Co[poly(ethylene terephthalate-p-oxybenzoate)] and Its Blends with Poly(ethylene terephthalate): Transesterification Reaction and Fractured Surface Morphology

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SYNOPSIS

A series of co[poly(ethylene terephthalate-p-oxybenzoate)] copolyesters, viz., P28, P46, P64, and P82, were synthesized. These copolyesters were blended with poly(ethylene terephthalate) (PET) at the level of 10 wt % at 293°C for different times. The results from proton NMR analysis reveal that a significant amount of the transesterification has been detected in the cases of PET/P28, PET/P46, and PET/P64 blends. The blending time necessary before any transesterification reaction could be detected depends on the composition of copolyester, e.g., a time less than 3 min is needed for both PET/P28 and PET/P46 blends, while a longer time of 8–20 min is needed for the PET/P64 blend. It is concluded that the higher the mol ratio of the POB moiety in the copolyester is the longer the blending time needed to initiate the transesterification. The degree of transesterification is also increased as the duration of melt blending is prolonged. Two-phase morphology was observed by scanning electron microscopy (SEM) micrographs in all the blends. It was observed that the more similar the composition between the copolyester and PET in the blends is the better the miscibility or interfacial adhesion between the two phases. Moreover, the miscibility can be markedly improved by the duration of melt blending. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The chemical structure of co[poly(ethylene terephthalate-p-oxybenzoate)] (POB–PET) consists of the following two moieties:

(1)POB   **(2)PET**
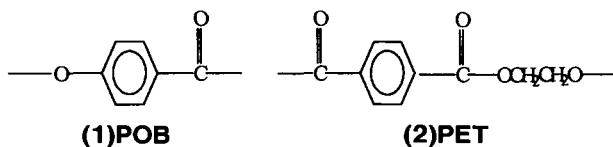
As polyesters readily transesterify near and above their melting points, the interchange reactions commonly occur between these two constituents. In fact, this is confirmed from the blends of normal PET with deuterium-labeled PET detected by small-angle neutron scattering (SANS).[1-5] It has been found also by many investigators that the transesterification in the polyester blends can play an important role in their miscibility and consequent properties. For instance, this reaction has been found to take place in many blends with PET such as PET/PBT,[6] PET/PC,[7,8] and PET/polyacrylate (PAr)[9,10] and in the blends with POB–PET copolyester such as PBT/POB–PET[11] and PC/POB–PET[12,13] systems as detected mainly by many techniques, such as differential scanning calorimetry (DSC), infrared spectroscopy (IR),[6,14,15] and nuclear magenetic resonance (NMR) analyses.[9,15,16] Among them, NMR is an powerful tool for the analysis of polymer miscibility and chemical change within polyester pairs.

Kotliar[17] reviewed the interchange reaction involving the condensation polymers, polyesters, and

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polyamides. The transesterification mechanism can be written as

$$\begin{array}{c} \text{——O——CO——} \\ + \\ \text{——CO——O——} \end{array} \rightleftharpoons \begin{array}{c} \text{——O} \\ | \\ \text{——CO} \end{array} + \begin{array}{c} \text{CO} \\ | \\ \text{O} \end{array}$$

The transesterification, therefore, can be readily facilitated with the following possibilities: It can open a new route to miscibility and preparation of a novel copolymer with a high degree of randomness and it can lead to a more uniform polymer by minimizing molecular weight fluctuations in a melt during polymerization and processing. It is well known that the transreaction in the polymer blends depends strongly on their initial compatibility and blending conditions. This includes temperature, duration of mixing, preparation method, viscosity match, and presence of catalysts[18] as well as inhibitors.[19-21] No significant transesterification has been detected in the PET/POB–PET blend within 1.5 min blending time as measured by DSC.[22]

The rate of PET crystallization analyzed by DSC can be significantly accelerated by the addition of 10 wt % POB–PET copolyesters as reported in our previous articles.[23,24] The purpose of this work was to detect the transesterification that occurred in this PET/POB–PET blend during blending and to determine the relationship between transesterification and the miscibility of the blends.

