

# A Study on Blends of Liquid Crystalline Copolyesters with Polycarbonate. I. Compatibility by Transesterification

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## SYNOPSIS

Blends of poly(bisphenol-A carbonate) (PC) and synthesized liquid crystalline poly(oxybenzoate-co-ethylene terephthalate 40/60) (P46) were prepared through melt-mixing in a Brabender mixer. The miscibility of the blends at different compositions and blending time was investigated with differential scanning calorimetry. The corresponding morphology of the blends was analyzed with scanning electron microscopy. It was found that for blends containing more than 20% P46 and mixed at 250°C or above the transesterification between PC and P46 took place. This transesterification was confirmed at a blend containing 40% P46 by nuclear magnetic resonance spectroscopy. The transesterification happened first between PC and the ester in the poly(ethylene terephthalate) (PET) block and then between PC and the ester in the polyoxybenzoate (POB) block. At 260°C and after 60 min' blending, the blend containing 30% P46 became an almost compatible system for appearing of a single glass transition temperature. This is also verified by the disappearing of P46 droplets in the PC matrix in the micrographs' observation. After 60 min' of blending, the compatibility of the system can be greatly improved even for the blend containing 40% P46 mixed at 260°C by the micrograph's observation. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Blending of polymers has been a major research focus in polymer science. In particular, polyester blends have been studied extensively because of industrial applications and academic interests. The interaction between components was the key factor in determining the miscibility of the blends. Coleman et al. found that the greater the intermolecular hydrogen bonding interaction the greater is the probability of miscibility.<sup>1</sup> Barlow and co-workers carried out a study on the miscibility of bisphenol-A polycarbonate (PC) in polyester blends.<sup>2-5</sup> They found that at an optimum density of ester groups in the polyester chain a maximum interaction between components is achieved. Ester exchange (transesterification) took place for polyester blends near or above their melting points. Kotliar<sup>6</sup> reviewed and discussed the interchange reactions, including

intermolecular alcoholysis, intermolecular acidolysis, and transesterification. Porter and Wang provided an overview on the compatibility and transesterification of various polymer blends.<sup>7</sup>

Blends of liquid crystalline polymers (LCP) with engineering plastics have become recently a major research effort. The motivation was to utilize their characteristics without incurring the high cost. Kiss<sup>8</sup> and Weiss et al.<sup>9</sup> discussed the major advantages of these LCP blends. The reduction of the matrix polymer viscosity and the reinforcement of the matrix polymer are the two benefits. However, thermodynamically, the enthalpy of mixing of LCPs with a flexible coil polymer was mostly positive, i.e., endothermic, and the entropy of mixing was small and positive. The free energy of mixing obtained was therefore mostly positive.<sup>7</sup> Consequently, phase separation occurred for the LCP blends during processing where high temperature and a high-stress environment existed. If there is strong interaction taking place between the LCP and the matrix polymer, a more compatible LCP blend will result. Since transesterification can happen in a polyester blend,

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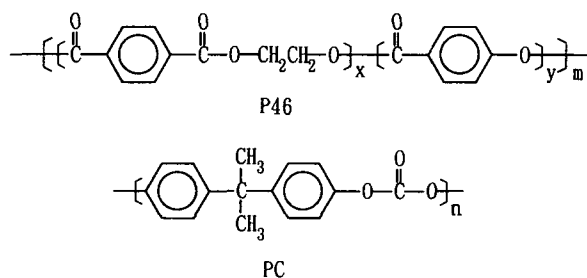
it can be utilized to enhance the miscibility of the liquid crystalline polyester blends.

One issue noted in the Porter and Wang's article is that as transesterification continues blends convert first to block copolymers and, finally, to random copolymers, whether at chain ends or at mid-chain. Therefore, to have some transesterification between the LCP and the matrix polymers without losing the liquid crystalline characteristics becomes very important. To control the extent of the transesterification, one has to understand the kinetics of the transesterification.

This article is concerned with the compatibility of the blends resulting from the transesterification between PC and liquid crystalline polyesters. The thermal properties of the blends were analyzed with differential scanning calorimetry. The corresponding blends' morphology was observed with scanning electron microscopy. A nuclear magnetic resonance spectroscopy study was also carried out to verify the transesterification.

## MATERIALS

Liquid crystalline poly(oxybenzoate-*co*-ethylene terephthalate) (POB-PET) was synthesized by adding *p*-acetoxybenzoic acid monomers to poly(ethylene terephthalate) (PET) following the method described in the literature.<sup>10</sup> The intrinsic viscosity of the PET used in the synthesis was 0.6 dL/g. The *p*-acetoxybenzoic acid monomer was purchased from Shang Hu Corp. The compositions of POB-PET were 40/60, and it was termed P46. P46 exhibited birefringence when it was heated up to 300°C and then cooled down. Polycarbonate (PC) was obtained from the Shin Kwang Corp. The weight-average molecular weight of the PC was 17,000. The chemical structures of P46 and PC are shown in Figure 1.



**Figure 1** The chemical structure of polycarbonate (PC) and poly(oxybenzoate-*co*-ethylene terephthalate) (40/60) (P46).

## EXPERIMENTAL

### Mixing

The powder of the liquid crystalline P46 and PC pellets was dried at 110°C under vacuum for 8 h prior to the mixing. The mixtures of P46 and PC were put into a Brabender mixer. The speed of the roller blade was 50 rpm. The blends containing 10, 20, 30, and 40% P46 were prepared. Three blending temperatures were chosen: 240, 250, and 260°C.

