

Transesterification and Compatibilization in the Blends of Bisphenol-A Polycarbonate and Poly(trimethylene terephthalate)

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Abstract: Melt blending of Bisphenol A polycarbonate (PC) and poly(trimethylene terephthalate) (PTT) was carried out over the entire composition range. The mixing time was varied up to 90 min. The resulting samples were analyzed by FT-IR, DSC, XRD, DMTA, ¹H NMR, and SEM. The process of transesterification between the two polymers and their resulting compatibilization were observed. The behaviors of the PTT-rich and PC-rich blends were different and an equilibrium was found to exist. Peculiar behavior, which was different from that of the PTT-rich and PC-rich blends, was exhibited by the 50/50 (PTT/PC) blend.

Keywords: poly(trimethylene terephthalate), polycarbonate, blend, transesterification, compatibilization.

Introduction

Blends of PC and polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) can have interesting properties and therefore has received attention from number of researchers.¹⁻¹⁶ The thermal resistance and dimensional stability of PC can be combined with ease of processing and chemical resistance of PET if a proper blend can be prepared. Lee *et al.*² have reported the transesterification between PC and PET and the resulting compatibility between PET and PC. Effect of blending sequence on the morphology and impact toughness of PET/PC blends has been studied by Wu *et al.*³ The compatibilization between PET/PC by the transesterification reaction has been demonstrated by Ma *et al.*⁴

Ignatov *et al.*⁵ have shown that activity of catalyst freshly added to the PET and PC just before melt blending was much higher for transesterification. The catalytic activity was also found to be a function of ligand structure which mainly influenced the solubility of polymer. Fiorini *et al.*⁶ have presented their results on the effect of different catalysts and mixing times on the transesterification process between PET and PC by analyzing the samples using the ¹H NMR and selective degradation technique. The chemical and physical properties of PET/PC blend prepared by one step

extrusion process have been reported by Ignatov and co-workers and they have evaluated the properties of transesterified product.^{7,8} The characterization of equimolar PET/PC blend using dynamic mechanical and thermal analysis as well as wide angle X-ray scattering has been carried out by Denchev *et al.*,⁹ and they have concluded that a random copolymers was formed due to transesterification.

Presence of PBT-rich and PC-rich phases and the difference in their behaviour have been reported by Delimoy *et al.* for a PBT-PC blend.¹⁰ They have also presented a phase diagram exhibiting spinodal-type phase composition. Transesterification in a polyblend of PBT and a liquid crystalline polyester has been followed quantitatively by Jo *et al.*¹¹ They employed ¹³C NMR and differential scanning calorimetry (DSC) techniques to study the extent of exchange reactions and have concluded that a random copolymers was formed for a 50/50 blend. Pompe *et al.*¹² have investigated equilibrium melting temperature in PBT/PC blends and have shown that melting temperature and PC concentration influenced the properties of blends. Bennecom *et al.*¹³ have observed that the partial miscibility between PBT and PC was not observed for amide modified PBT and PC system. Effect of transesterification catalyst on the crystallization behaviour of 50/50 blend of PBT/PC was investigated by Wilkinson *et al.*¹⁴ They characterized the blend using DSC and X-ray scattering (XRD) techniques. The ordered structure and progressive transesterification of PBT-PC 50/50 blend was studied by Hopfe *et al.*¹⁵ They have followed the

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tion through FT-IR and ^1H NMR spectroscopy. They have reported that transesterification improved the compatibility. Pompe and Hubler¹⁶ have also studied PBT/PC blend and demonstrated the formation of transesterified copolymer.

Montaudo *et al.*¹⁷ have studied the mechanism of exchange reactions between PET/PC and PBT/PC system. They found that the nature of end groups, namely hydroxyl (-OH) or carboxyl (-COOH) influenced the structure of copolymers formed. They found that PET/PC system needed temperatures higher than that for PBT/PC blend for the transesterification reaction. Formation of carbon dioxide and ethylene carbonate was observed when degradation of PET/PC blend took place after prolonged heating.

Recently a poly(trimethylene terephthalate) (PTT) has been made commercially available by Shell Chemical Company under the trade name COTERRA. The properties of this polyester and possible applications have been reported by Shell Chemical Company.¹⁸⁻²³ The semicrystalline nature of PTT can offer number of advantages offered by amorphous PET and crystalline PBT. The glass transition temperature of PTT is 45-65 °C compared with 80 °C for PET and 25 °C for PBT. On the other hand, the melting temperature of PTT is 228 °C as compared to 265 °C for PET and 225 °C for PBT. Thus PTT can improve the processability of PC in a better manner as compared to PET. There is no data available for the blends of PTT and PC. Besides, effect of time of blending on the characteristics of such blends has not received any attention. Therefore, present work is aimed at the study of extent of transesterification with blending time for the blend of PTT and PC over the entire range of compositions.