EXPERIMENTAL

Materials

Four types of co[poly(ethylene terephthalate-p-oxybenzoate)] copolyester (POB–PET), designated as P28, P46, P64, and P82, were synthesized according to the procedure reported in our previous articles.[25] These copolyesters contain different POB to PET mol ratios, e.g., P28 at 20–80, P46 at 40–60, P64 at 60–40, and P82 at 80–20 mol ratios. The PET resin with an intrinsic viscosity of 0.62 was supplied by the Far East Texile Co. (Taiwan). The intrinsic viscosity (I.V.) value was measured at 30°C in phenol/tetrachloroethane (60/40 by weight).

Blending Method

The PET/POB–PET blends in a 90 : 10 weight ratio were prepared using the following procedure: PET and copolyesters were dried at 105°C for 48 h in a vacuum oven prior to blending. The blends were made by melt compounding in a Brabender plasticorder in a batch-type roller mixer. The compounding was done at 293°C for different times at a rotor speed of 30 rpm. After blending, the sample was taken from the bowl and immediately thrown into liquid nitrogen to obtain the quenched samples.

NMR Spectra

For the NMR spectra, a 5–10 wt % solution of the blend in deuteriated trifluoroacetic acid (TFA) was prepared. The spectra were then taken within several hours of the sample dissolution and with tetramethylsilane (TMS) as the internal standard. NMR for the PET/P82 blend is not taken because the

Table I Codes of Copolyesters and Blends

(a) Codes of Copolyester Synthesized in Different Compositions

Copolyester (POB/PET)	Composition (Mol Ratio)	Code
POB/PET	0/100	PET
POB/PET	20/80	P28
POB/PET	40/60	P46
POB/PET	60/40	P64
POB/PET	80/20	P82

(b) Codes of Blends with a Blending Ratio of 90/10 (by Weight) in Different Blending Times

Blend	Blending Times (Min)	Code
PET/P28	3	BP2803
PET/P28	8	BP2808
PET/P28	20	BP2820
PET/P28	30	BP2830
PET/P46	3	BP4603
PET/P46	8	BP4608
PET/P46	20	BP4620
PET/P46	30	BP4630
PET/P64	3	BP6403
PET/P64	8	BP6408
PET/P64	20	BP6420
PET/P64	30	BP6430
PET/P82	3	BP8203
PET/P82	8	BP8208
PET/P82	20	BP8220
PET/P82	30	BP8230

P82 sample does not dissolve in TFA. The spectra were obtained by a Varian Model Unity-300 NMR spectrometer operating at 300 MHz for observing protons.

Scanning Electron Microscopy (SEM)

The SEM studies were carried out on the fractured surface of specimens prepared by snapping the material after cooling in liquid nitrogen. The specimens were sputter-coated with gold for the enhanced conductivity and observed by a Hitachi S-2500 scanning electron microscope.

Code

The codes for all samples examined in this study are listed as Tables I(a) and (b).

RESULTS AND DISCUSSION

NMR Study

Figure 1 illustrates the 300 MHz proton NMR spectrum of P46 showing the assignments for the resonances. The fraction of the POB repeat units that are bonded to a PET unit or to another POB unit can be determined from the spectra.[26,27] The peaks due to the proton of the POB–POB dyad and the POB–PET dyad are located at 7.5 and 7.4 ppm, respectively. The sharp signal at 8.2 ppm is due to the proton of the terephthalate group, while the spectrum of the methylene proton appears at 4.9 ppm.