### DSC

The thermal analysis of the blends was carried out with a DuPont 2000 differential scanning calorimeter (DSC). The samples were heated from 30–220°C at a heating rate of 20°C per min and maintained at 220°C for 1 min. Then, the samples were air-cooled down to 30°C. The samples were heated again from 30 to 300°C at the same heating rate. The DSC curves of the samples were taken the second time the samples were heated up at the heating rate of 20°C per min.

### NMR

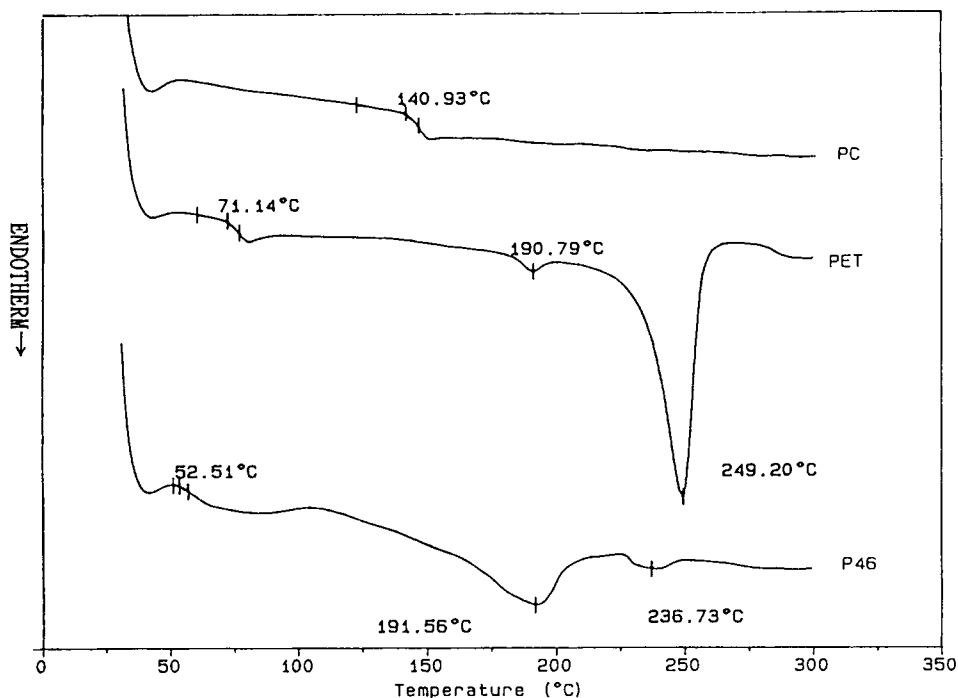
The blends were dissolved in deuterated chloroform for 4 h; then, the undissolved particles were filtered with a syringe filter. Tetramethylsilane was added to the solution as an internal reference standard, and the liquid mixture was put in a nuclear magnetic resonance (NMR) tube. A Varian Fourier Transformed NMR (unity-300) was used for this study.

### SEM

The blends were put in the DSC and heated up at a heating rate of 40°C per min to 220°C, staying at 220°C for 1 min, and air-cooled to room temperature. The samples were taken out of the DSC and quenched in liquid nitrogen. Then, the samples were fractured and coated with 10 nm-thick gold for scanning electron microscopy (SEM) study.

## RESULTS AND DISCUSSION

The DSC curves of PC, PET (used for synthesis), and P46 are shown in Figure 2. In Figure 2, the glass transition temperatures of PC and P46 are 140.93 and 52.51°C, respectively. There are two melting peaks for P46. The one at 191.56°C represents the diluted melting point of the POB block in P46. The

