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The effects of transesterification on structure development in PC-PBT blends

A. N. Wilkinson, D. Cole, S. B. Tattum

Department of Materials Technology, Manchester Metropolitan University,
Chester Street, Manchester M1 5GD, UK

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Summary

A series of polycarbonate - poly(butylene terephthalate) (PC - PBT) blends has been formed via reactive melt-blending in a torque rheometer. The degree of transesterification between the two homopolymers was controlled by the incorporation of an alkyl titanium catalyst. Resultant materials were characterised using DSC, DMA, FTIR and SEM. As the degree of transesterification increased composition of the blends became increasingly complex, comprising mixtures of the homopolymers and various AB-type block copolymers of PC - PBT, with concomitant changes in their thermal behaviour. A corresponding transformation in materials morphology was observed: the relatively coarse structure characteristic of essentially two-phase blends, developed into a more refined structure exhibited by blends containing significant volumes of interphase material. This morphological change was due to the formation of increasing concentrations of random block copolyesters.

Introduction

The main-chain transesterification of PC-PBT blends has been widely studied over the last two decades [1-4]. In this process, shown schematically in Figure 1, the homopolymers undergo an ester interchange reaction resulting in the formation of AB-copolymers. As transesterification proceeds the products are seen to increase in complexity from AB- to $(AB)_n$-type block copolymers, until eventually the block structure is lost and statistical AB-copolymer is produced. Transesterification in PC-PBT blends has been shown [3] to be catalysed by residual titanium catalyst in the PBT, and to be inhibited by the use of organic ligands such as diphosphites [3, 4], which are able to complex with the titanium so rendering it inactive. Commercial PC-PBT materials are termed "stabilised blends" because, during production, transesterification has been inhibited [3-6] yielding essentially immiscible blends with modified interphase properties, often termed compatibilised blends or polymer alloys. The efficiency of alkyl titanium compounds, added to PC-PBT blends to catalyse transesterification, has been documented [7]. The addition of these compounds allows high degrees of transesterification to be reached in relatively short blending times, reducing the likelihood of thermal degradation of the blend components. However, the use of these compounds for the control of morphology development in PC-PBT melt blends has not been widely studied. This paper presents preliminary results showing that controlled catalysis of transesterification leads initially to phase refinement within essentially two-phase blends, and finally to the generation of more complex mixtures of various AB-copolymers.

Table 1. Transitional behaviour of blends and homopolymers. The value of k indicates the degree of miscibility in the blends (see Eqn. 1).

	DSC Transitions (°C)			DMA (°C)	
Material	Tg	Exotherm	Endotherm	tan δ peaks	k
PC	140	-	-	160	
PBT	-	-	218, 224	80	
0T	122	-	214, 221	95, 138	2.92
50T	-	-	212, 221	100, 136	2.58
100T	-	-	220	110, 134	2.30
150T	-	-	218	115, 130	1.85
200T	-	120	190, 200	90	1.03
300T	80	-	-	NA	

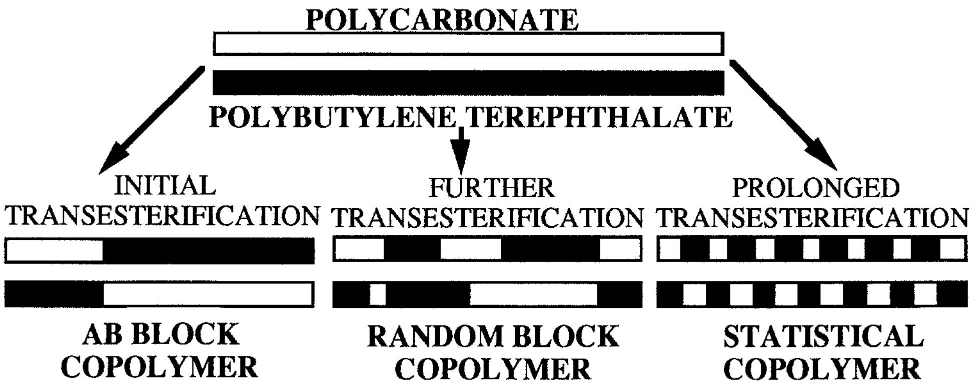


Figure 1. Schematic representation of melt transesterification (after [7])