If transesterification occurs, the ratio of POB–PET to POB–POB dyads of a blend compared with that of the virgin copolyester would be increased. The values of the ratios of dyads are given in Table II. It is seen that there is a trend of increasing of the ratios in both of PET/P28 and PET/P46
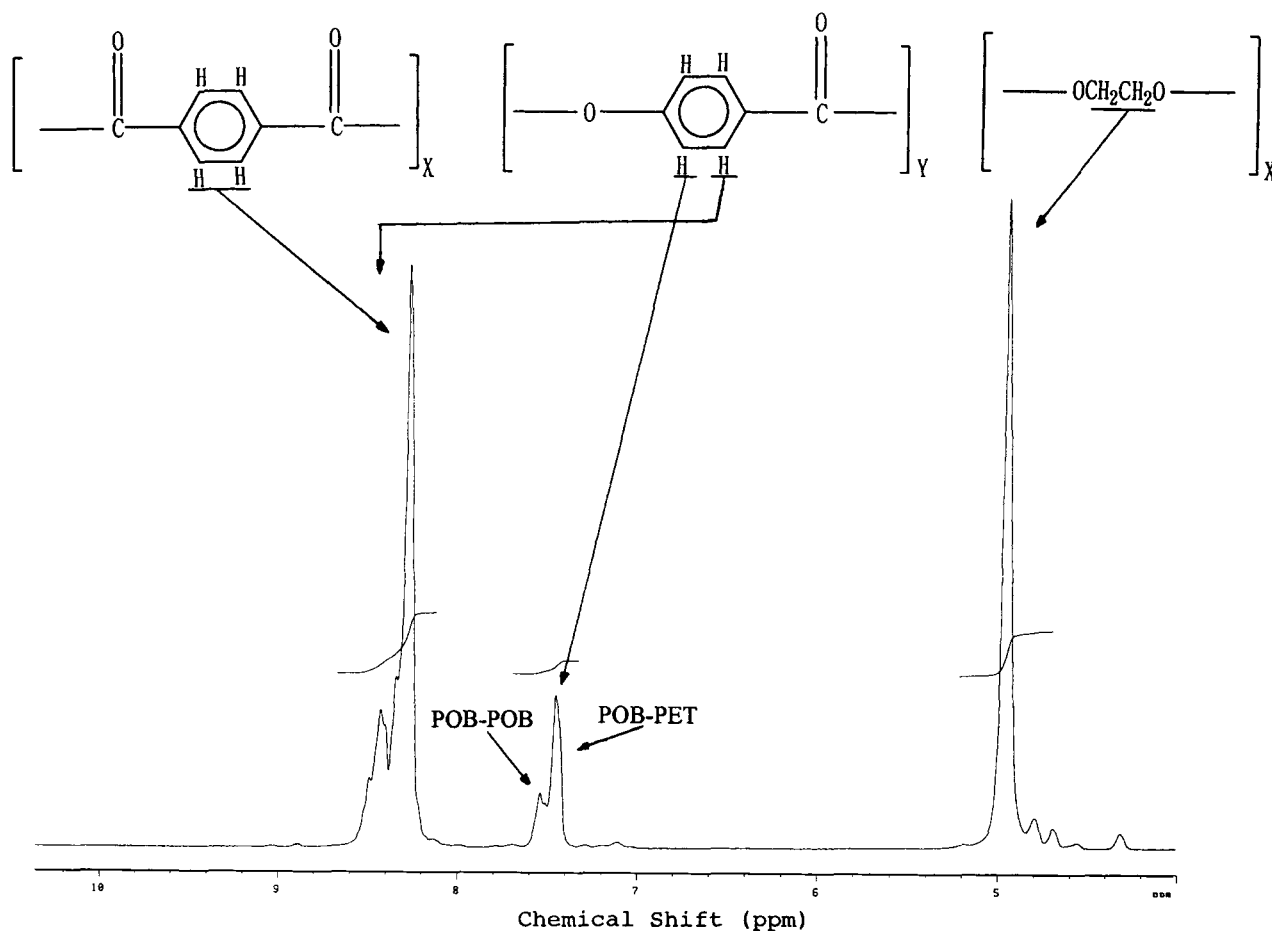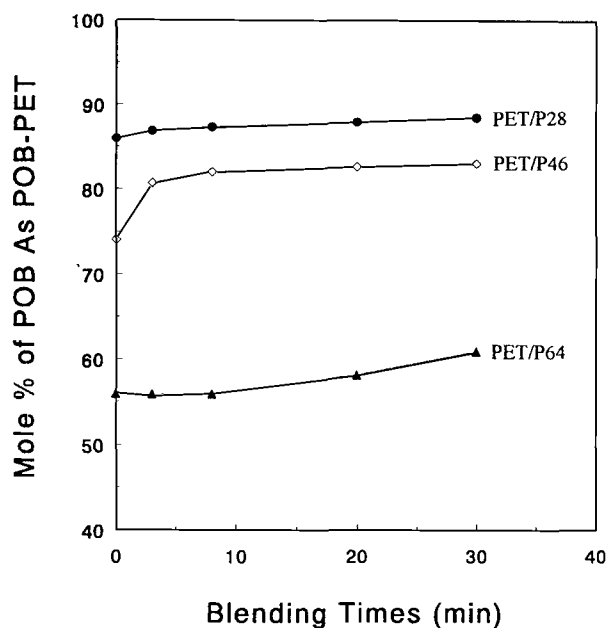

