

Blends of Poly(ethylene terephthalate)/polycarbonate by the Use of Lanthanum Acetyl Acetate Catalyst

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ABSTRACT: Blends of poly(ethylene terephthalate) (PET)/polycarbonate (PC) in the presence of lanthanum acetyl acetate catalyst that causes reactive mixing of two polymers were prepared, and mechanical and morphological properties were studied. For comparison reasons, simple blends of those two polymers (in the absence of catalyst) were also prepared. Compatibility strongly depends on the degree of transesterification at the interface of PET/PC, which leads to decrease of PET crystallinity,

and results reveal that at 40–50% of PC content in blends a fine microstructure is formed and impact strength reaches its maximum value. This phenomenon is attributed to the occurrence of transesterification reactions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2917–2922, 2008

Key words: compatibility; poly(ethylene terephthalate); polycarbonate; crystallization; catalyst

INTRODUCTION

Polymer blends are of considerable scientific and industrial interest, since blending is an effective way to improve the properties of polymers. Both poly(ethylene terephthalate) (PET) and bisphenol-A polycarbonate (PC) are important engineering plastics; in particular, PC has high impact strength and its solvent resistance is improved by mixing with PET. Both are polyesters and can react by transesterification in the molten state to form block or random copolymer, which will greatly alter the blend phase behavior and morphology.^{1–3} PET/PC blends have been extensively studied over the past two decades.^{4–8} Paul and coworkers^{9,10} reported that melt-mixed PET/PC blends formed an homogeneous amorphous phase for compositions with >70 wt % PET and an inhomogeneous amorphous phase for <70 wt % PET. On the other hand, others^{11,12} found that the blends were immiscible at all composition range. These discrepancies may result from a variety of factors such as the use of solvents in their preparation, ester exchange reactions, molecular weight differences, and the analytical techniques used to analyze and define compatibility.

In this work, two different sets of blends have been prepared with an internal brabender in the presence and absence of a transesterification catalyst,

lanthanum acetyl acetate hydrate,¹³ in order to determine what effect this reaction has in improving the material properties of the PET/PC blends.

EXPERIMENTAL

PET was supplied by Tondguyan Petrochemical as molding pellets. It has a number average molecular weight of 22.4 kg/mol and weight average molecular weight of 39.5 kg/mol. Bayer, Germany, provided PC (Makrolon2858). MFI of PC was 10 g/10 min. Lanthanum acetyl acetate hydrate was purchased from Aldrich Chemical (Pilsberg, The Netherlands) and used as obtained. Pellets of the two polymers were dried at 90°C for at least 12 h prior to blending in a brabender (plasti-corder pl2000) at 265°C and 60 rpm in the presence of catalyst and without it. The catalyst was mechanically dispersed throughout the PC pellets at a concentration of 0.075 wt %.

The blends were pressed at 280°C for 3 min at a pressure of 25 MPa to plates with dimensions of 125 mm × 125 mm × 3 mm. Amorphous plates were obtained by quenching into ice/water. Tensile dumbbell specimens were cut directly from the plaques.

The compatibilizing of PET/PC blends was investigated on a Perkin Elmer DSC 2. The samples, sealed in aluminum pans, were heated to 540 K and maintained at that temperature for 1 min to erase the thermal history and quenched to 300 K. They were then heated at a rate of 20 K/min to 540 K. The temperature was calibrated by the melting point of the ultrapure materials: stearic acid, indium, tin,

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and lead under different heating rates, corrections being made for thermal lag in the specimens.

A scanning electron microscopy (SEM), Joel 5410, was used to examine the extent of phase separation in the blends by examining the fracture surfaces of the blends. The samples were fractured in liquid nitrogen and etched with diethylene triamine (DETA) for about 1 min at ambient temperature to remove the PC. The specimens were rinsed by distilled water and coated by gold to eliminate surface changing. Silver paint was used to form a conducting pathway between the sample and the mounting block.