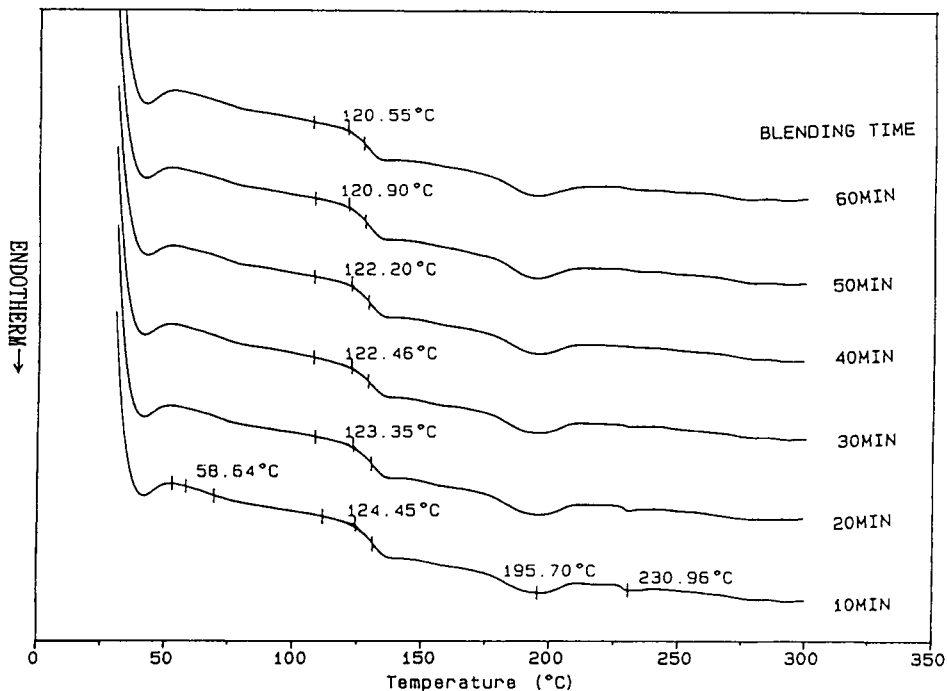


**Figure 2** The differential scanning calorimetry curve of PC, PET, and P46 at a heating rate of 20°C/min.

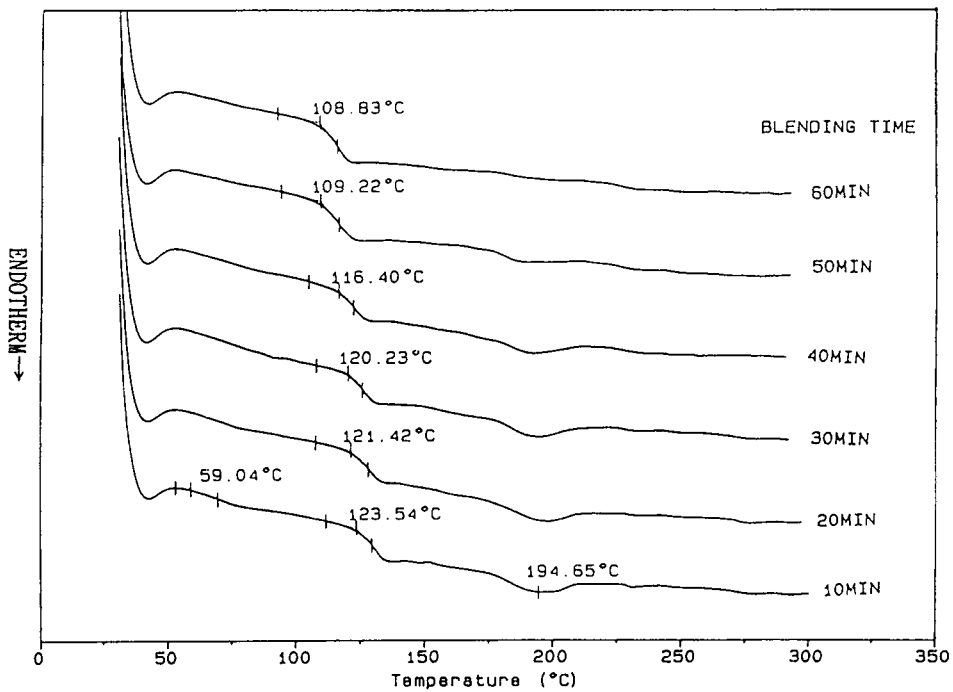
other one, at 236.73°C, is the melting point of the PET block in P46. Therefore, P46 synthesized in our laboratory should be a block copolymer. The DSC curves of the blend containing 30% P46 at different blending times are shown in Figure 3. At 240°C, the melting peak of the PET block in P46 disappeared in a 40 min blending time, whereas the melting peak of the POB block did not change even after a 60 min blending time. The glass transition temperatures ( $T_g$ ) of P46 and PC existed for all times. However, the  $T_g$  of PC decreased with the blending time. This indicated that at 240°C and 60 min, PC and P46 are still incompatible, and the decrease in the  $T_g$  of PC could possibly be caused by the plasticizing effect of P46 on PC.<sup>11</sup> For the blend of the same composition at a higher temperature, 260°C, the DSC curves are shown in Figure 4. In Figure 4, the melting peak of the PET block disappeared in 30 min of blending, and after 60 min of blending, the melting peak of the POB block also disappeared. In the same figure, after the first 10 min of blending, the two  $T_g$ 's, 59.04 and 123.54°C, are still quite distinctive and far apart. As the blending time increased, the two  $T_g$ 's shifted toward each other, and after 60 min of blending, only one  $T_g$  appeared at 108.83°C.

Based upon the above results, there are two points that can be deduced. First, the reaction between P46