Figure 1 Proton NMR spectrum at 300 MHz with the assignments of the absorptions for P46 dissolved in trifluoroacetic acid.

blends. These results reveal that the transesterification already occurs within 3 min of blending and the degree of transesterification increases with the blending time in these two blending systems. It is worthy to note that the ratio of POB–PET to POB–POB dyads remains constant at 1.27 for both the PET/P64 blend at 3 min blending time (i.e., BP6403) and the PET/P64 blend at 8 min blending time (i.e., BP6408) and then increases to 1.39 for the PET/P64 blend at 20 min blending time (i.e., BP6420) and to 1.56 for the PET/P64 blend at 30 min blending time (i.e., BP6430), respectively. These results reveal that the transesterification can take place only after 8–20 min blending in the PET/P64 blend. The blending time necessary for the transesterification seems to increase with the mol % of POB in the copolyesters. This fact might be attributed to the increased stiffness of the polymer backbone chains due to the increased POB composition in the polymer structure. Figure 2 shows the mol % of POB units bonded to the PET unit as a function of blending time for PET/P28, PET/P46, and PET/P64 blends. The slope of the line between 0 and 3 min can be regarded as the initial rate of transesterification. The values of the slopes are 2.97×10^{-1}, 2.22, and 0 [%/min] for the PET/P28, PET/P46 and PET/P64 blends, respectively. From these data, the initial transesterification rate of the PET/P46 blend seems to be faster than that
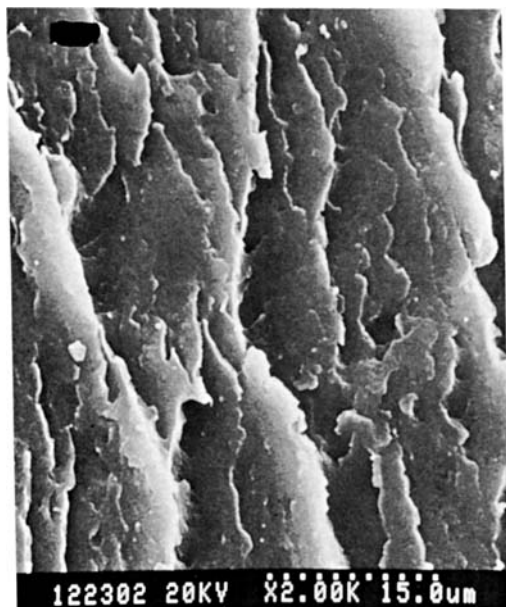

Figure 2 Mol % of POB connected to PET (i.e., POB–PET dyad) after different blending times in the PET/P28, PET/P46, and PET/P64 blends.

of the PET/P28 blend within 3 min of blending. On the contrary, no detectable transesterification occurs in the PET/P64 blend within 3 min of blending. The values of the slope at the period between 3 and 30 min are 5.93×10^{-2} and 8.52×10^{-2} [%/min] for the PET/P28 and PET/P46 blends, respectively. It is seen that the transesterification rate of the PET/P46 blend is also larger than that of the PET/P28 blend during this period. The fraction of POB units bonded to a PET or to another POB unit for the PET/P82 blend was not measured because of its insolubility to TFA. So, the amount of transesterification of the PET/P82 blend remains undetermined. However, it is reasonable to assume that a very small amount of transesterification may take place for the PET/P82 blend during the measured period because of its large POB moiety content in its composition.

