

Spectroscopic studies of the crystallization behaviour in poly(ether imide)/poly(ethylene terephthalate) blends

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The crystallization behaviour of poly(ethylene terephthalate) in poly(ether imide) (PEI)/poly(ethylene terephthalate) (PET) blends was investigated using Fourier transform infrared spectroscopy. Thin films of PEI/PET blends were prepared by solution blending, and many characteristic bands for the PET crystalline region were observed as a function of the annealing time of PEI/PET blends at 225°C. It was found that the C=O stretching band shifted up to 5 cm⁻¹ in PEI/PET blends due to the increase in crystallinity of PET. This C=O band shift is in agreement with the increase for the characteristic crystallization band of PET, and the band shift width is proportional to the PET weight fraction in PEI/PET blends. Crystallization of PET occurs immediately by annealing for PEI/PET blends with a high PET weight fraction (2/8 and 4/6 PEI/PET blend composition). In the case of PEI/PET blends with a low PET weight fraction (6/4 and 8/2 PEI/PET blend composition), crystallization of PET occurs in the PET-rich phase only after the amorphous phase is separated into PET-rich and PEI-rich phases. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Polymer blending has been studied extensively as an important technique for improving the cost-performance of various polymers^{1,2}. These blend systems may be homogeneous, phase separated or a bit of both. Semi-crystalline polymer blend systems have, in particular, attracted much attention in recent years^{3–9}.

The poly(ether imide) (PEI)/poly(ethylene terephthalate) (PET) blend is one of these crystalline/amorphous polymer blends. PEI is a linear amorphous polymer that has high thermal stability with T_g at 220°C, and excellent mechanical properties. However, the high processing temperature due to the aromatic polymer backbone, and its poor solvent resistivity, restrict the wide application of PEI. Blends of PEI with many polymers such as poly(aryl ether ether ketone)¹⁰, poly(aryl ether ketone)¹¹ and polybenzimidazole¹² have been attempted. Among these polymers, PET, which is a semicrystalline polymer with T_g at 75°C and T_m at 250°C, is studied as a potential polymer for blending with PEI. Although a relatively low T_g and fast crystallization behaviour are disadvantages of PET, blending of PEI and PET is expected to induce excellent synergistic effects such as a lowering of the processing temperature of PEI, enhancement of the solvent resistance of PEI, and reduction of the crystallization rate of PET. To achieve these attractive properties, basic studies on the PEI/PET blend are continuously required.

In this study we investigate the crystallization behaviour of PET during the annealing of the PEI/PET blend by using FTi.r. spectroscopy. The various spectral changes due to the crystallization of PET in the PEI/PET blends were used to monitor the change in crystallinity of PET as a function of the annealing time. The effect of blend composition on the crystallization mechanism of PET in the PEI/PET blends is also discussed.

EXPERIMENTAL

Materials

The PEI used in this study was Ultem 1000 (General Electric Co., $M_n = 20\,000$), and the PET was supplied from Tongyang Nylon Co. (Korea) and has a relative viscosity of 0.64 μl g⁻¹ in 1,1,2,2-tetrachloroethane (TCE).

Sample preparation

The PEI/PET blend was obtained by solution blending. A TCE and phenol mixture (1:1 by volume ratio) was used as a co-solvent, and PEI/PET (2/8, 4/6, 6/4, 8/2 by weight ratio) was dissolved at 100°C to form a 1 wt% solution. These dissolved blends were precipitated in a 20-fold excess volume of methanol, washed with methanol, and vacuum dried to remove the residual solvents at 100°C for 24 h. After drying, the precipitants were melt pressed using a laboratory press at 275°C into a thin film and quenched. The first d.s.c. scan showed that the heat of cold crystallization was almost equal to the heat of melting. Therefore, the resulting films were in an almost amorphous state.

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The annealing of PEI/PET blend films was accomplished by placing a Teflon sheet/film/Teflon sheet sandwich in a furnace pre-equilibrated to 225°C, at which temperature the annealing is most effective. The samples were cooled at room temperature after the annealing with various treatment times.

FTi.r. spectroscopy

The attenuated total reflectance (ATR) technique was used to investigate the crystallization behaviour of PET in the PEI/PET blend. The spectra of PEI/PET blend films with various compositions at different annealing times were obtained by using a germanium (incident angle 45°) crystal at 2 cm⁻¹ resolution and 100 scan number.