Experimental

Materials. Polycarbonate was procured from Aldrich and it had number average molecular weight of 19,000. PTT was synthesized in the present investigation as described below: PTT was synthesised by a transesterification reaction between 1,3-propanediol (PDO) and dimethylterephthalate (DMT). Both of these chemicals were procured from Aldrich. Mole ratio of PDO:DMT was 3:1 and the catalyst was $\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$ (Aldrich) used at the concentration level of 5.0×10^{-3} mol/mol of DMT. The experimental set up is shown in Figure 1. The speed of agitation was maintained at 100 rev/min and reaction temperature was 180 °C. The methanol formed during the reaction was removed, condensed and collected in a measuring cylinder. At the end of reaction (80 min) when no more methanol was formed the reaction was stopped. The reactor contents were cooled rapidly and the resulting lump of PTT was finely pulverized. The powder was washed with trifluoro acetic acid and then with methanol. After washing, the residual solvent was removed by drying the PTT powder in vacuum at 110 °C for

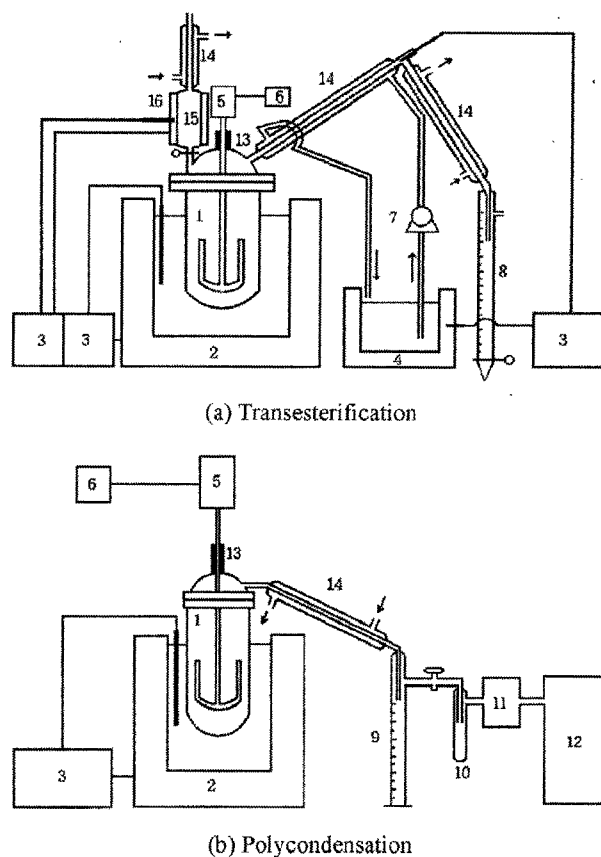


Figure 1. Schematic diagrams of transesterification and polycondensation apparatus. 1) Reactor 2) Oil bath 3) Temperature controller 4) Water bath 5) Motor 6) Ammeter 7) Pump 8) Bürette 9) Graduated measuring cylinder 10) Vacuum trap 11) Vacuum gauge 12) Vacuum pump 13) Vacuum adaptor 14) Condenser 15) PDO tank 16) Heating mantle.

12 h.

Blend Preparation. Both PTT and PC were dried at 110 °C for 12 h and PTT powder and PC pellets were charged to the vessel used as a reactor for synthesis of PTT. The blending temperature was 275 °C and speed of agitation was 40 rev/min. Blending times were varied up to 90 min for some blends, however, all the blends were mixed at least for 30 min. The blending was carried out under vacuum so as to avoid the oxidative degradation.

The blended samples were cooled and compression moulded using a pressure of 25 MPa and temperature of 250 °C, into thin sheets measuring $30 \times 5.5 \times 1.5$ mm. The sheet was then cut into small sizes suitable for further characterization.

Characterization. All the samples were dried *in vacuo* 150 °C for 12 h to remove any moisture before analysis was carried out. All the samples were analysed by FT-IR spectroscopy (Bruker KFS-66), FT-NMR spectroscopy (JF JNM-LA 30), DSC (TA Instruments, DSC 2010), *dyr*

mechanical thermal analysis (DMTA, Polymer Laboratories, Mark II), scanning electron microscopes (SEM, JEOL, JSM-840 A) and wide angle X-ray diffraction (RIGAKU-GEIGER WXR, 30 kV and 10 mA, Ni filtered $\text{CuK}\alpha$ radiation) covering 0 to 50° at the scanning rate of 2°/min.