Tensile properties were measured on an Instron model 5566 interfaced to a computer. The crosshead speed was 2 mm/min. Standard dumbbell-shaped specimens were cut directly from molded plate. An average of at least five specimens was measured for each determination. The energy to failure at high strain rate (3.5 m/s) was also investigated using a Zwick impact tester. Dumbbell-shaped specimens used were identical to those used in Instron test. An average of at least eight specimens was used. All these tests were carried out at a constant temperature of 297 ± 1 K and constant relative humidity of $32 \pm 1\%$.

RESULTS AND DISCUSSION

Glass transition temperature

Since the glass transition temperature, T_g , depends on the rate at which the glass was formed, a standard quench rate was adopted and corrections were made for thermal lag by linear extrapolation to zero heating rate at constant sample weight. By this method, the T_g of PET and T_g of PC were measured as 349 and 413 K, respectively.

It is believed that during mixing of PC and PET in the presence of catalyst, a transesterification reaction occurs resulting in a copolymer in the interface. This formed copolymer is poly(terephthalate caprolactone-*co*-ethylene terephthalate) (TCET). The formation of this copolymer has been reported by Ma et al.¹⁴

The TCET50 copolymer with 50 wt % ethylene terephthalate content was determined by the solubility test, it is compatible (miscible) with both PET and PC in almost the entire composition range.¹⁴ Figure 1 shows the DSC thermogram of the PET50/PC50/TCET50 ternary blends after the samples were melted for 1 min and quenched from 540 K.

Because of the overlap between the cold-crystallization of the PET component and the glass transition of the PC-rich phase (>90 wt % PC), in the DSC thermogram of the PET/PC/TCET50 (low TCET50 copolymer content (<25 wt %)), the higher glass transition temperature, which belongs to the PC-rich

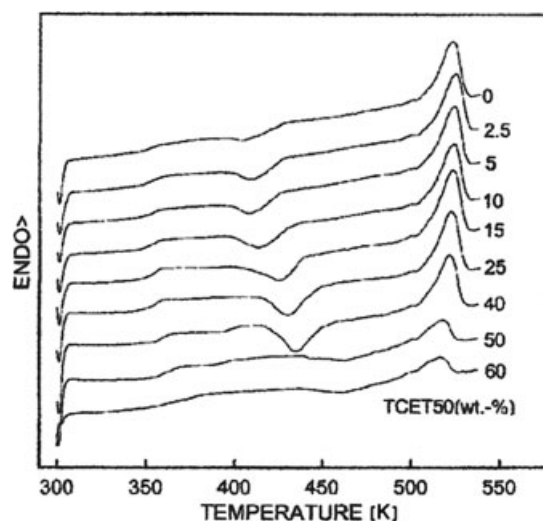


Figure 1 The DSC thermograms of the PC50/PET50/TCET50 ternary blend samples with different TCET50 copolymer content.

phase, is very difficult to determine. By increasing the content of the TCET50 copolymer in the blends, the lower T_g that belongs to the PET-rich amorphous phase increases a little. The melting temperature and the area of the melting endotherm of the PET component decrease slightly, while the cold-crystallization exotherm moves drastically to high temperature. These phenomena once again prove the fact that the TCET50 copolymer is compatible with PET. The crystallization of the PET component in the blends has been impeded. Only with a higher TCET50 copolymer content in the blends, e.g., 40 wt %, the cold-crystallization exotherm of the PET component moves to a high enough temperature, so the T_g of the PC-rich phase can also be detected in the DSC thermogram, which is somewhat lower than that of the pure PC component. When the TCET50 copolymer content in the ternary blends reaches 60 wt %, only one glass transition temperature can be observed, reflecting the compatibilizing effect of the TCET50 copolymer between the PC and PET component in the presence of catalyst. However, differences were observed with the blends prepared without the presence of the transesterification catalyst. Two glass transition temperatures are observed, one close to that of PET, which can be attributed to the PET-rich phase and the other to that of PC, which can be attributed to the PC-rich phase. Catalyst causing the crystallization of the PET is inhibited and occurs at a much higher temperature, above 425 K rather than 400 K. This takes it out of the temperature region of the second glass transition, enabling it to be observed.