Experimental

Melt blending of PC (Makrolon 2405, ex. Bayer) and PBT (Pocan B1505, ex. Bayer) was performed in a Brabender PL2000 plasticorder fitted with a W50 mixing chamber. Rotor speed, mixing time, chamber temperature and fill ratio were maintained, respectively, at 75 rpm, 10 minutes, 260°C and 0.8 (based on measured melt density). All blends consisted of 50:50 by weight PC:PBT and increasing levels of an alkyl titanium catalyst (tetrakis(2-ethylhexyl)titanate, Tyzor TOT, ex. Du Pont) were used to vary the phase development in each blend. A strong transesterification inhibitor [2], di-n-octadecyl phosphite (DNOP, ex. Janssen Chimica), was added to each blend following the desired mixing time, to inhibit further transesterification during subsequent heating. Addition levels of alkyl titanium catalyst were calculated based on the percentage of titanium in TOT. Levels ranging from 50 ppm titanium up to 300 ppm were used, and materials were designated as 0T (no addition), 50T, 100T, 150T, 200T and 300T, to indicate the addition level of catalyst. After blending, each material was compression moulded into a plaque (100 x 100 x 3 mm) at 260°C. Samples cut from these plaques were characterised using DSC, DMA, FTIR and SEM. DSC measurements were made using a Perkin Elmer DSC7, calibrated using indium and zinc standards. Samples (~ 5 mg), were encapsulated in aluminium pans and heated between 50 and 250°C at 20°C/min under flowing nitrogen, with an empty sample pan as an inert reference. DMA data were obtained using a Du Pont 982 DMA. Samples were run at an oscillation amplitude of 0.2 mm between -150°C and 180°C, to obtain storage modulus (E') and mechanical damping (tan δ) as functions of temperature. IR spectra were obtained using a Nicolet 510 P FTIR, fitted with a Spectratech diffuse reflectance cell. For analysis, samples were lightly abraded onto silicon carbide paper and inserted into the cell. For each sample, 150 scans were taken to produce a spectrum, from which the background spectrum was subtracted. A Cambridge stereoscan 250 SEM was used to obtain micrographs of blend structures. Samples for SEM were first cryo-fractured from liquid nitrogen and the fracture surfaces were then exposed to dichloromethane (a good solvent for PC) for one hour at room temperature, dried, and coated with gold/palladium alloy.

Results and discussion

Differential scanning calorimetry. Figure 2 shows a family of DSC curves showing the initial heating cycle of the homopolymers and blends, and the derived transition data are summarised in Table 1. Over the experimental temperature range (50-250°C), PC exhibits only a glass transition at 140 °C (onset of endothermic baseline change). PBT shows a double melting endotherm with the main peak at 224°C, and a smaller peak at 218°C which may be ascribed to melting of thin lamellae formed during secondary crystallisation [8]. Blend 0T (with no added catalyst) shows behaviour indicative of the homopolymers: a shallow baseline shift between 122 and 140°C, ascribed to the T_g of the PC-dominated phase, and a dual endotherm similar to PBT. The shift in T_g (140 to 122°C) shows that some phase mixing has occurred. This shift corresponds to a homogeneous mixture of PC with 15% PBT calculated from the Fox equation [9] (using T_g values of 318 and 413 K for PBT and PC, respectively), which agrees well with a value of 12% reported previously [10]. The blends with 50 to 150ppm catalyst show no discernible glass transition, and with increased catalyst level they exhibit a slight lowering of the endothermic peak temperatures and the disappearance of the low temperature endotherm. This behaviour may be attributed to an increased quantity of phase-mixed PC present in the PBT phase, reducing the efficiency of the primary crystallisation process and inhibiting secondary crystallisation. In contrast, the 200T and 300T blends show vastly different behaviour to the others: 200T exhibits only a vestige of the semi-crystalline behaviour of PBT, with a shallow exotherm between 105 and 130°C and a broad, diffuse endotherm between 165 and 210°C; 300T displays no discernible crystallinity but only a T_g at 80°C, which agrees well with the value of 86°C predicted by the Fox equation for a homogeneous 50:50 material.