Intrinsic viscosity of PTT at 30°C was measured using a mixed solvent comprising of TFA and chloroform in a ratio of 70/30 (v/v). Both solvents were GR grade procured from Aldrich. Additional details are reported by Na.²⁴

Results and Discussion

FT-IR Analysis. Figure 2 shows the IR spectra of PC, PTT and their blends mixed for 90 min at 275°C. The wavenumbers of 1728 and 1784 cm^{-1} correspond to C=O stretchings for PTT and PC, respectively. As the amount PC increases, there seems to be shifts of C=O at 1728 cm^{-1} to lower wavenumbers. The change in this band has been commonly used to identify the exchange reaction between PC and PET.^{25,26} The peak at wavenumber of around 1710 cm^{-1} corresponds to an aromatic ester structure of phenoxybenzoyl.

¹H NMR Analysis. NMR is very useful for obtaining information about the extent of transesterification reaction. This technique is, however, limited by its low sensitivity to the very first formation of block copolymers, when the concentration of joining links between PC and PTT segments is very low. Figure 3 compares the ¹H NMR spectra for PTT, PC and their blends. Three distinct peaks at 8.22, 4.75 and 2.5 ppm correspond to terephthalate, oxy methylene and middle methylene group protons of PTT. Similarly, peaks at

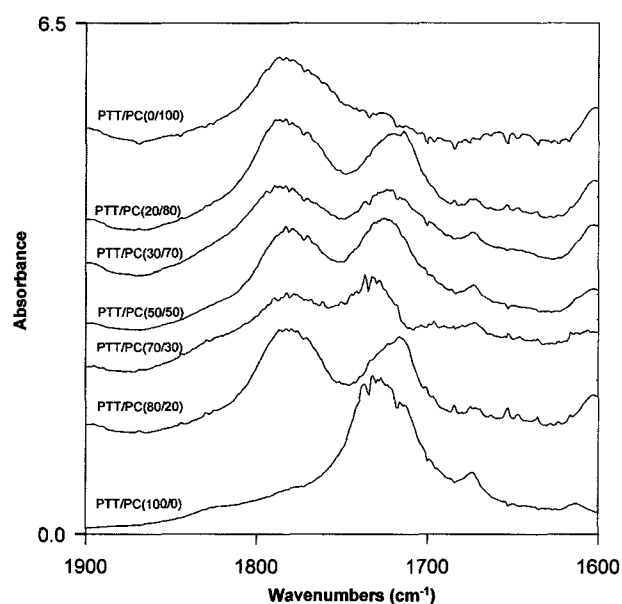


Figure 2. IR spectra of PC, PTT and their blends mixed for 90 min at 275°C.

1.75 ppm and those between 7.19 and 7.37 ppm represent 6 methyl protons and aromatic protons of PC, respectively.

For the PTT/PC blend, new peaks around 4.6 and 4.08 ppm are observed which can be due to transesterification as the new peaks show characteristic delta values for CH_2 protons adjacent to ether linkage (Figure 4). Similar peak for PET-PC blend has been observed at 4.1 ppm by Ignatov *et al.*⁵ Since PET environment in transesterified PET-PC copolymer is different as compared to PTT in PTT/PC exchange reaction, there will be small difference in peak

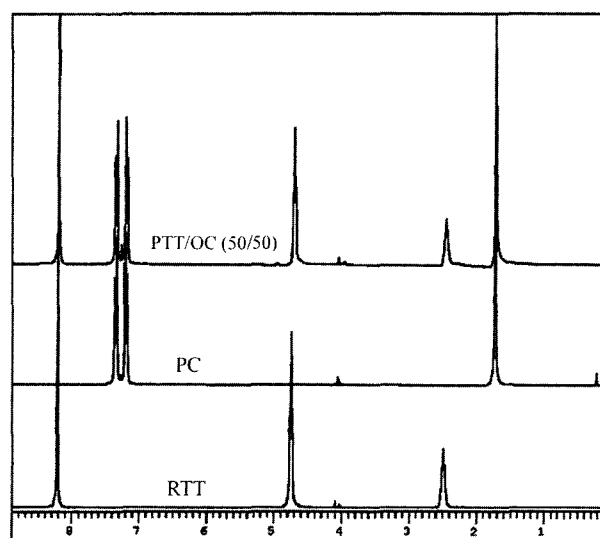


Figure 3. ¹H NMR spectra of PTT, PC and their PTT/PC (50/50) blend.