Fracture Morphology

Figure 3 is an SEM micrograph of the fracture surface of PET showing a smooth but not a fibrous structure. The SEM micrographs of the PET/P28 blends are presented in Figure 4. The P28 components are observed as dispersed phases in dark circles as seen in Figure 4(a). These spots of dispersed phases are around 5–10 μm in size. After 30 min blending, the spots of P28 are no longer exhibited

**Table II Dyad Ratio and Mole % of POB Connected to PET in the Samples After Different Blending Times**

Sample	POB–PET / POB–POB	Mol % of POB as POB–PET
P28	6.14	85.99
BP2803	6.62	86.88
BP2808	6.91	87.36
BP2820	7.30	87.95
BP2830	7.68	88.48
P46	2.85	74.03
BP4603	4.18	80.69
BP4608	4.56	82.01
BP4620	4.74	82.58
BP4630	4.88	82.99
P64	1.27	55.95
BP6403	1.27	55.95
BP6408	1.27	55.95
BP6420	1.39	58.16
BP6430	1.56	60.94

Figure 3   SEM micrograph of fracture surface of PET (×2000).

but disintegrate to dark striped shapes [see Fig. 4(b)]. Moreover, the phase boundaries between the matrix PET and dispersed P28 phases as shown in Figure 4(a) and (b) indicate a good interfacial

adhesion, because of the good miscibility between PET and P28 due to the relatively similar compositions.

The SEM micrographs of the fractured surface of the PET/P46 blends after 3 and 30 min blending are shown in Figure 5(a) and (b), respectively. Fine droplet dispersions of P46 are embedded into the PET matrix and are seldom "loose" from the matrix during the fracture. These micrographs illustrate the good adhesion between these two phases. After 30 min blending, the droplets become finer than those observed in Figure 5(a) after 3 min blending. This fact reveals that the transesterification reaction during the melt blending is a possible approach to interfacial adhesion and miscibility as evidenced by the previous NMR analysis. In fact, Wang et al.[28] reported that the miscibility of PET/PC blends was found to be markedly improved by the addition of as little as 2% of the copolyester due to the transesterification as detected by FTIR and NMR analyses.