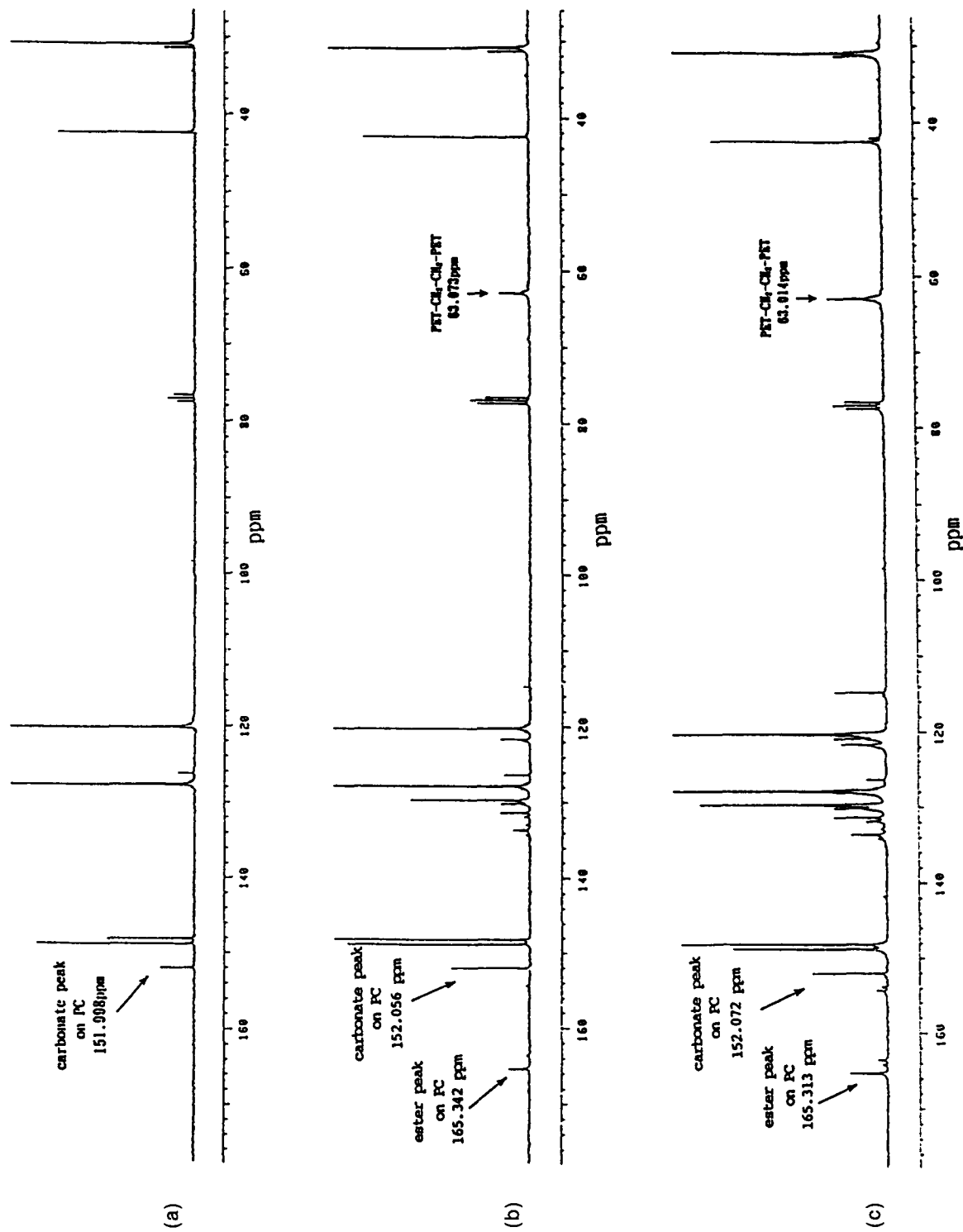
and PC started from the PET block and PC and then continued to the POB block and PC. Second, the blend containing 30% P46 became a compatible system after 60 min of blending at 260°C. Kosfeld et al.<sup>12</sup> carried out solution casting of the P46 and PC mixture and annealed the sample at 270°C for 60 min. He confirmed that there was ester exchange between P46 and PC with the <sup>13</sup>C-NMR technique. For this study, a blend consisting of 40% P46 was measured with the <sup>13</sup>C-NMR technique. The NMR results are shown in Figure 5(a)–(c). In Figure 5(a), the NMR spectroscopy of PC was used to establish a base-line. Since deuterated chloroform dissolved only PC in the blend, the NMR data indicated the chemical structure change of PC during the blending. In Figure 5(b), a blend of a composition of 40% P46 that experienced 10 min of blending at 260°C showed two major new peaks. The first one is at 165.342 ppm, and it is the ester peak. The second one is at 63.072 ppm, and it is the ethylene peak from the PET block in P46. This is direct evidence that the ester group from the PET block in P46 was attached to PC molecules. As the blending time increases to 60 min, the two peaks grew much bigger simultaneously. This indicated that the amount of ester exchange increased with time. Therefore, the ester exchange between P46 and PC at this composition and in this condition has been confirmed.



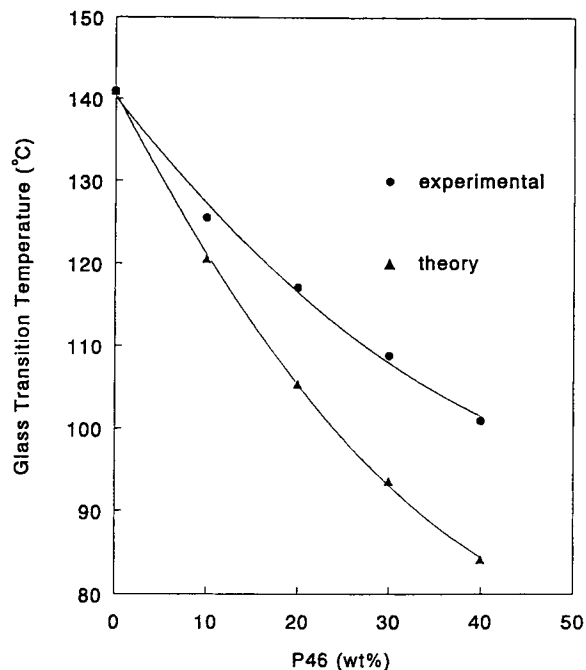
**Figure 3** The differential scanning calorimetry curves of the blend containing 30% P46 after being mixed for different times at 240°C.



**Figure 4** The differential scanning calorimetry curves of the blend containing 30% P46 after being mixed for different times at 260°C.



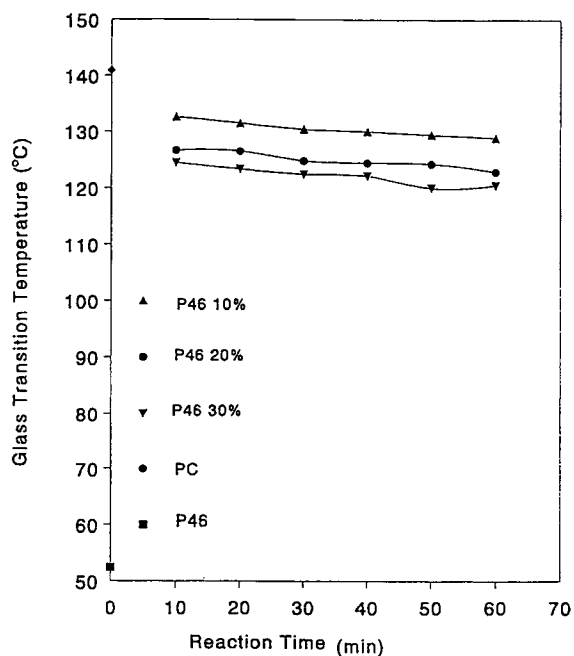
**Figure 5** (a) <sup>13</sup>C-NMR spectroscopy of PC. (b) <sup>13</sup>C-NMR spectroscopy of the blend containing 40% P46 mixed at 260°C for 10 min extracted with deuterated chloroform. (c) <sup>13</sup>C-NMR spectroscopy of the blend containing 40% P46 mixed at 260°C for 60 min extracted with deuterated chloroform.