Thermal analysis

D.s.c. was used with a Perkin Elmer DSC-4 to measure the crystallinity of PET in the PEI/PET blends, and the results obtained from d.s.c. were compared with i.r. spectra. The scan rate used was 20°C min⁻¹ and a second scan was not recorded because the annealing history was eliminated during the first scan. Dynamic mechanical thermal analysis (d.m.t.a.) was also performed to observe the shift of the glass transition temperature (*T_g*) because it was difficult to detect *T_g* of PEI/PET blends by d.s.c. in the case of low PET content and high crystallinity of PET.

RESULTS AND DISCUSSION

The PEI/PET blend is known to be miscible in the melt over the total composition range¹³. In this study, blending of PEI and PET was accomplished by solution precipitation, and the precipitants were pressed resulting in a thin film.

Figure 1 shows the glass transition temperatures of PEI/PET blends with different compositions. The glass transition temperatures of PEI/PET blends were assigned to the highest point of the d.m.t.a. loss modulus peak. Single glass transition temperatures were measured for all PEI/PET blend compositions and the shift of the

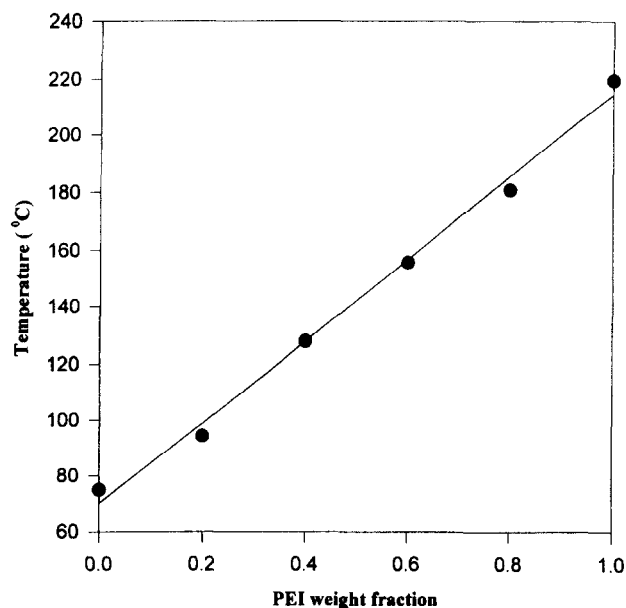


Figure 1 *T_g*-composition variation of amorphous PEI/PET blends before annealing

glass transition temperature has a linear relationship with PEI composition in the PEI/PET blends. This result means that the PEI/PET blend is miscible throughout the composition range, and it also indicates that solution blending for the PEI/PET system is an effective method.

The FTi.r. spectra for amorphous PET and PEI are shown in Figure 2. In the spectrum of PET, the band at 1720 cm⁻¹ is due to the C=O stretching vibration, and the peak at 1260 cm⁻¹ is due to the C(=O)-O stretching vibration. In addition, the bands at 1098 and 726 cm⁻¹ correspond to C-O stretching of the ethylene glycol residue and the C-H bending vibration (aromatic out-of-plane) of PET, respectively. As the characteristic bands for PEI, the bands at 1722 and 1356 cm⁻¹ are assigned to the C=O stretching and C-N stretching vibration modes, respectively. The bands at 1274 and 1237 cm⁻¹ are attributed to asymmetric C-O-C stretching vibration of PEI.

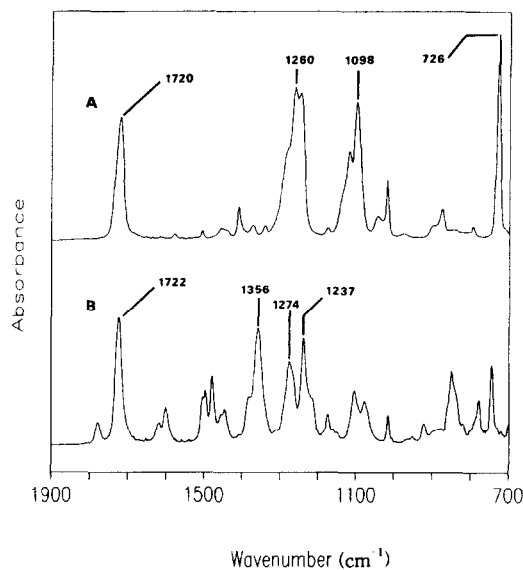


Figure 2 FTi.r. spectra of pure PET and PEI used for PEI/PET blends: (A) amorphous PET and (B) PEI

