of PC, PET and PC/PET = 5/5 mixture before and after melt processing. The absorption bands noted in this study

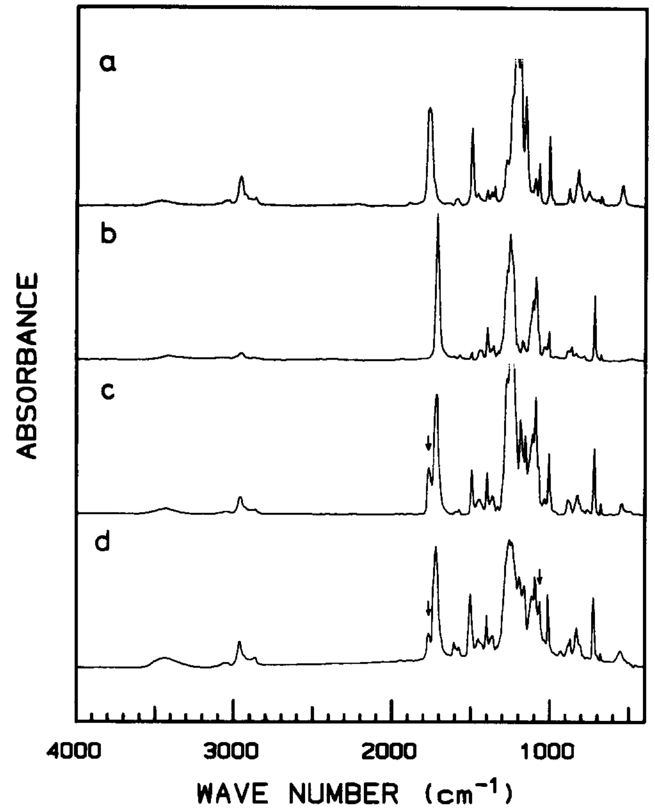


Figure 8 *FT*i.r. spectra: (a) PC; (b) PET; (c) PC/PET = 5/5 (by weight) before melt processing; (d) PC/PET = 5/5 after 3890 min at 270°C. Arrows indicate 1775 cm^{-1} and 1070 cm^{-1} band peaks

Table 2 Assignment of i.r. bands in PC/PET

Wavenumber (cm^{-1})	Assignment
727	Mixed vibration in a terephthalate unit
≈1070	Vibration in an aromatic ester group
1724	Carbonyl stretching of aliphatic ester
≈1740	Carbonyl stretching of aromatic ester
≈1770	Carbonyl stretching of mixed aliphatic–aromatic carbonate
1768	Carbonyl stretching of aromatic carbonate (crystalline)
1775	Carbonyl stretching of aromatic carbonate (amorphous)

are summarized in *Table 2* with their assignments[16–19]. The relative amounts of aromatic carbonate triads in amorphous state (1775 cm^{-1} band) for all terephthalate units (727 cm^{-1} band) and aromatic ester dyads (1070 cm^{-1} band) for all terephthalate units (727 cm^{-1} band) are represented by absorbance ratios of bands, A_{1775}/A_{727} and A_{1070}/A_{727}, respectively[7,8,19]. *Figure 9* shows the temporal changes in the absorbance ratios in *FT*i.r. spectra during melt processing. The A_{1070}/A_{727} ratio reflects the extent of transesterification, and the A_{1775}/A_{727} ratio reflects the extent of both transesterification and degradation of carbonates. Usually, crystallization of PC is induced by solvent[20], and PC is partially crystallized during the solvent-casting process[16]. The 1775 cm^{-1} peak of the aromatic carbonates in amorphous state decreases and a shoulder at 1768 cm^{-1} corresponding to aromatic carbonates in crystalline state increases with increasing crystallinity[16]. Therefore, the A_{1775}/A_{727} ratio also reflects the crystallinity of solvent-cast films. For PC/PET = 9/1, 8/2 and 5/5, A_{1775}/A_{727} slightly increases with decreasing crystallinity for the solvent-cast films of the melt-processed samples. Because of difficulties in resolving the overlapped peaks, the absorbance ratios were not proportional to the relative amounts. However, transesterification causing the disappearance of 20–30% of the aromatic carbonates is probably enough for the homogenization of the blends. The 1070 cm^{-1} peak was not detected for PC/PET = 9/1, 2/8 and 1/9 over the time range studied. The 1070 cm^{-1} peak was detected only for PC/PET = 8/2 and 5/5 samples after 2000 min processing. This means that the drastic change in chemical structure occurred after the homogenization. In other words, even a slight extent of transesterification, which means that long PC or PET blocks exist in copolyester products, can increase the miscibility drastically.