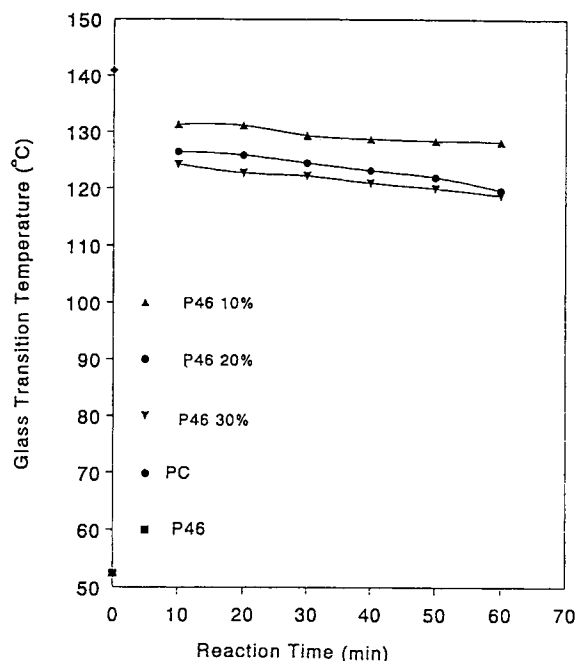
**Figure 6** The glass transition temperatures of different P46 compositions in the blends of P46 and PC predicted by the Fox equation and measured after 60 min of blending time.

The single  $T_g$  of a totally compatible binary polymer blend can be predicted by the Fox equation:

$$1/T_g = W_1/T_{g,1} + W_2/T_{g,2} \quad (1)$$



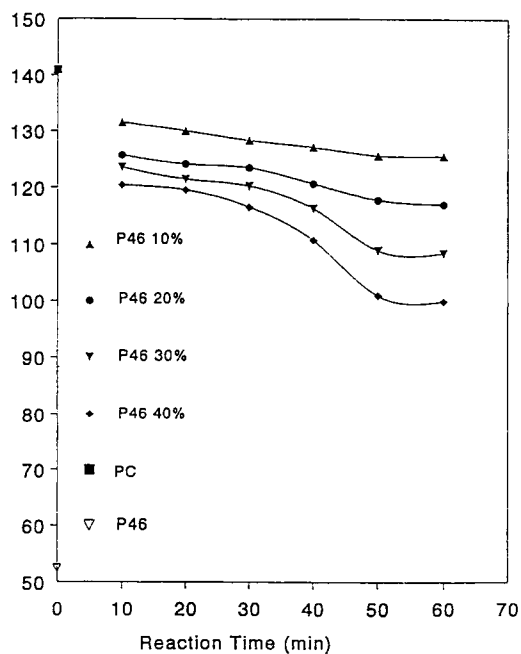
**Figure 7** The glass transition temperatures of the P46/PC blends mixed at 240°C for different times.



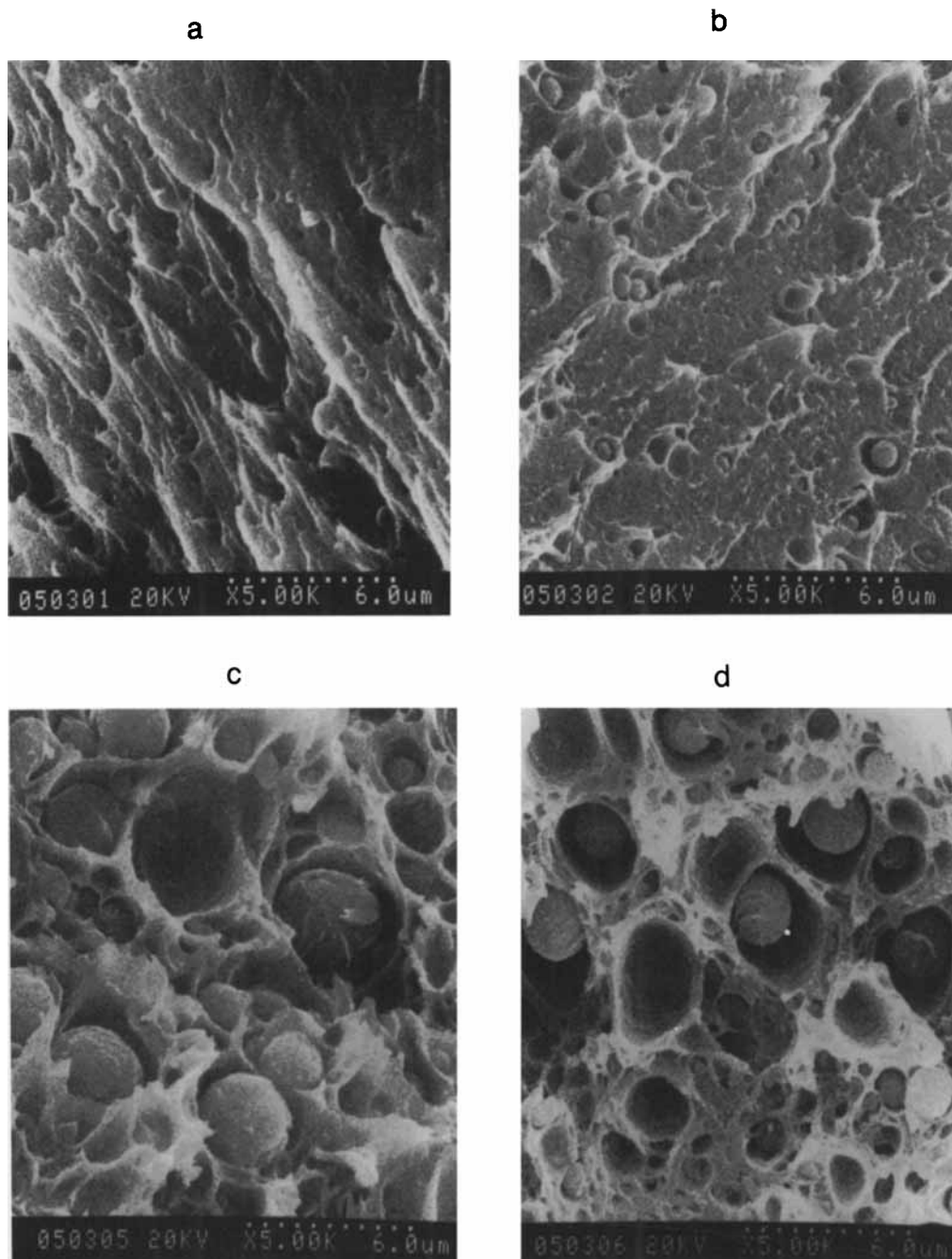
**Figure 8** The glass transition temperatures of the P46/PC blends mixed at 250°C for different times.