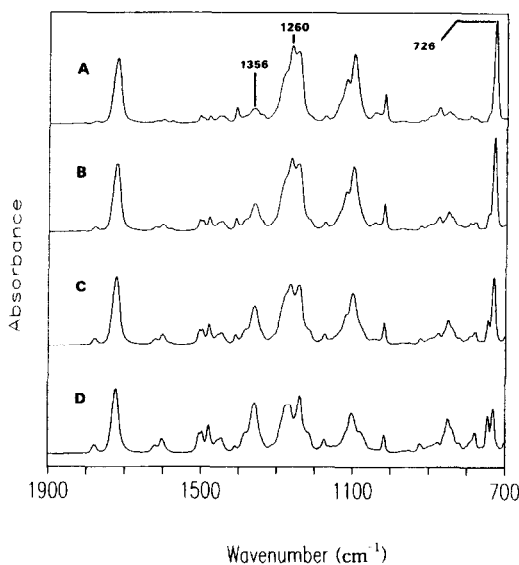


Figure 3 FTi.r. spectra of PEI/PET blends with various compositions: (A) 2/8, (B) 4/6, (C) 6/4 and (D) 8/2

Figure 3 shows the FTi.r. spectrum of the PEI/PET blend with various compositions (PEI/PET = 2/8, 4/6, 6/4 and 8/2) in the range 1900–700 cm^{-1} . The band at 1356 cm^{-1} increases, and the peaks at 1260 and 726 cm^{-1} decrease on going from spectra (A) to (D). Comparing these spectra of PEI/PET blends with the spectra of pure PEI and PET in Figure 2, it is evident that the relative intensities of characteristic peaks for each component vary according to the PEI/PET blend quantitative composition.

In Figure 4, the i.r. spectra of the PEI/PET blend with the 2/8 composition are shown for various annealing times. It is observed that the apparent change for some peaks occurs in the i.r. spectra of the PEI/PET blends on annealing. The bands at 1343, 1118, 973 and 848 cm^{-1} become more intense as the annealing time increases, and the bands at 1360, 1099, 1042 and 898 cm^{-1} become

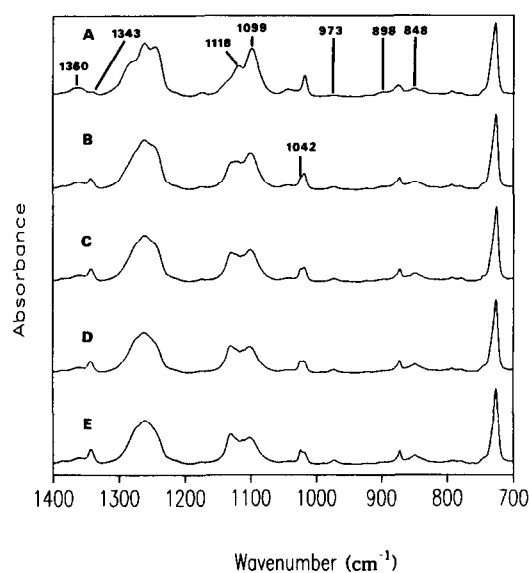


Figure 4 Effect of annealing at 225°C on the FTi.r. spectra of PEI/PET blends with 2/8 composition: (A) 0 min, (B) 10 min, (C) 20 min, (D) 30 min and (E) 60 min

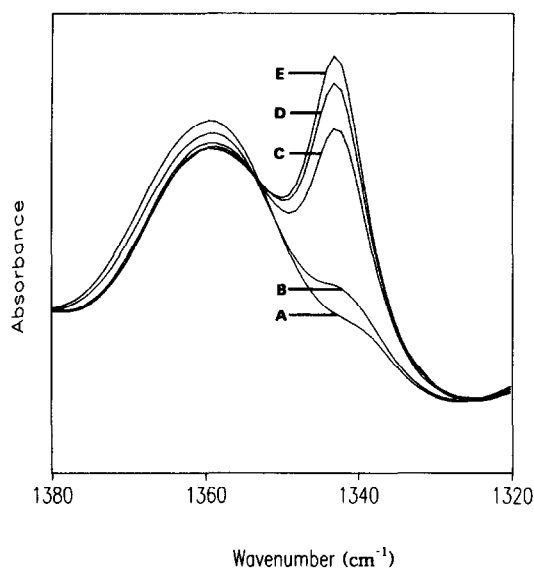


Figure 5 The change of crystalline bands of PET in PEI/PET blends after annealing at 225°C for (A) 0 min, (B) 10 min, (C) 20 min, (D) 30 min and (E) 60 min