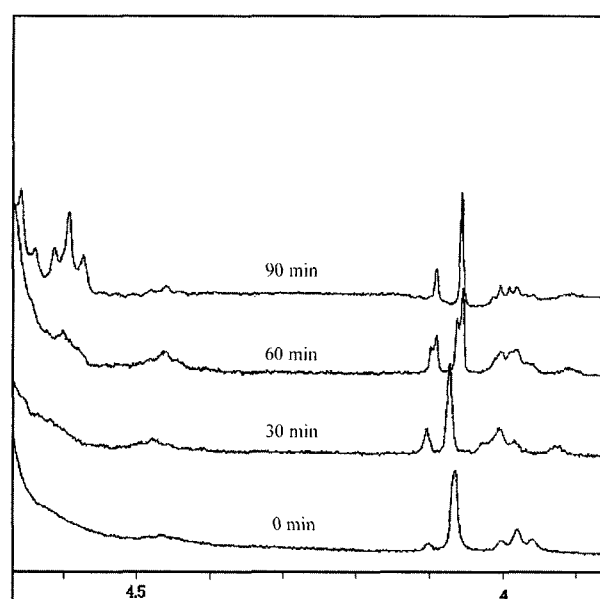


Figure 4. ¹H NMR spectra at up-field of the PTT/PC (50/50) blend heat treated at 275°C.

values. The new peaks around 8.29 and 8.39 ppm also are indicative of change of environment for terephthalate moiety of PTT adjacent to ether group (Figure 5). The shift becomes more predominant as % PTT increases which is not shown here.

DSC Analysis. Figure 6 shows the DSC thermograms of PTT and PC. PTT shows an exotherm around 70 °C indicating cold crystallization, while melting endotherm was around 228 °C. These observations are similar to those reported by Pyda *et al.*²³ The glass transition temperature (T_g) of PTT and PC were respectively 45.8 and 152.9 °C. Figure 6 com-

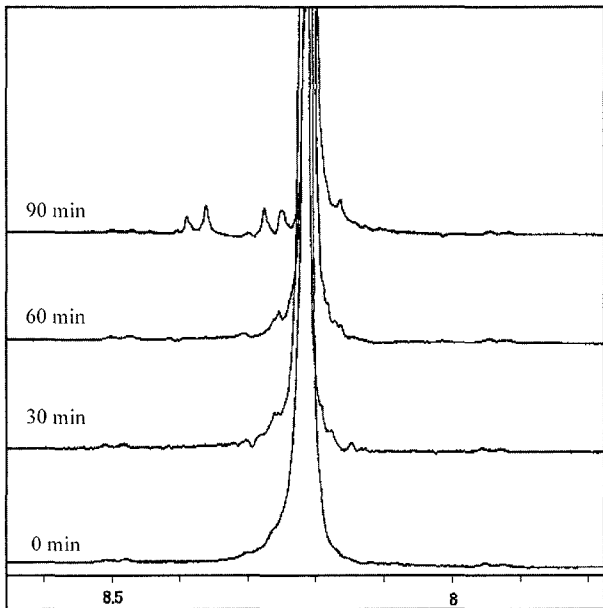


Figure 5. ¹H NMR spectra at down-field of the PTT/PC (50/50) blend heat treated at 275 °C.

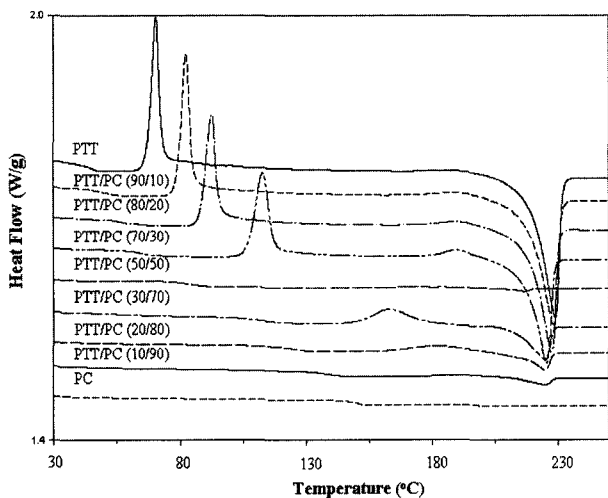


Figure 6. DSC thermograms of PTT/PC blends with various compositions for time, 90 min.

pare the DSC thermograms of PTT-rich blends namely 90/10, 80/20, and 70/30 compositions after 90 min of blending. As PTT content has reduced or PC content increased, the glass transition temperature steadily increased, and the temperature at which exotherm corresponding to cold crystallization occurred also increased. The enthalpy change (ΔH) at this temperature as well as at PTT melting temperature (T_m) decreased as PC contents increased. This suggests that amorphous nature of blends is increasing. Figure 7 shows the effect of blending time on DSC thermogram for blend of 70/30 (PTT/PC) composition. The glass transition temperature of blend increased as the mixing time increased.

The results in Figure 6,7 indicate that presence of PC has not eliminated the preordering of PTT. Increase in T_g indicates the formation of copolymer through transesterification which induces loses crystallinity.¹⁴ As PC content increased, crystallinity decreased further as evident from decreased ΔH values.

For 70/30 blend, increase in T_g with time of blending indicates change of composition as more PC may be induced due to compatibilization. After 60 and 90 min of melt mixing, the formation of new exotherm at high temperatures closer to melting of PTT, suggests that PC-rich copolymer could have been formed. PTT-rich copolymer formed initially could have some phase in equilibrium with PC-rich domains, which are favored as time progresses when PC was a minor component. The PC-rich blends, therefore, may be analyzed in this direction.