Compatibilizing effect of transesterification products on PC/PET

In some cases, A–B random copolymer plays a role in a compatibilizer for A/B polymer blends[21]. For polyester/polyester blends with transesterification, copolyester products are considered to be compatibilizers[22]. We made transesterification products of PC/PET by melt processing at elevated temperature in the d.s.c. pan, and examined the miscibility between the homopolymer and the products by phase-contrast microscopy, to check the effect of the products as a homogenizer. *Table 3* shows the conditions for making transesterification products, miscibility of the products with homopolymers and absorbance ratios obtained by *FT*i.r. spectroscopy with KBr tablets of the products. For the products with high transesterification ratios, the homopolymer/products blends were not always miscible. Generally, ternary polymer blends containing more than two immiscible pairs are immiscible[23]. Therefore, these copolyester products, which are not simple A–B random copolymers, are not efficient as a compatibilizer. We conclude that homogeneous transesterification over most polymer chains is necessary for homogenization of PC/PET. At the homogenization, most of the molecules in PC/PET probably have long PC and PET sequences which are chemically connected to each other.

Phase structure of solvent-cast PC/PET

The phase diagram for the ternary system of PC/PET/HFIP is shown in *Figure 10*. Since the crystallization of polymer is induced at high concentration, miscibility in the high concentration range is not clear. However, the wide unstable region in the phase diagram indicates that homogeneous mixing of PC/PET by solvent-casting is impossible in the temperature range studied. The T_gs for solvent-cast PC/PET blends are shown in *Figure 11*. The detection of T_g was not easy on account of the crystallization of polymers, and the T_g data are rather scattered. However, *Figure 11* demonstrates the absence of homogeneous single amorphous phase for the solvent-cast blends. It is consistent with the phase diagram shown in *Figure 10*. If the unstable region in the PC/PET/HFIP phase diagram shown in *Figure 10* is extrapolated simply to 0% solvent, the miscibility gap of PC/PET binary blends will be

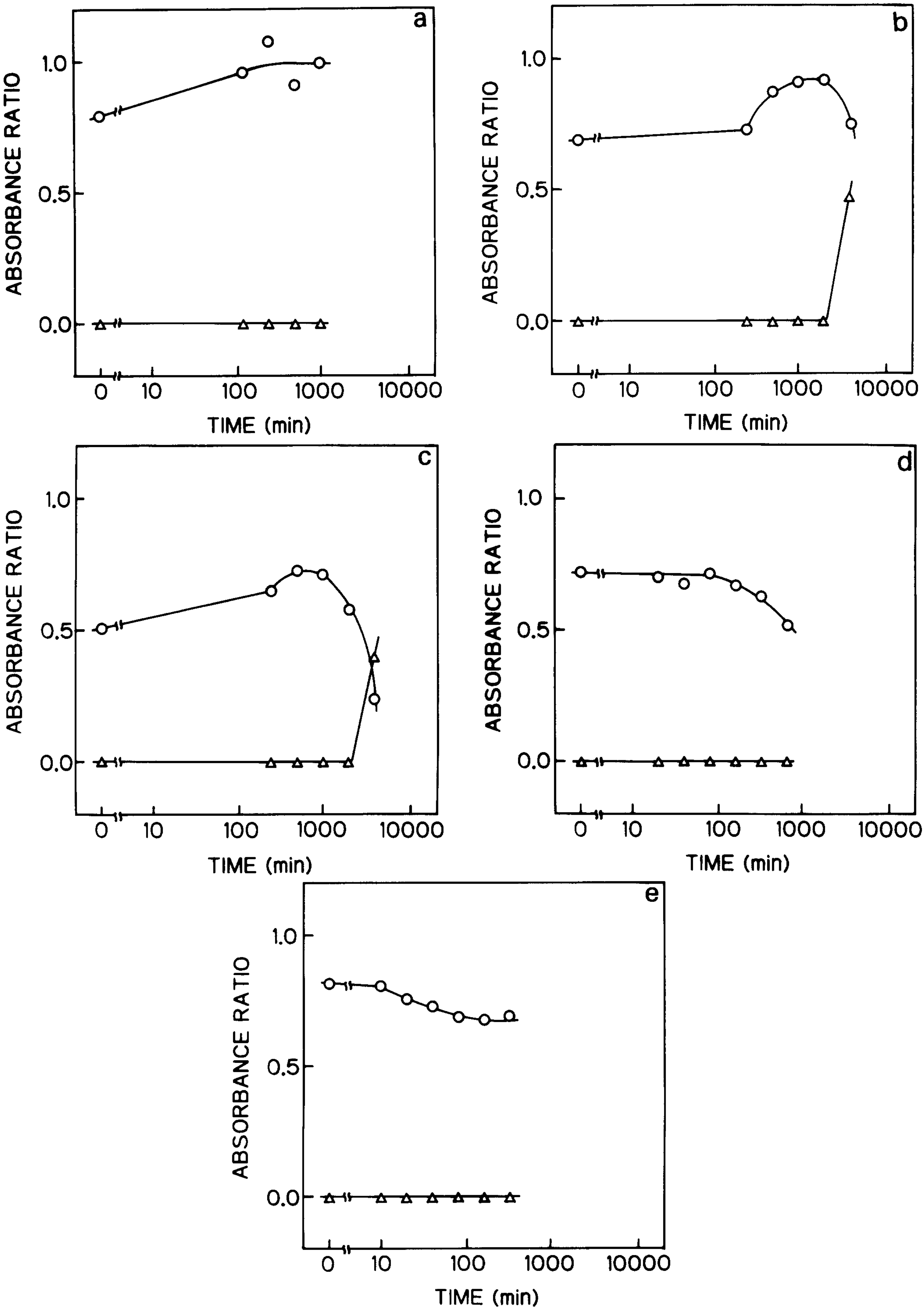


Figure 9 Temporal changes of normalized absorbance ratios: ○, (A_{1775}/A_{727}); ×, (PET/PC); △, A_{1070}/A_{727}. (a) PC/PET = 1/9; (b) PC/PET = 8/2; (c) PC/PET = 5/5; (d) PC/PET = 2/8; (e) PC/PET = 1/9 (by weight)