The SEM micrographs of the fractured surface of the PET/P64 blend are shown in Figure 6. In this case, the shapes of the dispersed droplets after 3 min blending are in spherical or elliptical geometries with the domain sizes ranging from 1 to ∼ 4 μm in diameter [see Fig. 6(a)]. When increasing the blending time from 3 to 20 min, the dispersed droplets become smaller and more uniform in size
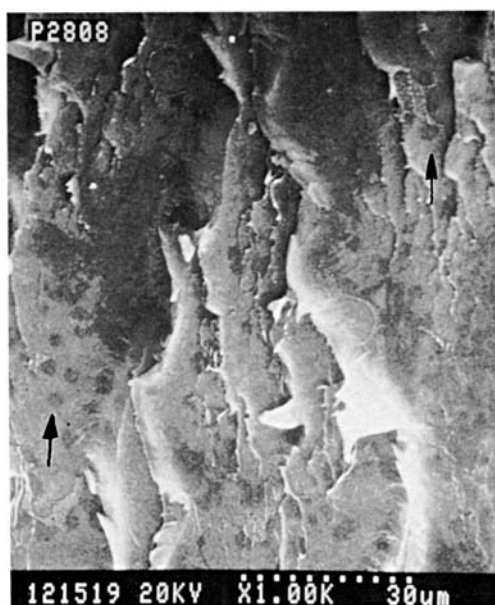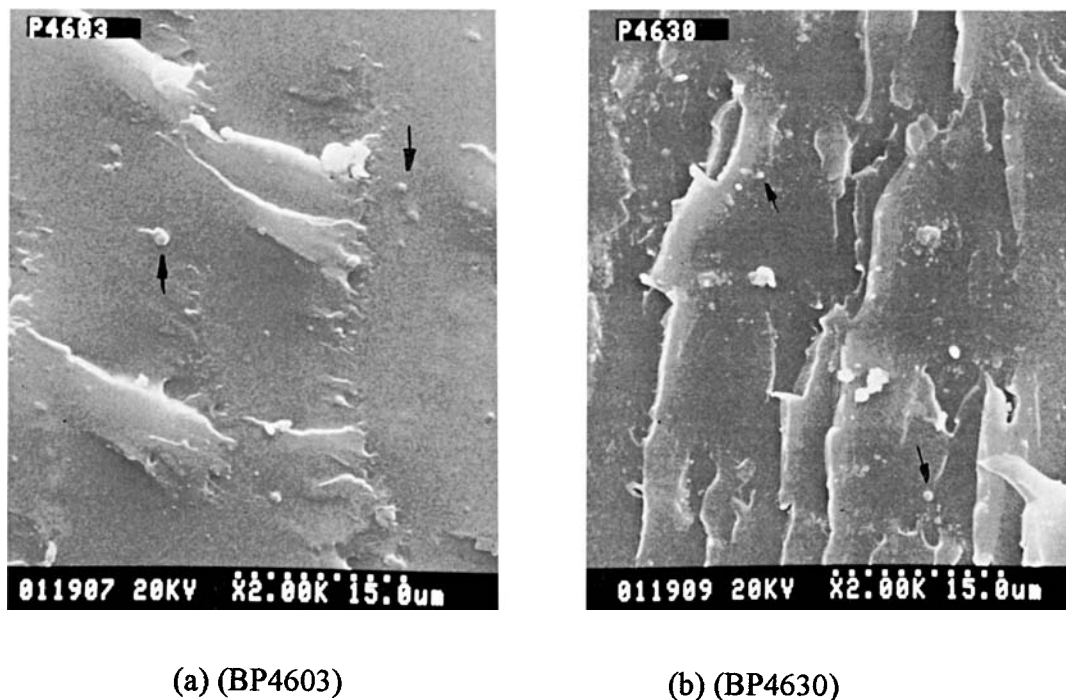
(a) (BP2808)   (b) (BP2830)

Figure 4   SEM micrographs of fracture surface of PET/P28 blend (×1000) after (a) 8 min and (b) 30 min blending.

(a) (BP4603)   (b) (BP4630)

Figure 5   SEM micrographs of fracture surface of PET/P46 blend (×2000) after (a) 3 min and (b) 30 min blending.

by reducing their diameters to about 0.5 μm on average. All the micrographs of the fracture surface of PET/P64 blends exhibit sharp and distinct phase boundaries, as well as many voids resulting from the P64 domains that were detached during the fracture. The loose P64 droplets lying on the fracture surface can also be observed. These observations suggest poor interfacial adhesion between the two phases and the pulling out of P64 droplets after fracture in the case of the PET/P64 blend. These results reveal that the interfacial adhesion between PET and P64 is poorer than that between PET and P46.
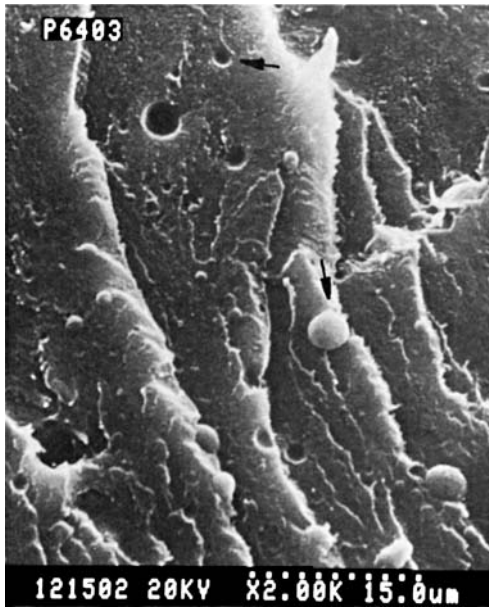
The SEM micrographs of the fractured surface of the PET/P82 blend are shown in Figure 7. These morphologies are similar to those of the PET/P64 blend, but exhibit a little difference between them. First, almost all of the dispersed P82 droplets are loose-lying on the surface even after 30 min blending [see Fig. 7(d)]. Second, the dispersed P82 droplets still vary widely from 0.5 to 5 μm in diameter even after 30 min blending. These results indicate that the texture of the dispersed P82 phase can not be homogenized even by increasing blending time and exhibits a very poor interfacial adhesion between PET and P82. We predict that P82 is completely incompatible with PET and that the transesterifi-

cation, if it occurred, does not take place to an appreciable extent.