Figure 8 compares the effect of time of blending for 50/50 blend. The behaviour is very similar in nature as that of 70/30 blend. Complete absence of cold crystallization exotherm after 90 min is indicative of formation of random copolymer having predominantly amorphous nature. A random copolymers, 50/50 compositions for PET/PC, PBT/PC and PBT/liquid crystal polymer have been reported in literature.^{9,11,14}

Figure 9 depicts the behaviour of 30/70 and 20/80 blends.

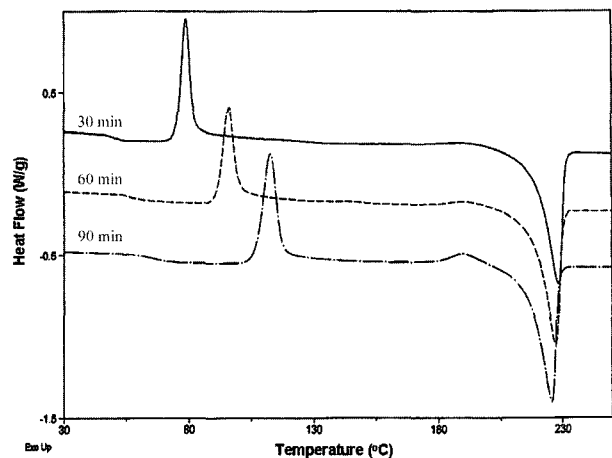


Figure 7. DSC thermograms of PTT/PC (70/30) blend with various mixing times.

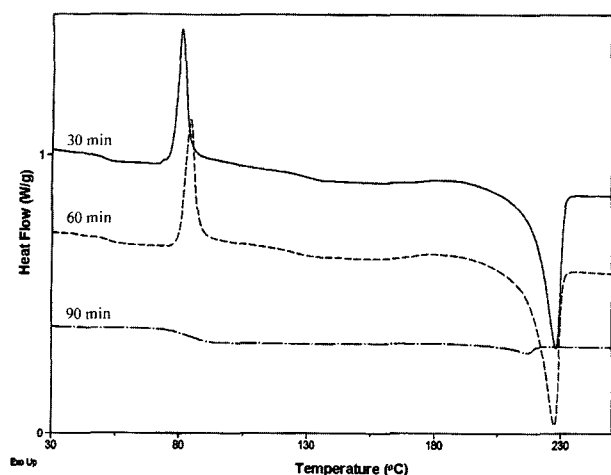


Figure 8. DSC thermograms of PTT/PC (50/50) blend with various mixing times.

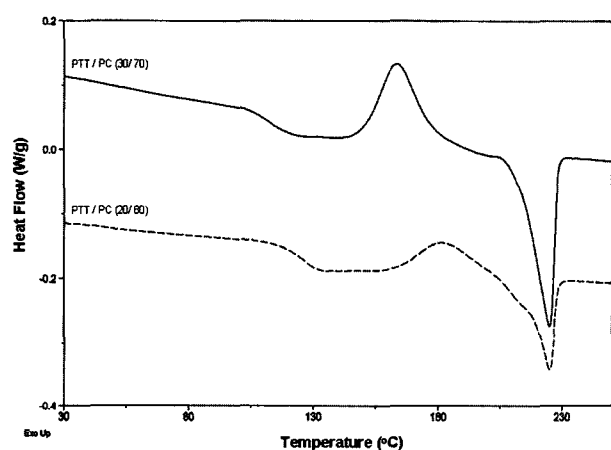


Figure 9. DSC thermograms of PTT/PC blends with compositions of (30/70) and (20/80) for mixing time, 30 min.

As PC content increased substantially, the presence of high temperature exotherm was observed even after 30 min of blending. The presence of two exotherm for PC-rich blends even at initial stages positively suggest that nature of copolymer formed are different from those of PTT-rich blends. The presence of PC has not eliminated the preordering but it has influenced it differently. PTT-rich copolymer was more ordered than PC-rich copolymer. PC being more amorphous, it has induced higher T_g for both PTT-rich and PC-rich blends.

When both PTT and PC are blended, there can be, initially, some PTT-rich domains and some PC-rich domains for all the compositions. As transesterification take place, the crystallinity of PTT would decrease. As transesterification product can bring in compatibilization, more PC or PET may become miscible depending upon composition. The shift of temperature for PTT-rich or PC-rich blends in oppo-

site direction confirms this. The equilibrium between these two may be a function of initial composition. The preordering temperature seems to increase with time, for PTT-rich blends while it seems to decreased for PC-rich blends. The nature and equilibrium between these two types of copolymer needs to be studied. However, if one is preparing these blends through extrusion process which allows smaller times for blending, the characteristics of PTT-rich copolymer or PC-rich copolymer only may be observed depending upon initial composition.