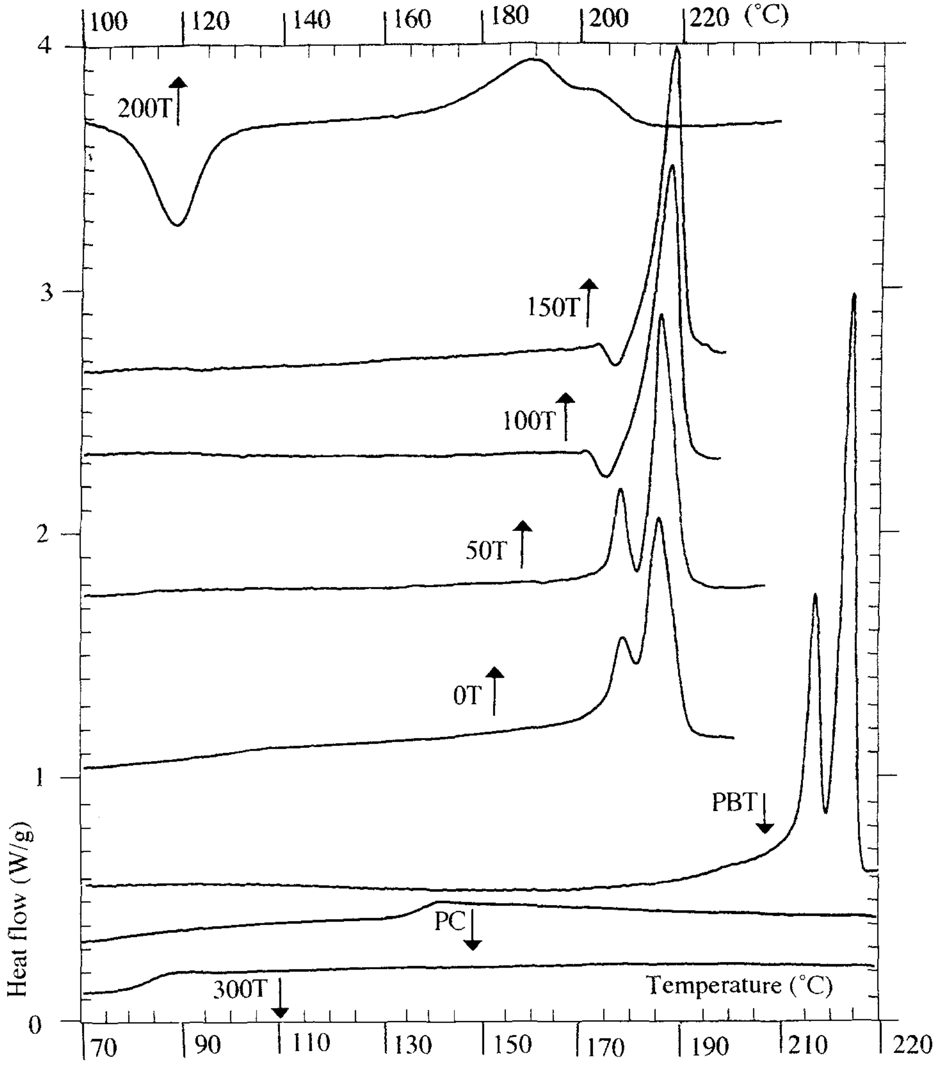


Figure 2. DSC curves for the homopolymers and blends. PC, PBT and 300T are shown over the temperature range 70 - 230°C (lower x-axis scale), whereas the other blends are displayed on a displaced scale 100 - 240°C (upper x-axis scale).