The variation in the T_g with composition is shown in Figure 2, where the dash line represents the compositional variation in T_g for a miscible blend sys-

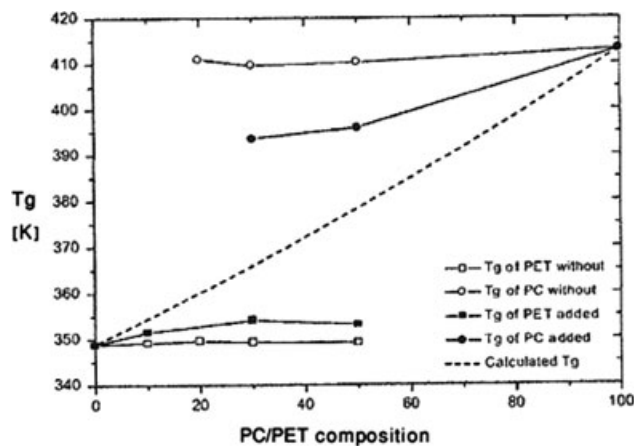


Figure 2 The effect of PET/PC blend composition on T_g ; dash line is the T_g calculated by Fox equation.

tem, assuming that the Fox equation¹⁵ applies. It can be seen that for the blends without added catalyst, both glass transition temperatures are almost independent of composition. For the blends with added catalyst, two glass transition temperatures could be

observed in the 50/50 and 60/40 blends. The T_g of PET-rich phase is slightly higher than that of 100% PET and increases with PC content increase, while the T_g of PC-rich phase is somewhat lower than that of PC and also increases with PC content increase. The values of glass transition temperatures suggest that there is only 0.5–0.7% PC in the PET-rich phase for 50/50 and 60/40 blends prepared without added catalyst, while there is 8–10% PC in the PET-rich phase for corresponding blends with added catalyst. This clearly indicates that the blends prepared without added catalyst are immiscible, on the other hand, these blends prepared in the presence of catalyst show a partial miscibility. The T_g values also confirm that there is more PET contained in the PC-rich phase rather than PC in the PET-rich phase.⁸

Morphology of the blends

The morphology of the blends was investigated by SEM from the appearance of the fracture surfaces after etching with DETA. DETA has a good selectivity to etch PC without attacking PET.¹⁶ The SEM micro-