In eq. (1),  $W_1$  and  $W_2$  are the weight fractions of polymer 1 and polymer 2, respectively.  $T_{g,1}$  and  $T_{g,2}$  are the glass transition temperatures of polymer 1 and polymer 2, respectively.

In Figure 6, the  $T_g$ 's of the blends of various P46 compositions after 60 min of blending at 260°C were



**Figure 9** The glass transition temperatures of the P46/PC blends mixed at 260°C for different times.

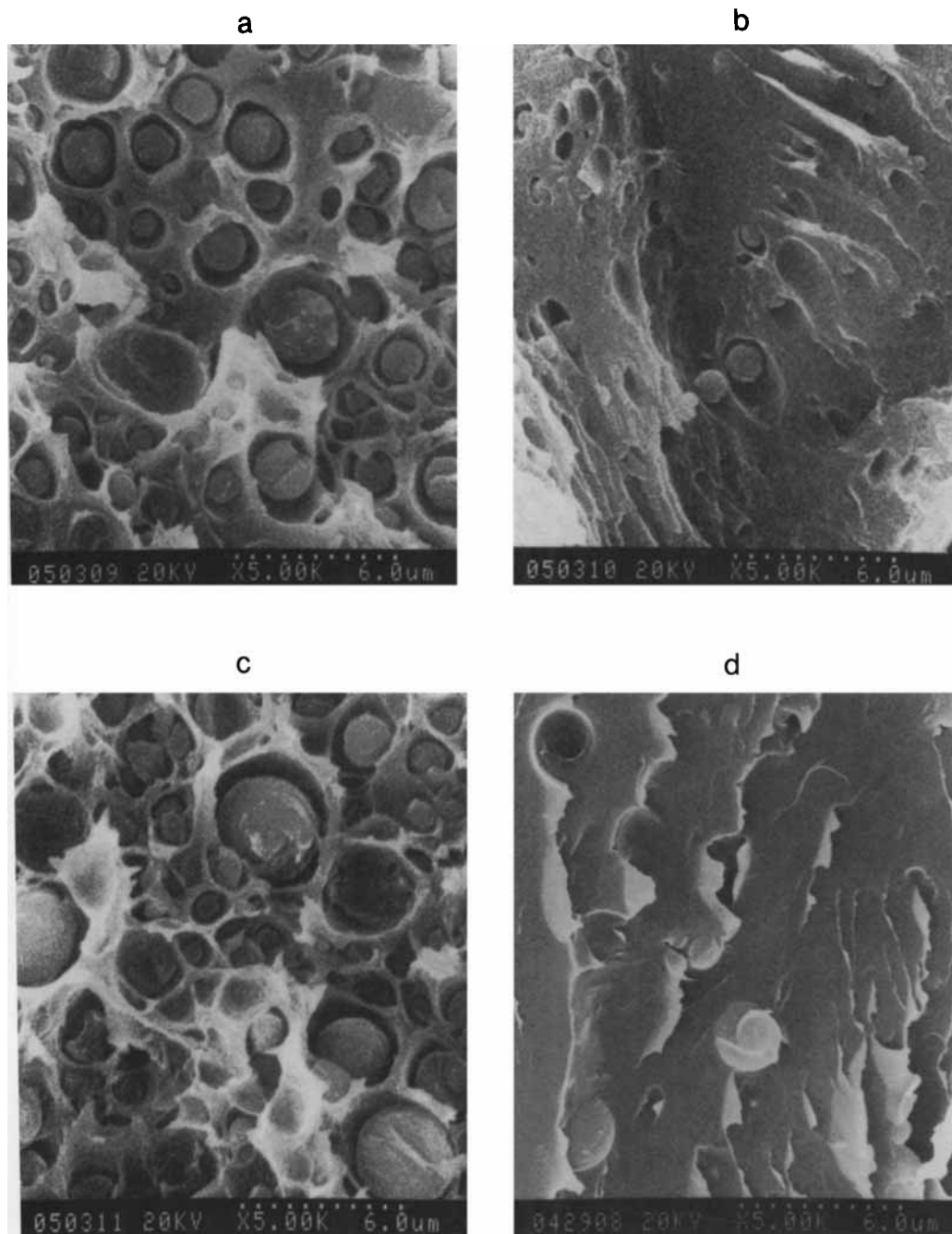


**Figure 10** (a) SEM micrograph of 10% P46 blend mixed at 240°C for 10 min. (b) SEM micrograph of 10% P46 blend mixed at 240°C for 60 min. (c) SEM micrograph of 30% P46 blend mixed at 240°C for 10 min. (d) SEM micrograph of 30% P46 blend mixed at 240°C for 60 min.

plotted. The predicted  $T_g$ 's were always lower than those of the experimental ones. There are two possible causes: The difference between the experimental and calculated ones is due to the fact that after transesterification the molecules were rearranged. The second one was that it took more time for the