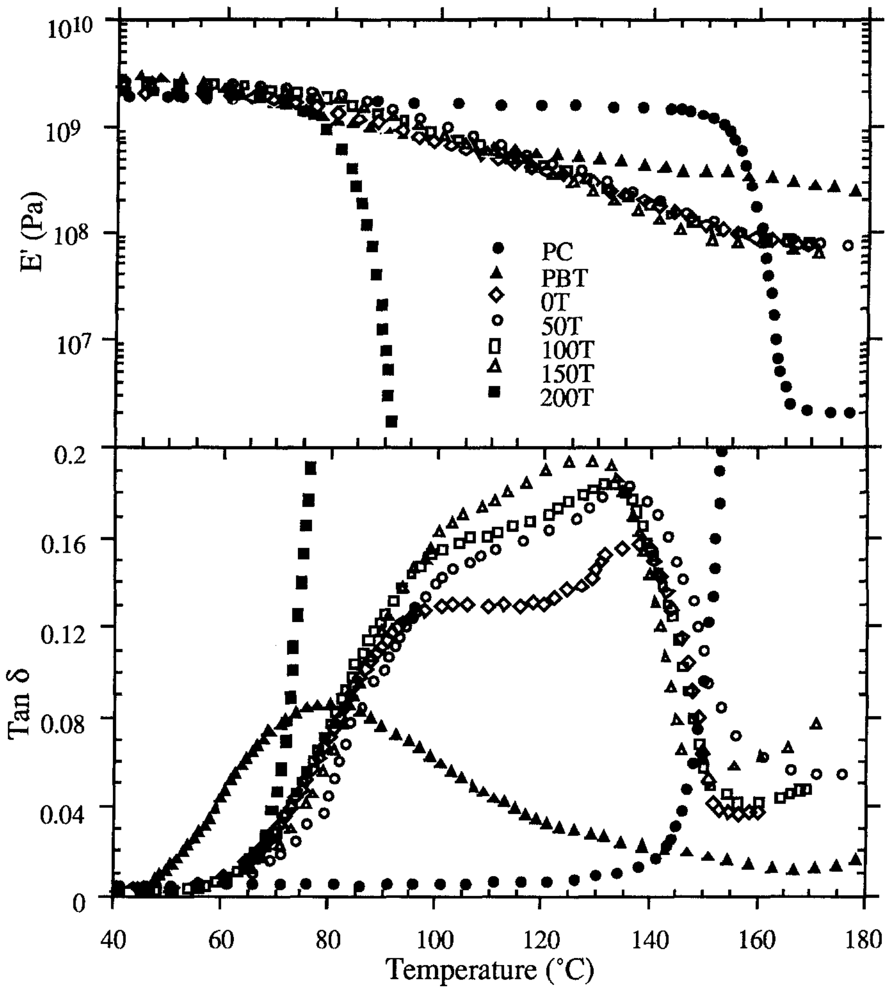


Figure 3. Dynamic flexural modulus (E') and mechanical damping (tan δ) versus temperature for the homopolymers and blends.

Dynamic mechanical analysis. The curves in Figure 3 show storage modulus (E') and damping (tan δ) versus temperature data for the homopolymers and blends. Table 1 summarises the essential transition data derived from these curves. The onset of the glass transition in PBT and PC, observed as a rise in tan δ and a concomitant drop in E', occurs at ~140 (peak at 160°C) and 45°C (peak at 80°C), respectively. At T_g, the amorphous PC exhibits a typical three decade drop in E', whilst the semi-crystalline PBT exhibits a much smaller drop of around half a decade. Blend 0T shows a broad, merged damping curve with an onset temperature of ~60°C, a distinct peak at 138°C and a shoulder at approximately 95°C, ascribed to PC- and PBT-dominated relaxations, respectively. The significant temperature shifts of the transition peaks indicate that some phase mixing has occurred during melt blending [5, 10, 11]. In addition, the broadening of the transition region results from transesterification at the phase boundaries, producing AB-block copolymers of PC-PBT which promote interphase mixing [12, 13] and result in thickening of the interphase region [14]. Thus, the 0T material has the structure of a compatibilised blend or alloy with a multiphase morphology of PC- and PBT-dominated phases and a significant interphase volume. The PBT phase is still capable of a high degree of crystallinity as evidenced by DSC and the modulus plot in Fig. 3, which shows a high value of E' (~10^8 Pa) maintained at temperatures >160°C. Adding further catalyst results in a higher degree of transesterification during the 10 minute mixing cycle. Thus, as the catalyst level is increased the "blends" actually comprise increasingly complex mixtures of the homopolymers and various AB-type block and statistical copolymers of PC and PBT. The damping curves for the 50T, 100T and 150T blends show that the peak and shoulder exhibited by the 0T material merge into one broad peak, indicating that the addition of catalyst causes an increase in phase mixing resulting from higher degrees of transesterification. However, the modulus-temperature behaviour of these blends is very similar to that of 0T indicating that the degree of crystallinity of the PBT-based moieties is essentially unchanged, in agreement with the DSC data. Upon the addition of 200 ppm of TOT, the DMA curves show no indication of multiphase behaviour only the rapid rise in damping and drop in modulus indicative of an essentially single-phase material. Thus, the degree of transesterification in 200T has increased to a point where predominantly statistical and short random-block copolymers are formed which do not crystallise on cooling, but vitrify to produce an amorphous glass. A qualitative measure of miscibility in blends can be obtained using the Utracki-Jukes equation [15]:

$$w_1 \ln(T_g/T_{g1}) + k\, w_2 \ln(T_g/T_{g2}) = 0 \qquad (1)$$

where w_i and T_{gi} are the weight fractions and glass transitions of the homopolymers. A value of $k \approx 1$ indicates a miscible system, and the proximity to unity of a k value calculated from one of the glass transitions of an immiscible blend indicates the degree of phase mixing. Thus, k values calculated from the DMA data for the blends (see Table 1) show increased miscibility with catalyst content, with k varying from 2.92 for 0T to 1.03 for 200T, indicating the latter to be an essentially homogeneous mixture.

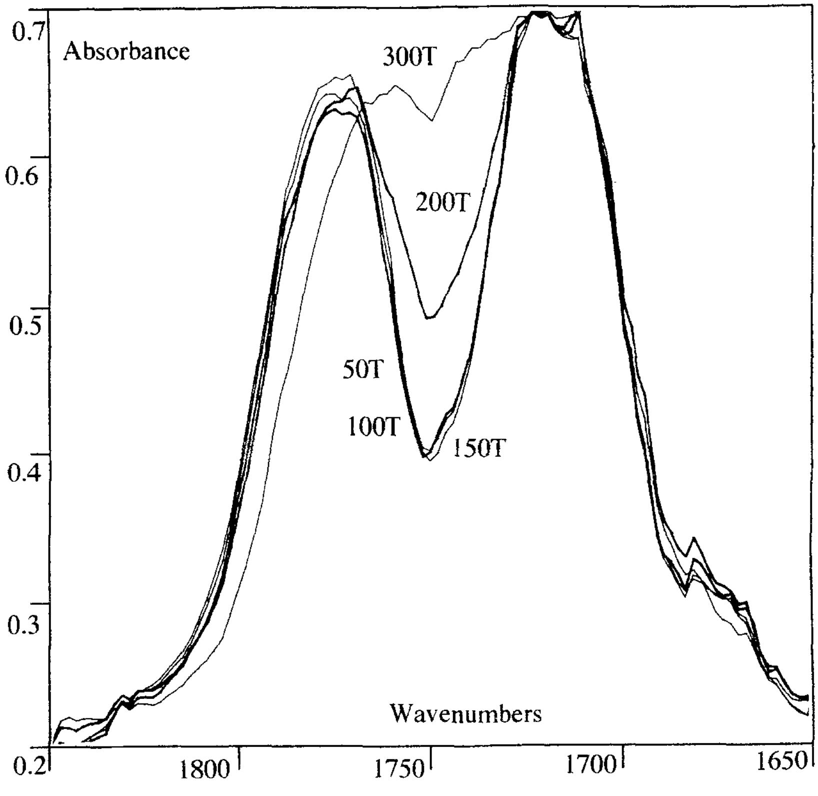
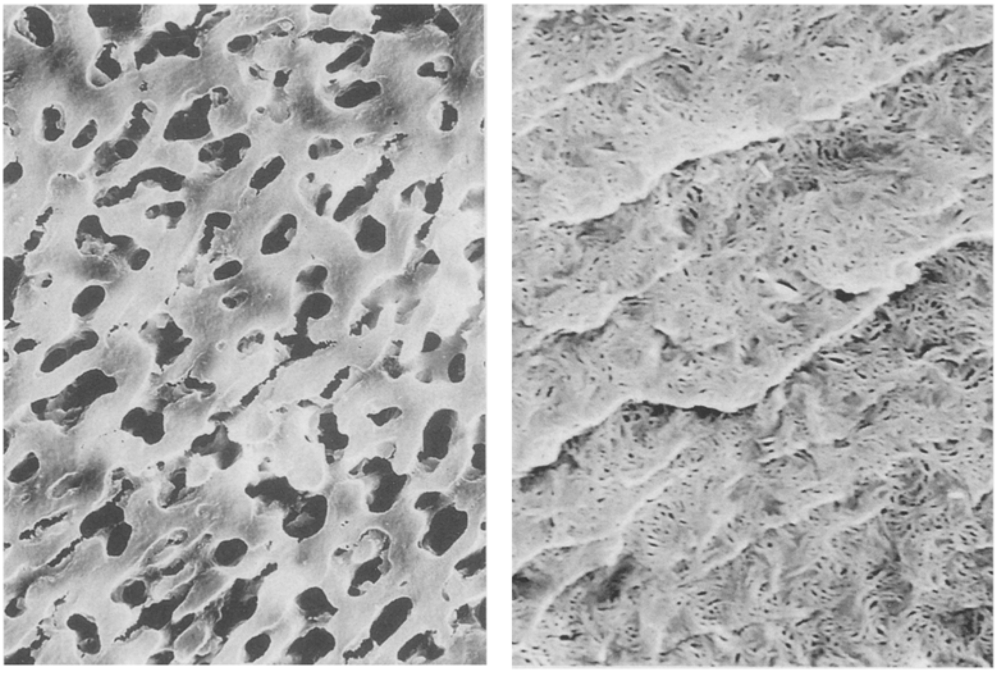