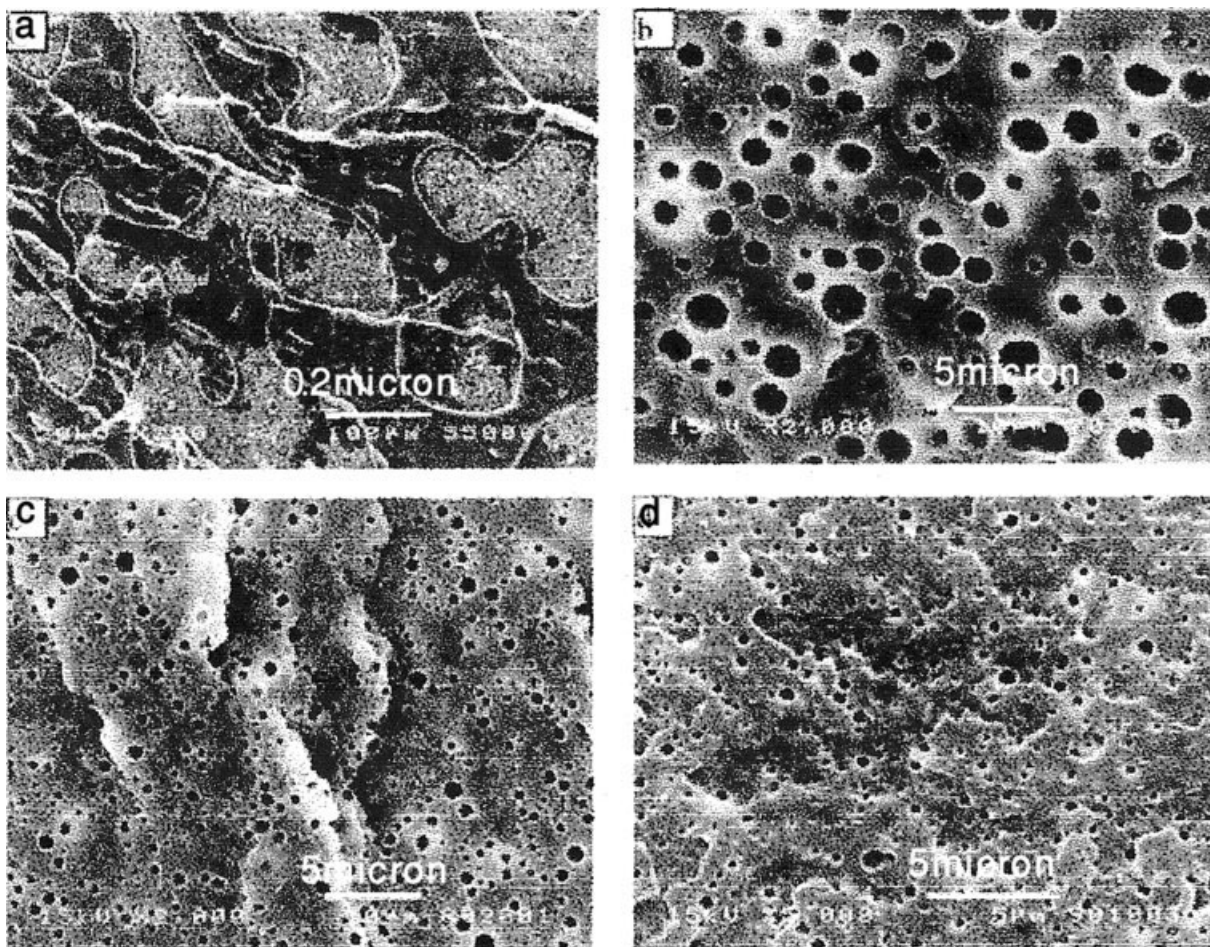


Figure 3 SEM micrographs of cryofracture surface of PET/PC blends prepared without added catalyst etched by DETA for 1 min: (a) PET50/PC50; (b) PET60/PC40; (c) PET80/PC20, and (d) PET90/PC10.