weaker in intensity. These variations of the band intensities are associated with a change of molecular conformation, especially rotational isomerism of the ethylene glycol residue of PET^{14,15}. The band at 1343 cm^{-1} corresponds to the *trans* CH₂ wagging vibration of PET, and makes a couple with the *gauche* CH₂ wagging band at 1360 cm^{-1} . The increase of the band intensity at 1343 cm^{-1} , and the decrease at 1360 cm^{-1} , signify that the conformation of the ethylene glycol residue changes from *gauche* to *trans*. The bands at 973, 1099 and 1042 cm^{-1} are assigned to the C–O stretching vibration of PET in *trans* (B_u type), *gauche* (B Type) and *gauche* (A type) conformation, respectively. The bands at 848 and 898 cm^{-1} correspond to the *trans* and *gauche* vibrations of CH₂ rocking, respectively, and the band at 1118 cm^{-1} seems to correspond to the CH₂ twisting vibration mode.

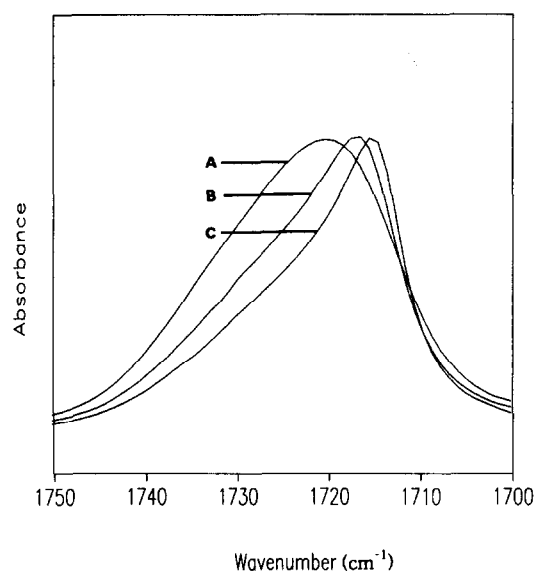


Figure 6 FTi.r. spectra pure of PET in the C=O stretching region after annealing at 225°C for (A) 0 min, (B) 10 min, (C) 20 min, (D) 30 min and (E) 60 min

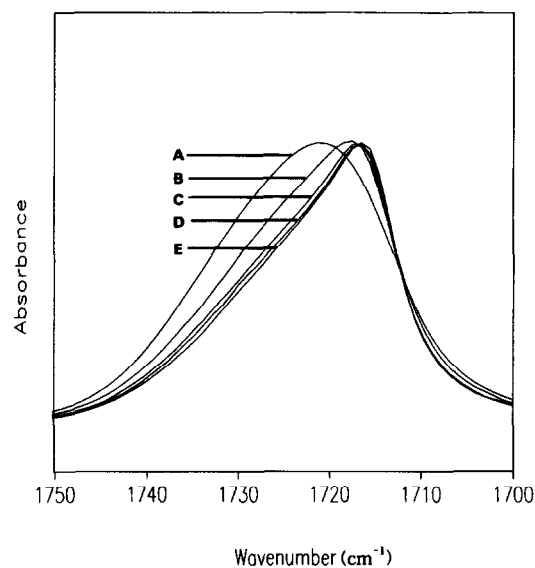


Figure 7 C=O stretching bands of PEI/PET blends with the 2/8 composition after annealing at 225°C for (A) 0 min, (B) 10 min, (C) 20 min, (D) 30 min and (E) 60 min

Figure 5 shows the increase of the PET crystalline band at 1343 cm^{-1} in the i.r. spectra of PEI/PET blends with the 6/4 composition. The trend of increasing wavenumber for these peaks is in accordance with the crystallinity change of PET measured from the T_m peak area in the d.s.c. thermogram. In general FTi.r. spectroscopy offers more specific and microrange information for molecular interactions (molecular structure) and quantitative analysis. This characteristic crystallization band in the i.r. spectrum can be used as a specific parameter to investigate PET crystallization behaviour in the PEI/PET blend system.