transesterification to be completed at higher P46 concentrations. Sixty minutes of blending was not long enough for the ester exchange reaction to be completed in the 30 and 40% P46 cases.

The  $T_g$  of the blends at different blending times is plotted in Figures 7–9. In Figures 7 and 8, at 240



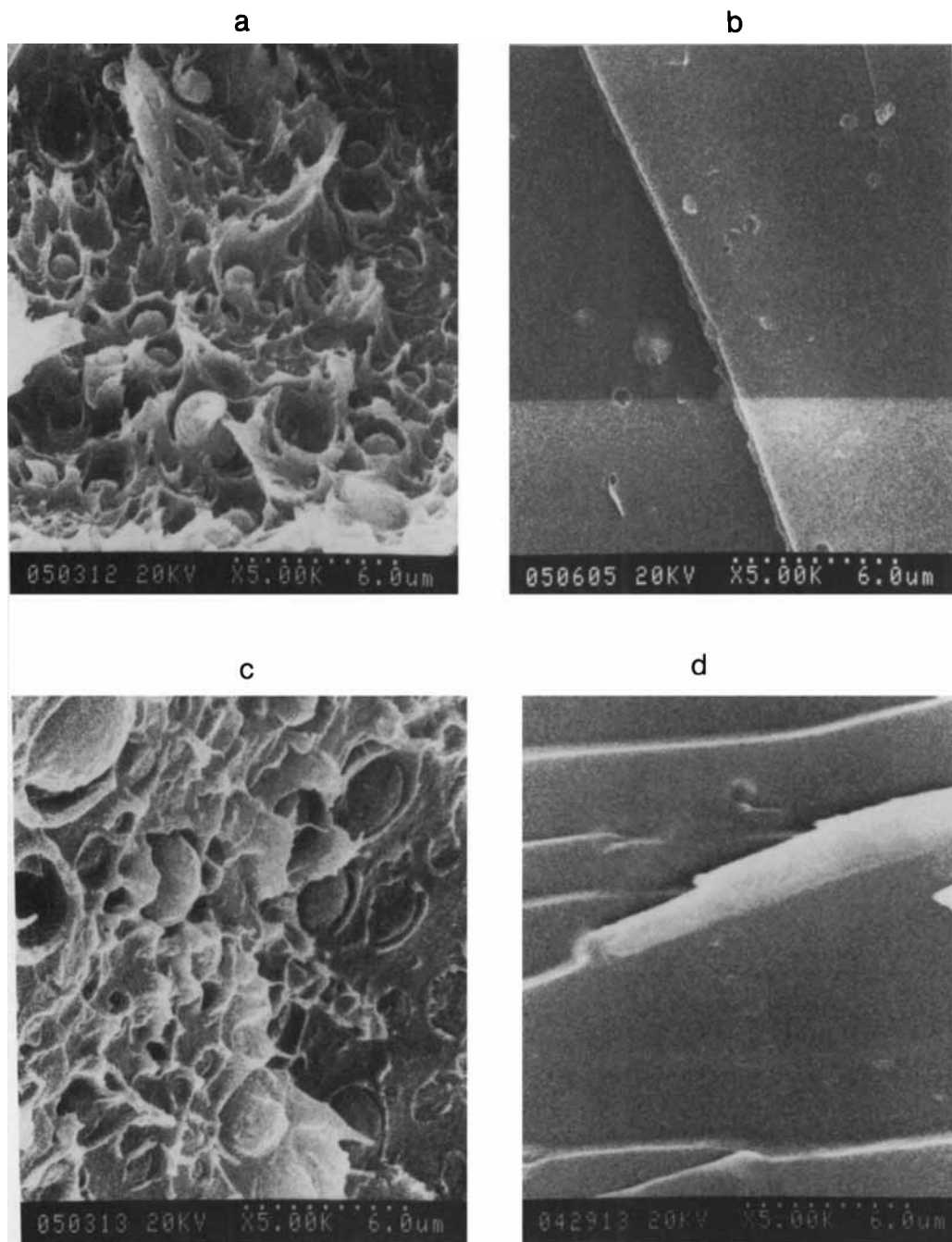
**Figure 11** (a) SEM micrograph of 20% P46 blend mixed at 250°C for 10 min. (b) SEM micrograph of 20% P46 blend mixed at 250°C for 60 min. (c) SEM micrograph of 30% P46 blend mixed at 250°C for 10 min. (d) SEM micrograph of 30% P46 blend mixed at 250°C for 60 min.

and 250°C, the decreases in the  $T_g$  of the blends are due to the plasticization effect of P46 in PC. As the mixing time increases, this effect became more apparent. However, when the blending temperature increased to 260°C and P46 composition was more than 20%, the effect of the ester exchange on the  $T_g$

took over after 30 min of blending time, as shown in Figure 9.