Table 3 Melt processing conditions and miscibility of PC/PET transesterification products with homopolymers

PC/PET (by weight)	8/2	5/5	2/8
Processing temperature (°C)	300	300	300
Processing time (h)	48	48	24
I.r. absorbance ratio			
A_{1070}/A_{727}	1.3–1.5	0.38	0.10
$(A_{1775}/A_{727}) \times$ (PET/PC)	0.52	0.35	0.0
Miscibility with PC[a]	○	×	×
Miscibility with PET[a]	×	×	○

[a] ○, homogenizing; ×, immiscible

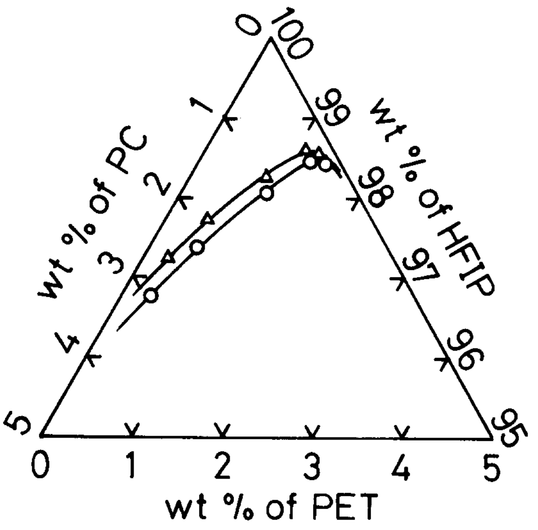


Figure 10 Cloud points for PC/PET/HFIP: ○, 25°C; △, 60°C

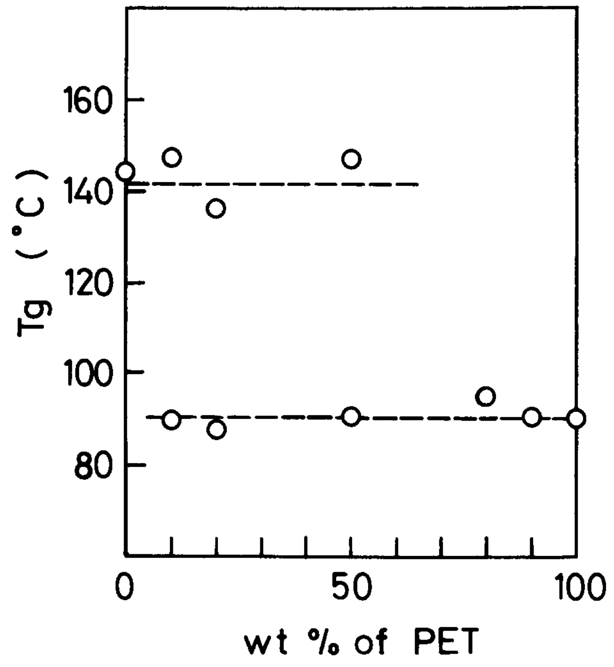


Figure 11 T_g for HFIP-cast PC/PET blends at various compositions

extremely wide. The unstable region up to low concentration (≈98 wt % solvent) and the wide miscibility gap of PC/PET indicate rather large, positive values of the Flory–Huggins χ parameter[24] for PC/PET in this temperature range, although the χ parameters for PC/HFIP and PET/HFIP are unknown. According to Cruz *et al.*[3], the heat of mixing between diphenyl carbonate and dimethyl terephthalate, which are the analogues of the structural units of the polymers, is rather exothermic at 85°C, and the interactional energy[25] between PC and PET is expected to be rather negative. This indicates that the large, positive value of χ expected is mainly due to the free volume effect[25] of the polymers.

CONCLUSIONS

PC/PET is immiscible in almost the entire composition and accessible temperature range. This is supported by the phase diagram for PC/PET/solvent systems. The chemical reactions involving transesterification between PC and PET are brought up for molten PC/PET at elevated temperature or prolonged heat treatment. The reaction proceeds even if the system is phase separated. Homogenization of the system is caused only by homogeneous transesterification over most of the polymer chains, because the copolyester products of the reactions are not efficient as a homogenizer. Over the wide temperature range, the Flory–Huggins χ parameter for PC/PET is expected to be rather large and positive from the immiscibility between PC and PET over the extremely wide composition range. Crystallization of the polymers is strongly suppressed by the change of chemical structure (copolymerization) and the blending effect.

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