The C=O peak analysis of PET was also performed to investigate the effect of annealing time on the PEI/PET blend. Figure 6 shows i.r. spectra for PET between 1750 and 1700 cm^{-1} at various annealing times. It is clear that the C=O peak shifts to lower wavenumber, and the peak width becomes narrower, as the annealing time

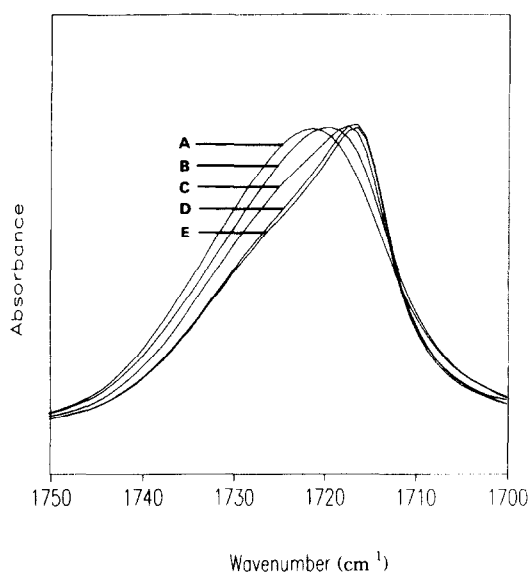


Figure 8 C=O stretching bands of PEI/PET blends with the 4/6 composition after annealing at 225°C for (A) 0 min, (B) 10 min, (C) 20 min, (D) 30 min and (E) 60 min

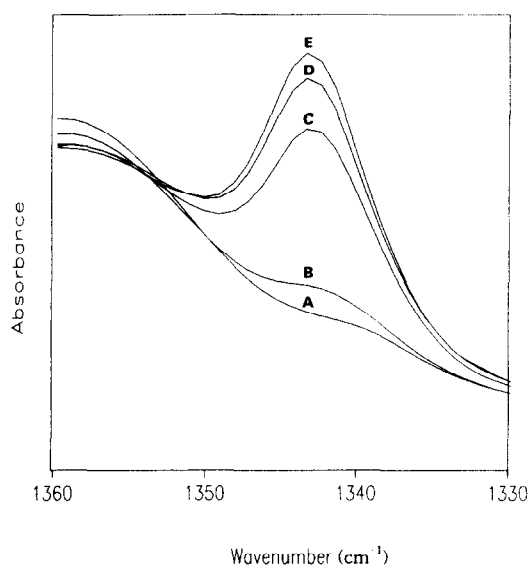


Figure 9 Crystalline bands of PET in PEI/PET blends with the 4/6 composition after annealing at 225°C for (A) 0 min, (B) 10 min, (C) 20 min, (D) 30 min and (E) 60 min

increases. The C=O peak of PET appears at 1720 cm^{-1} for the initial amorphous state before annealing. As the crystallinity of PET increases on annealing, the C=O stretching motion of PET becomes restricted in the crystalline field and the C=O peak shifts up to 1715 cm^{-1} . In contrast, it is confirmed that the C=O stretching peak of PEI appears at 1722 cm^{-1} , and is not affected by annealing.

Figure 7 shows the change in i.r. spectra of PEI/PET blends with the 2/8 composition as a function of annealing time. The shift of the C=O stretching peak is similar to that of pure PET. In addition, the shift width of the C=O stretching peak of PEI/PET blends is proportional to the weight fraction of PET in the blend.

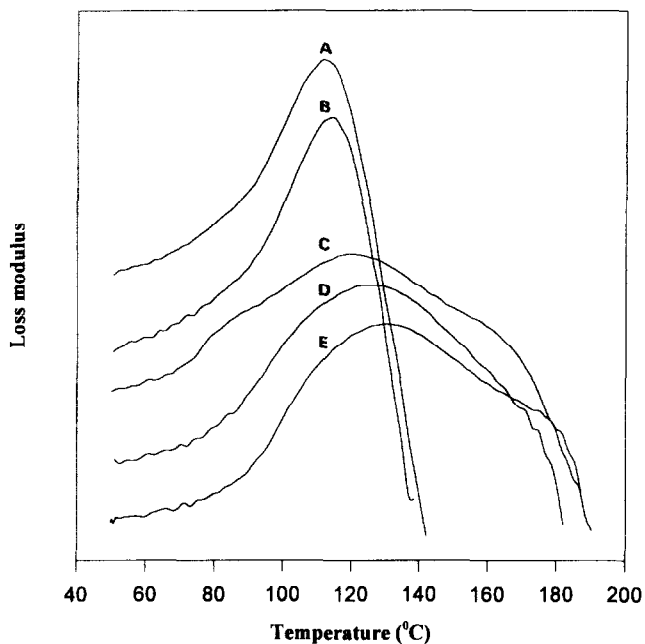


Figure 10 D.m.t.a. thermogram for the change of T_g with annealing time in PEI/PET blends with the 4/6 composition: (A) 0 min, (B) 10 min, (C) 20 min, (D) 30 min and (E) 60 min