XRD Analysis. Figure 10 shows XRD data for PTT and PC. The diffraction pattern of neat PTT is typically characterized by five strong reflection position in the 2θ region of 15-30°. PC showed typical amorphous nature. Figure 11

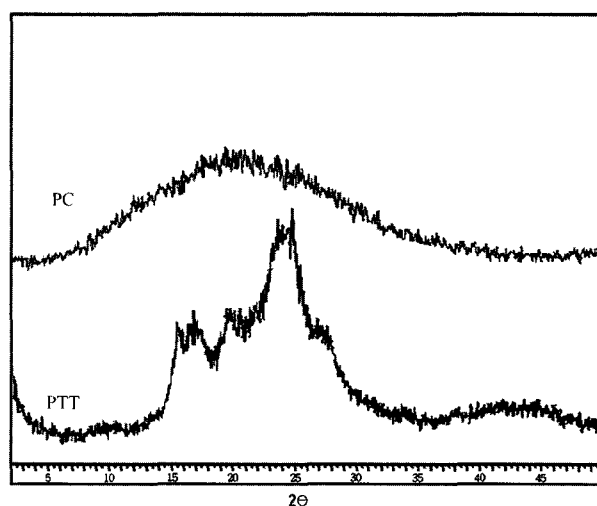


Figure 10. X-ray diffraction patterns of PTT and PC.

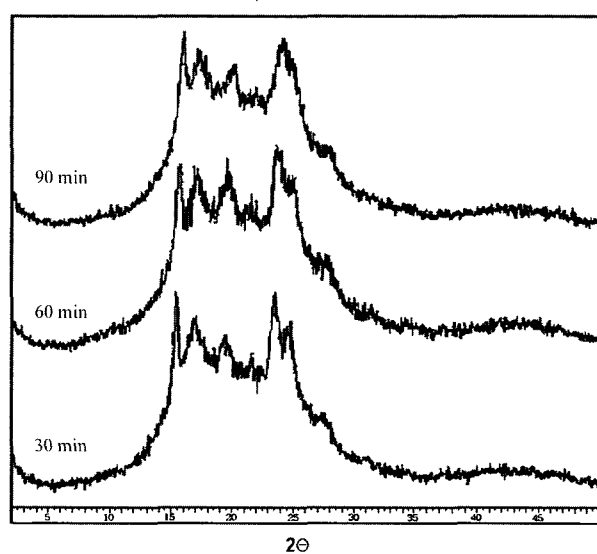


Figure 11. X-ray diffraction pattern of PTT/PC (70/30) blend at various mixing times.

shows the XRD for 70/30 blend mixed for three different times of 30, 60 and 90 min. As time of blending increased, the pattern has moved towards more amorphous behaviour of the blend. This loss of crystallinity can be more vividly seen for 50/50 blend as shown in Figure 12. For blends of higher PC contents similar behaviour was observed.²⁴

DMTA Analysis. The loss of crystallinity was shown by XRD analysis. The DMTA data can explain the amorphous behaviour in a better fashion. Figure 13 shows the DMTA

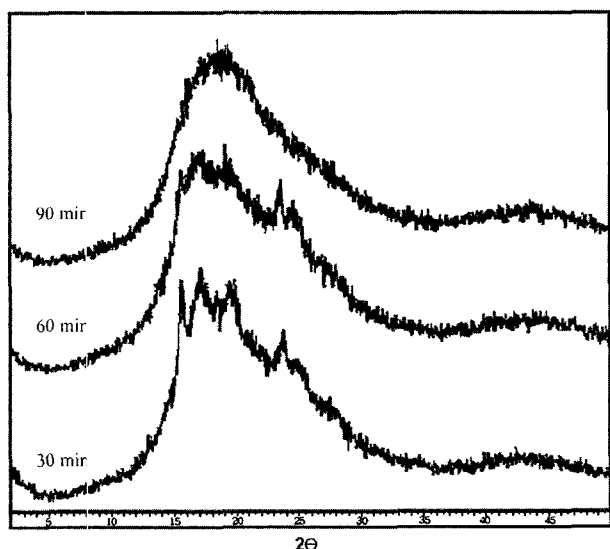


Figure 12. X-ray diffraction pattern of PTT/PC (50/50) blend at various mixing times.