The micrographs of the blends from the SEM study are shown in Figure 10(a)–(d). From comparing the cases of 10 and 30% P46 in the blends at 240°C, it was found that after 10 min, small (about

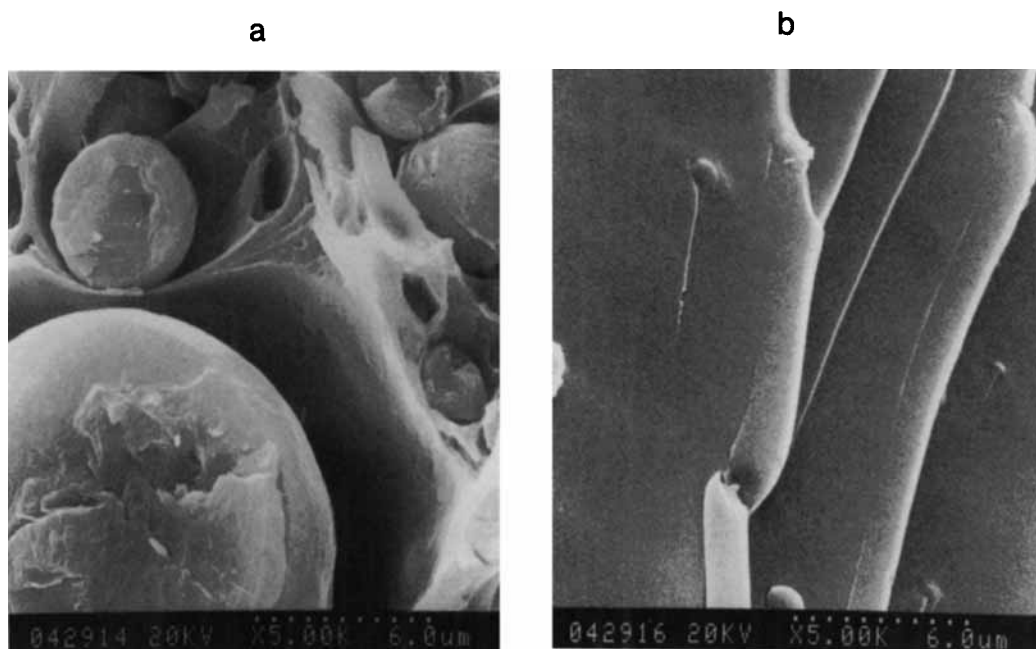




**Figure 12** (a) SEM micrograph of 20% P46 blend mixed at 260°C for 10 min. (b) SEM micrograph of 20% P46 blend mixed at 260°C for 60 min. (c) SEM micrograph of 30% P46 blend mixed at 260°C for 10 min. (d) SEM micrograph of 30% P46 blend mixed at 260°C for 60 min.

0.9 micron) and big (about 3 microns) droplets of P46 existed in the matrix of PC. When the blending time increased to 60 min, the size of P46 droplets reduced somewhat and the number of the smaller droplets increased. This is a result of mixing. Whereas in the case of 20 and 30% P46 in the blends,

the change in the blends' morphology between 10 and 60 min of blending is dramatic, as shown in Figure 11. In Figure 11, for the 20% P46 case at 250°C, the size of P46 droplets reduced to about 0.5 micron at 60 min of blending from about 1.5 micron at 10 min of blending. Also, after 60 min of blending,



**Figure 13** (a) SEM micrograph of 40% P46 blend mixed at 260°C for 10 min. (b) SEM micrograph of 40% P46 blend mixed at 260°C for 60 min.

the number of P46 droplets decreased greatly. The same trend appeared and became almost a single phase for the case of 30% P46 at 260°C, as shown in Figure 12. To match the NMR spectroscopy of the blend containing 40% P46, the SEM micrographs of the blend after 10 and 60 min of blending are shown in Figure 12(a) and (b). In Figure 12(a) and (b), large P46 droplets (about 1.5 microns) disappeared totally after 60 min of blending at 260°C. In Figure 13, the same phenomenon appeared for the case of 40% P46 blend.

## CONCLUSIONS

Blends of P46 and PC at various compositions were studied to understand their compatibility at different blending temperatures and time. Thermal analysis and scanning electron microscopy were used to investigate the physical as well as the transesterification between the two polymers at different conditions.

At low temperature (240°C) and low P46 composition (10% or 20%), a progressive shifting of the glass transition temperature of the PC matrix to lower temperature was observed. This was attributed to the plasticization of PC by PET-rich P46. However, as the temperature increased to 250°C or above, there was a larger drop in the glass transition tem-

perature of the PC matrix. This is due to the ester exchange reaction between PC and P46. The transesterification is verified by the NMR in the case of 40% P46 at 260°C. The drop in the glass transition temperature of the blend became larger as the blending time was more than 30 min. From the thermal analysis data, the transesterification took place first between PC and the ester functional group in the PET block of P46. As the reaction continued, PC then reacted with the ester group in the POB block of P46. At 260°C and for the blend containing 30% P46, it seemed that the blend became a compatible system. This is further confirmed through the micrograph observation in the SEM study. In the SEM micrographs, P46 appeared as droplets in the PC matrix at 240°C. However, at 260°C and after 60 min of blending, almost all P46 droplets disappeared for both the 30 and 40% P46 cases.

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