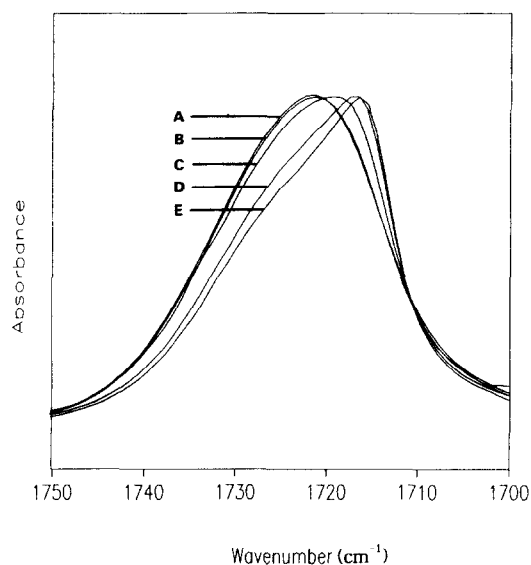


Figure 11 C=O stretching bands of PEI/PET blends with the 6/4 composition after annealing at 225°C for (A) 0 min, (B) 10 min, (C) 20 min, (D) 30 min and (E) 60 min

Consequently, the increase in PET crystallinity plays a major role in the C=O peak shift of PEI/PET blends. It is noteworthy that the shift width of the C=O peak for each annealing time is congruent with the increase of the crystalline peak of PET in PEI/PET blends. This means that the C=O peak shift can be used as another indicative parameter of PET crystallization in the PEI/PET blend.

Although this C=O peak shift of PEI/PET blends was observed for all compositions except for pure PEI, there is some difference for each blend composition. Figures 8 and 9 show the C=O peak shift and the increase of the crystalline peak of PET in the PEI/PET blend with the 4/6 composition, respectively. For the PEI/PET blends

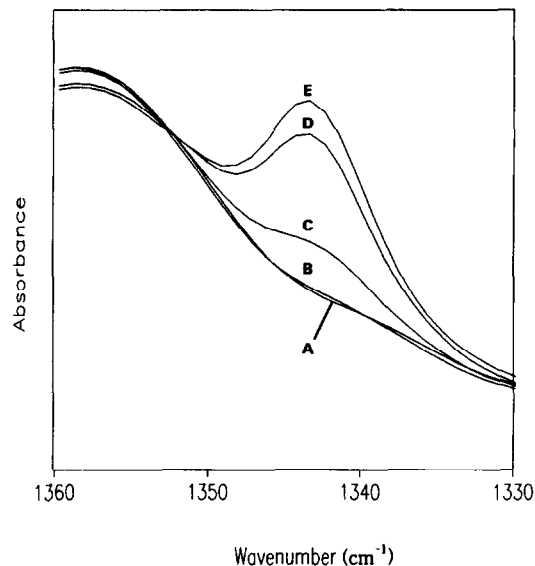


Figure 12 Crystalline bands of PET in PEI/PET blends with the 6/4 composition after annealing at 225°C for (A) 0 min, (B) 10 min, (C) 20 min, (D) 30 min and (E) 60 min