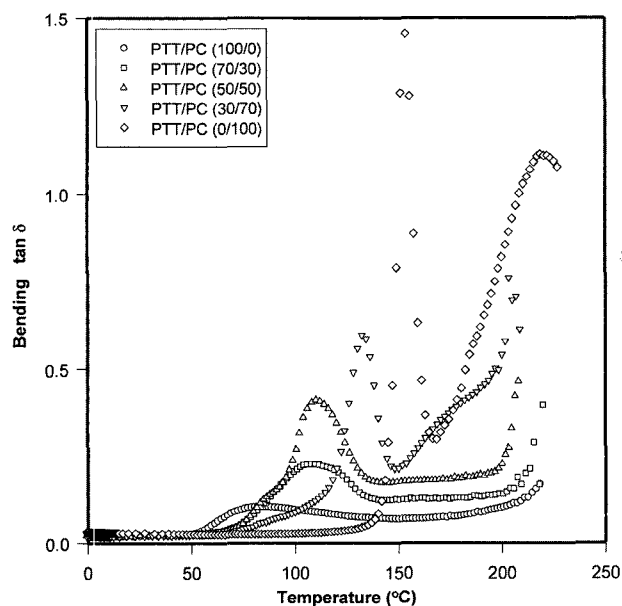


Figure 13. DMTA spectra of the PTT/PC blends at a heating rate of 1°C/min and frequency of 1 Hz.

data of different blend compositions in terms of $\tan \delta$ as function of temperature. $\tan \delta$ is a ratio of loss modulus (E'') to elastic modulus (E') at a given frequency and a measure of viscoelasticity of polymer blend systems. PC showed a sharp peak at 155°C and PTT exhibited a broad peak at 82°C. These are the T_g for these two polymers. The peaks became progressively sharper as PC content increased and peaks also appeared at temperatures that increased steadily with PC content. This indicates increase in T_g of the blend. The transesterification is known to reduce crystallinity.²

Figure 14 shows the effect of mixing time on $\tan \delta$ for 70/30 blend. After 30 min of mixing, PTT-rich blends exhibited two T_g 's corresponding to two principal components. But beyond 60 min of melt mixing, only one peak ($\geq 100^\circ\text{C}$) was obtained. This kind of single peak may indicate the presence of random copolymer in the system.⁹ Generally detection of signal peak also indicates miscibility. Since PTT and PC are well known for immiscibility, it can be assumed that transesterification has brought about some degree of compatibilization.

Morphology Analysis. Figure 15 shows the effect of mixing time for 70/30 blend. The dispersed domain size decreased significantly when mixing time increased from 30 to 90 min. This change in solubility with increasing transesterification has been ascribed to the formation, at the low degrees of reaction, of block copolyesters with reduced solubility followed, at higher degrees of reaction, by completely soluble statistical copolymers.¹⁴ Figure 16 similarly shows change in morphology with mixing times for a 50/50

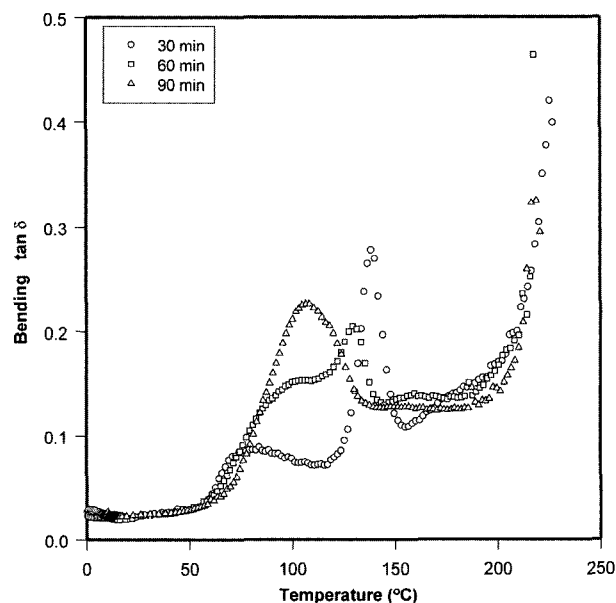


Figure 14. DMTA spectra of the PTT/PC (70/30) blend prepared for mixing times at a heating rate of 1°C/min and frequency of 1 Hz.