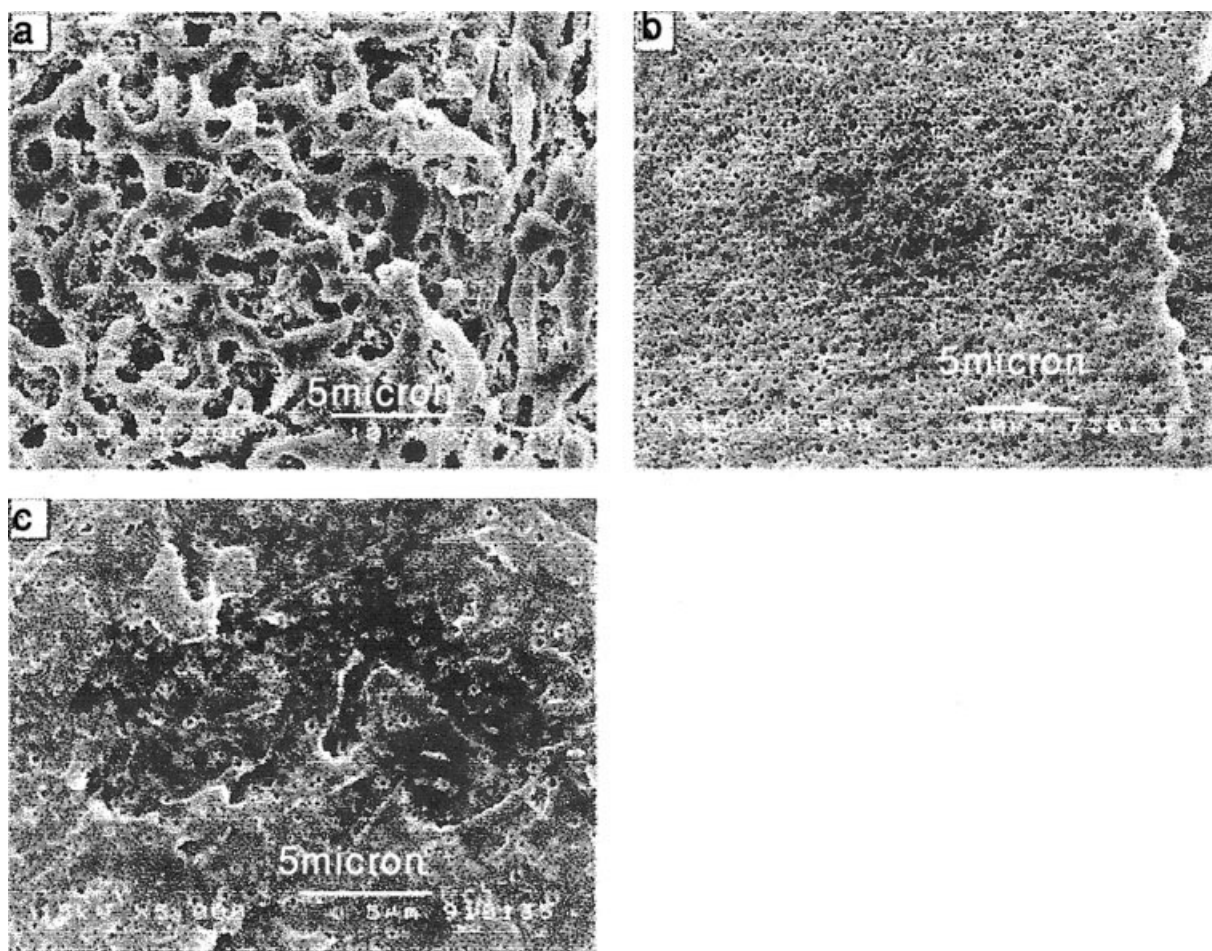


Figure 4 SEM micrographs of cryofracture surface of PET/PC blends in the presence of catalyst etched by DETA for 1 min: (a) PET50/PC50; (b) PET60/PC40, and (c) PET90/PC10.

graphs of the blends prepared without added catalyst are shown in Figure 3. All the blends exhibited a binary structure and at 50/50 composition a cocontinuous morphology was observed. At compositions less than 50 wt % PC, spherical PC particles were distributed uniformly throughout a continuous PET matrix. The etched spherical cavities had sharp boundaries, and there was no evidence of an inter-

facial layer between the PET matrix and PC domains. The PC particles decreased in size from about 3–5 μm in 60/40 to 1–2 μm in 90/10 PET/PC blends.

In the blends prepared with added catalyst, it can be seen from Figure 4 that the 50/50 blend shows a cocontinuous morphology and a similar trend with increasing PET composition from 60/40 to 90/10 of

TABLE I
Mechanical Properties of PET and PC and Their Blends

Sample	Young's modulus (GPa)	Elongation at break (%)	Ultimate strength (MPa)	Impact strength (kJ/m^2)
PC	2.41	85	70.3	0.89
PET50/PC50 without catalyst	2.67	158	50.4	0.44
PET50/PC50-added catalyst	3.74	186	52.1	0.51
PET60/PC40 without catalyst	2.83	200	53.7	0.36
PET60/PC40-added catalyst	3.75	260	79	0.33
PET90/PC10 without catalyst	3.27	120	74	0.36
PET90/PC10-added catalyst	3.86	155	77.6	0.36
PET	3.43	35	52.3	0.34