Figure 4. FTIR spectra of blends with added catalyst (50T, 100T, 150T, 200T, 300T)

FTIR spectroscopy. Figure 4 shows the evolution in the IR spectra from 1650 to 1850 wavenumbers for the blends with added catalyst. The blends with < 200 ppm TOT show essentially identical spectra corresponding mainly to the carbonyl stretching absorptions of PC and PBT at 1780 and 1720 wavenumbers [2], respectively. At higher degrees of transesterification other carbonyl absorptions evolve at 1740 and 1770 wavenumbers, which are characteristic of aromatic ester units and mixed aliphatic-aromatic carbonates formed during the reaction [2, 3]. The growth of these reaction-induced absorptions in the spectra of the 200T and 300T blends results in the peaks becoming increasingly convoluted until for 300T, only a virtually lone, broad carbonyl peak is observed. Thus, the FTIR results indicate that significantly higher degrees of transesterification occur only at catalyst addition levels of >150 ppm, in accordance with the results from thermal analysis.

Scanning electron microscopy. The effect of the degree of transesterification on blend morphology is illustrated clearly in Figure 5, which shows SEM micrographs of the solvent-etched 0T and 50T blends. Blend 0T exhibits a relatively coarse bicontinuous morphology in which the PC-based phase has a size scale of ~5 µm, whereas the 50T blend shows a much finer, sub-micron, bicontinuous morphology. The morphologies of the other blends were not amenable to solvent etching as both 100T and 150T were unaffected by the solvent, whereas 200T and 300T appeared to be completely soluble. This change in solubility with increasing transesterification has been ascribed [3] to the formation, at low degrees of reaction, of block copolyesters with reduced solubility followed, at higher degrees of reaction, by completely soluble statistical copolymers. The preliminary results on catalysed systems reported in this study agree with this evolution in structure and indicate that as the degree of transesterification increases, the blends comprise increasingly complex mixtures of the homopolymers and various AB-block copolymers, with concomitant changes in their thermal behaviour.



Blend 0T ___ 5 µm Blend 50T ___ 1 µm

Figure 5. SEM micrographs for 0T (no added catalyst) and 50T (+50ppm of TOT).

Acknowledgements

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