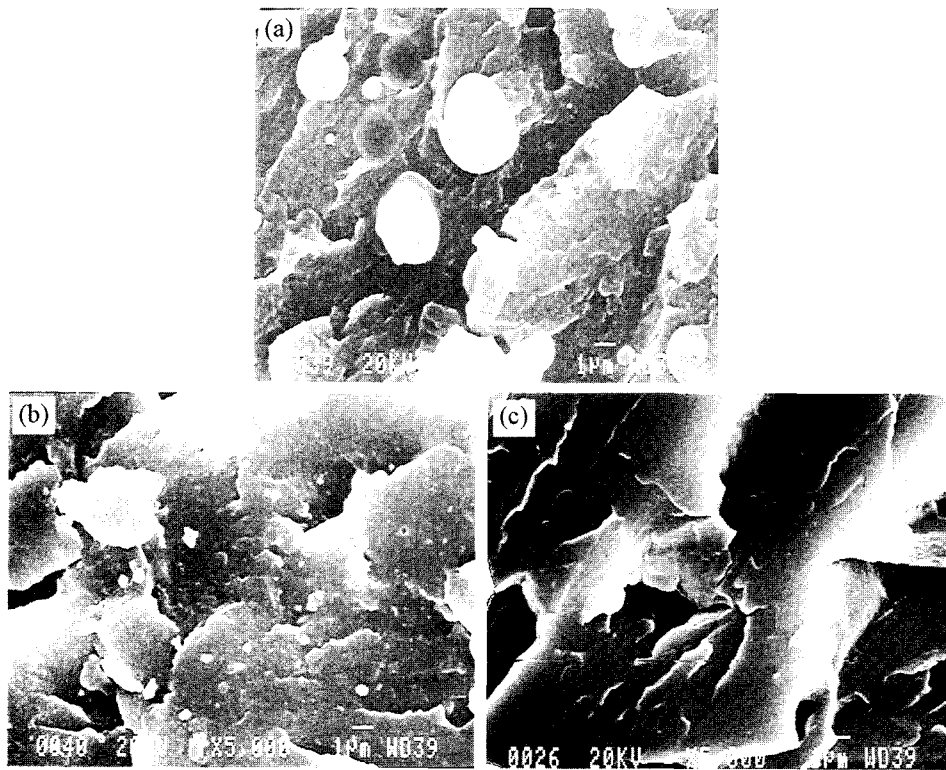


Figure 15. SEM photographs of PTT/PC (70/30) blend at a mixing time of ; (a) 30 min, (b) 60 min, and (c) 90 min.

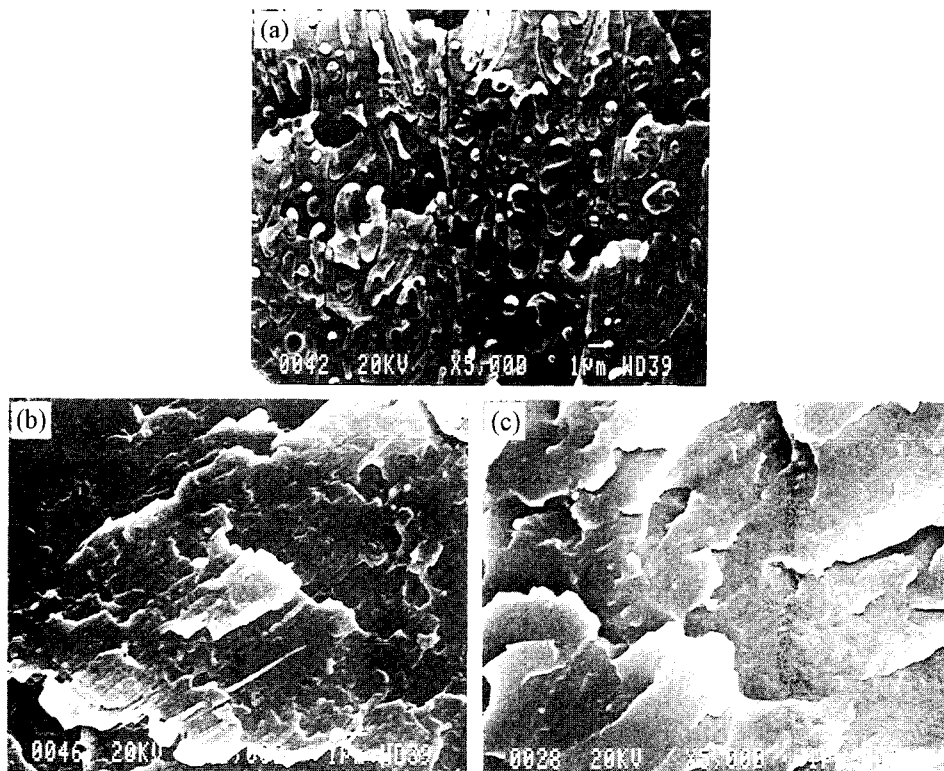


Figure 16. SEM photographs of PTT/PC (50/50) blend at a mixing time of ; (a) 30 min, (b) 60 min, and (c) 90 min.

blend. Elongated particles initially observed seem to be disappearing and formation of co-continuous phase with increase in time is very characteristically shown in this figure. Particles or big domains observed in Figure 16 could be attributed to higher viscosity of PC which would render difficulties in dispersing PC into PTT.

Conclusions

PTT and PC seem to form the transesterified product. The behaviour of PTT-rich and PC-rich blends seems to be different and equilibrium between the two types of copolymer can exist depending upon blend composition and blending time. The transesterified product appears to be more amorphous as evident from XRD, DMTA and DSC data. The transesterification has also improved the compatibilization.

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