It is concluded that all the PET/P28, PET/P46, PET/P64, and PET/P82 blends consist of two phases. The microstructure are dependent on the composition of the copolyester and blending time. The compatibility and interfacial adhesion between PET and the copolyester seem to decrease with increasing the POB mol % in the copolyester. The textures of the dispersed phase can be homogenized, however, by increasing the blending time, especially in the cases of PET/P28 and PET/P46 blends.

CONCLUSIONS

From NMR analysis and SEM micrograph observations on the PET/POB–PET blends, some of the salient conclusions of this study are the following: First, the more POB content in the copolyester backbone chain, the longer time needed to initiate the transesterification. Second, the more similar the composition between PET and the copolyester, better compatibility and interfacial adhesion are indicated in the blending systems. Third, the texture of
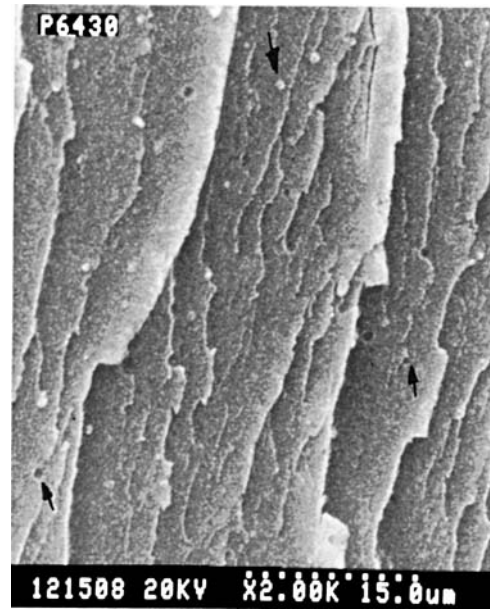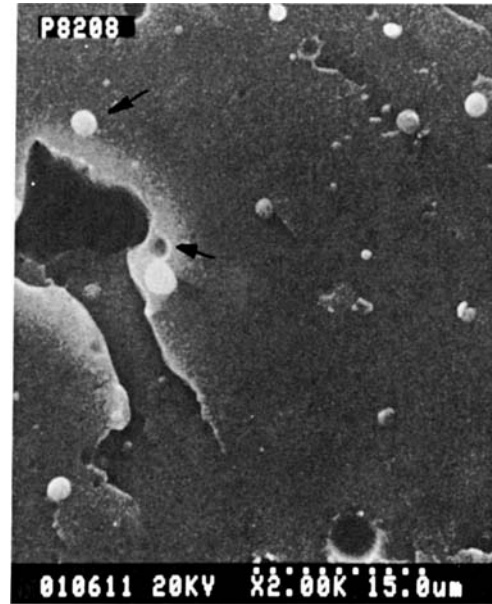
(a) (BP6403)
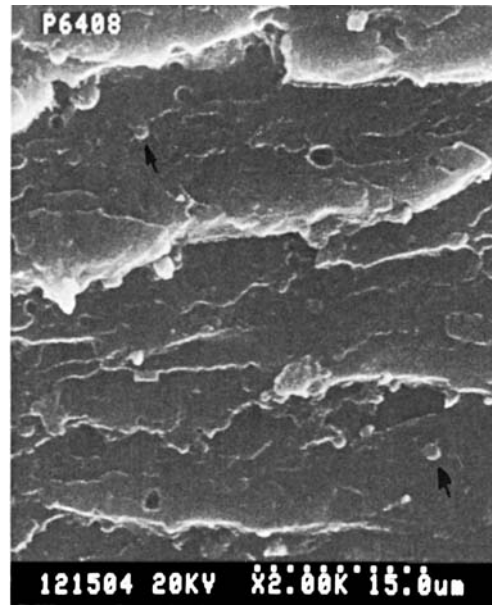
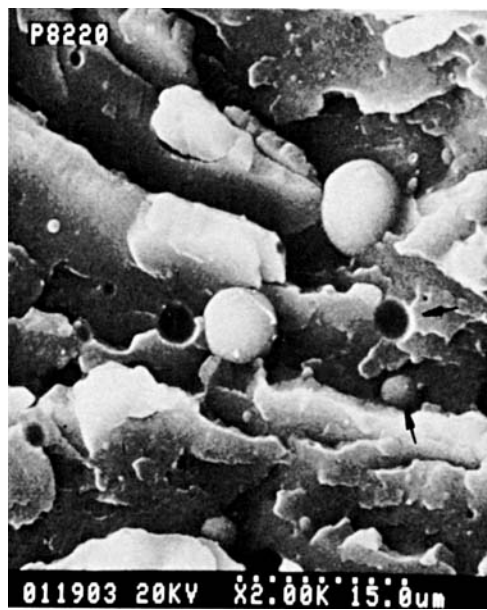(b) (BP6408)
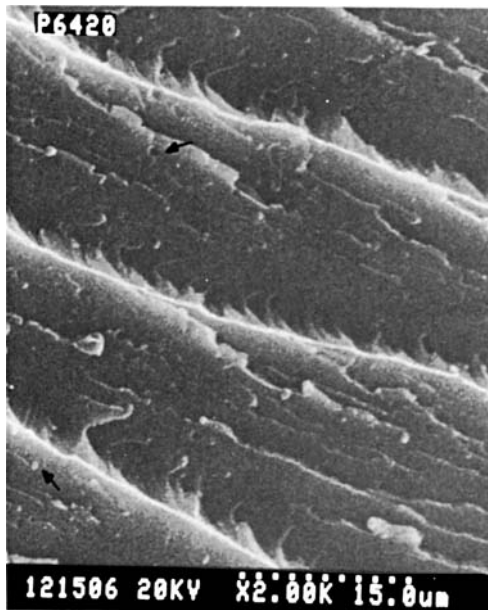
(c) (BP6420)