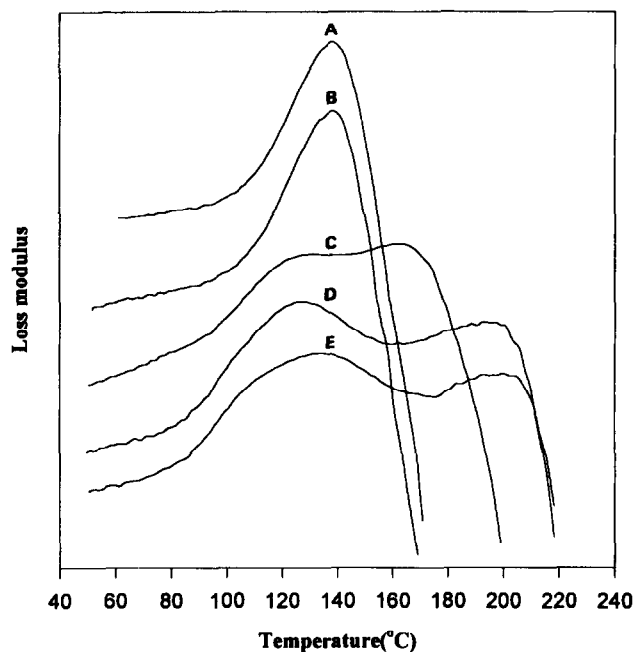


Figure 13 D.m.t.a. thermogram for the change of T_g with annealing time in PEI/PET blends with the 6/4 composition: (A) 0 min, (B) 10 min, (C) 20 min, (D) 30 min and (E) 60 min

with a high PET weight fraction (2/8 and 4/6 PEI/PET blend composition), the C=O peak shift of PEI/PET blends and the PET crystalline peak increase occur almost simultaneously on annealing.

Figure 10 is the d.m.t.a. loss modulus data of the PEI/PET blend with the 4/6 composition at various annealing times. As shown in figure, the T_g of the blend increased as the annealing time was increased because the PET content decreases in the amorphous phase due to the amorphous PET consumption in the crystallization process. These results indicate that the PET crystallization occurs immediately on annealing in the case of PEI/PET blends with a high PET weight fraction.

Figures 11 and 12 show the C=O peak shift and the increase of the crystalline peak of PET in the PEI/PET blend with the 6/4 composition. In case of PEI/PET blends with a low PET weight fraction (6/4 and 8/2 PEI/PET blend composition), the C=O peak shift started more slowly than the C=O peak shift of PEI/PET blends with a high PET weight fraction. As the PET fraction is small in absolute quantity, the total width of the C=O peak shift may become narrower.

However, this slow starting of the C=O peak shift may not be explained by the small quantity of PET. Figure 13 shows d.m.t.a. loss modulus data of the PEI/PET blend with the 6/4 composition at various annealing times. It is an interesting result that two T_g s of the blend appear at an annealing time of 20 min, and that these two T_g s became more apparent as the annealing time increased. This behaviour is contrary to the result from PEI/PET blends with a high PET weight fraction. In addition, it is also noted that the appearance of two T_g s during an annealing time of 10–20 min is accompanied by the start of the C=O peak shift.

From these results, it is concluded that amorphous–amorphous phase separation occurs in the PEI/PET blend with a low PET weight fraction. In the case of the 6/4 composition of the PEI/PET blend, a high T_g due to the large amount of PEI hinders the crystallization of PET before 10 min of annealing. Therefore, the C=O peak shift of the blend or the increase of the crystalline peak of PET is not observed. After this stage, the amorphous phase separates into PET-rich and PEI-rich phases. The formation of a PET-rich phase contributes to the low T_g at 20 min of annealing, and the PEI-rich phase to a high T_g . Eventually, crystallization of PET starts in the PET-rich phase and a shift of the C=O peak of PEI/PET blends is observed. Because crystallization of PET starts as soon as the PET-rich phase is formed, the PET content in the PET-rich region also rapidly decreases. This is the reason for the small decrease of low T_g at 20 min of annealing and the increase of T_g after 20 min of annealing.

CONCLUSIONS

The crystallization behaviour of PET in the PEI/PET blend during annealing was studied using FTi.r. spectroscopy.

FTi.r. spectroscopy could be used as an effective method to investigate PET crystallization behaviour in the PEI/PET blend. The crystallization of PET occurs by annealing at 225°C, and characteristic i.r. bands of crystalline PET increase obviously as a function of annealing time. Also, due to the restriction of molecular vibration in the PET crystal region, the C=O stretching

peak of the PEI/PET blend shifts to low wavenumber on annealing.

The crystallization mechanism of PET on annealing in PEI/PET blends varies according to the composition of the PEI/PET blend. At a high weight fraction of PET (2/8 and 4/6 PEI/PET blend composition), crystallization of PET in PEI/PET blends occurred immediately on annealing. At a low weight fraction of PET (6/4 and 8/2 PEI/PET blend composition), crystallization of PET in the PEI/PET blends is hindered by PEI, and crystallization of PET starts after the PET-rich phase is formed by phase separation of the amorphous phase.

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