small PC particles embedded in a PET matrix. However, the PC particles are significantly smaller than that observed previously with the blends prepared without the catalyst. The particle sizes are submicron and much more dispersed. It is difficult to accept that 30 and 10% of the sample is present as the dispersed phase. The SEM analysis is in agreement with DSC result that the PET/PC blends prepared without added catalyst are completely immiscible and exhibit a clear two-phase structure. However, the blends prepared in the presence of added catalyst show partial miscibility because of much smaller phases. These demonstrate that the two materials appear to be more compatible as a result of the treatment with the transesterification catalyst.

The mechanical properties of the blends

In the tensile tests, all the amorphous blends exhibited ductile failure with a yield point followed by the development of a neck and strain hardening before finally failing. The tensile properties of both sets of blends are listed in Table I. The elastic modulus of the blends, in the presence of catalyst shows a synergistic effect, i.e., the modulus of PET90/PC10 in the presence of catalyst has highest value. The highest increase in modulus was obtained at 10% composition of PC. The ultimate strengths were also higher in these blends, although the trend is somewhat different to that of modulus. Strength increases with increasing PET content, reaches a maximum at PET60/PC40, and then decreases again.

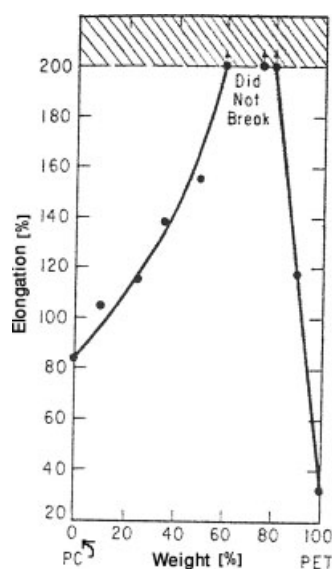


Figure 5 Elongation at break for injection molded blends. Maximum available crosshead equivalent to >300% elongation.

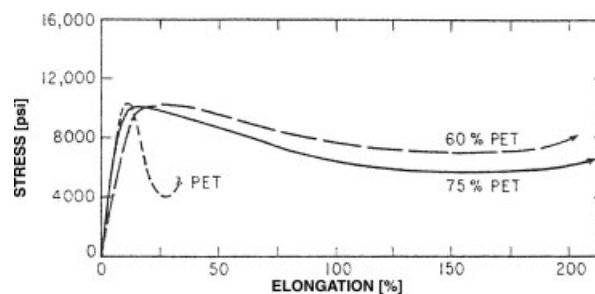


Figure 6 Typical stress-strain diagrams illustrating high ductility of 60 and 75% PET blends.

The elongation at break was also higher in the blends prepared with catalyst (Figure 5). Maximum elongation at break occurs at 70% composition of PC samples, which had elongation in the range of >300%. The stress-strain diagrams for two compositions with that of pure PET are compared in Figure 6.

It is perhaps significant that elongation at break has a very high value in the presence of catalyst compared to that of blends prepared without catalyst.

All specimens on the left branch of the curve in Figure 5 had two glass transitions, while those on the right branch had a single glass transition.

CONCLUSIONS

Blends of PET/PC produced without added catalyst have two glass transition temperatures independent of composition and a binary morphology. However, for the blends prepared with added catalyst, two glass transition temperatures close to each other are observed over a limited concentration range. The mechanical properties of PET-PC are quite good and do not show any significant negative departures from the additive rule typical for many phase-separated blends while catalyst is used. In fact, there is an interesting increase in the elongation at break. Being completely compatible or compatible to a certain degree with the homopolymers, random copolymers can act as efficient compatibilizers for the corresponding homopolymer blends, resulting in the reduction of the interfacial tension and the improvement of the interfacial adhesion. This has been indicated by the compatibilizing effect of the transesterification products, the TCET copolymers, in the PC/PET/TCET blends.

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