(d) (BP6430)

Figure 6   SEM micrographs of fracture surface of PET/P64 blend (×2000) after (a) 3 min, (b) 8 min, (c) 20 min, and (d) 30 min blending.
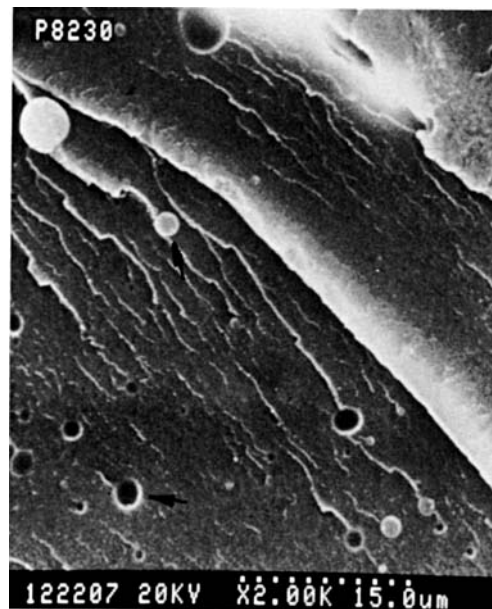
(a) (BP8203)

(b) (BP8208)

(c) (BP8220)

(d) (BP8230)

Figure 7 SEM micrographs of fracture surface of PET/P82 blend (×2000) after (a) 3 min, (b) 8 min, (c) 20 min, and (d) 30 min blending.

the two-phase morphology of the blends is dependent on composition of the copolyester and blending time. It is believed that the miscibility of the PET/POB–PET blend can be improved owing to the transesterification.

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