Novel poly(butylene terephthalate)/poly(vinyl butyral) blends prepared by in situ polymerization of cyclic poly(butylene terephthalate) oligomers

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Abstract

Blends of in situ polymerized PBT from cyclic oligomers (c-PBT) and PVB were prepared with varying compositions and compared with mechanical blends of conventional PBT and PVB. The materials were characterized by a variety of techniques including DSC, DMTA, DETA, FTIR, NMR and GPC. It was found that the in situ prepared blend of c-PBT/PVB has one glass transition temperature and shows evidence of miscibility. In contrast, the conventional blend of PBT/PVB shows incompatibility after blending. The cause of miscibility in the in situ prepared PBT/PVB blends is thought to be the formation of a graft copolymer. These results show that there are unique possibilities for in situ processing by combining polymerization of cyclic polyester oligomers with blending.
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Keywords: Cyclic polymers; Blending; PBT

1. Introduction

Polyesters such as poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) are being increasingly used in products ranging from packaging to automotive components, and now account for some 11% of the annual volume of engineering plastics [1]. PBT in particular, with its high stiffness, strength and dimensional stability together with low water absorption and good chemical and electrical resistance finds wide application in engineering, especially in automotive, construction and structural applications [2]. It is estimated that the total world consumption of PBT in moulded products was 193,000 tonnes in 1996 with an average growth rate of 8% per year [1]. However a consequence of such increasing use is a growing problem of waste management and an increasing desire for recycling options, especially for the automotive sector. Recycling is often not cost competitive and the recycled plastics usually suffer some degradation in properties, though some recycling of PBT-PC blends from automotive applications has been developed commercially [3].

Recently, a unique and effective method to convert waste polyesters to cyclic polyester oligomers has been developed. Linear high molecular weight PBT has been depolymerized and converted to cyclic oligomers [4–8]. A variety of cyclic polyester oligomers have been successfully prepared by ring/chain equilibration (cyclo-depolymerization) of the corresponding polymers in dilute solution with various catalysts. These cyclic oligomers are then readily polymerized to high molecular weight polyesters in the presence of initiators within a few minutes.

The conditions of polymerization of cyclic PBT oligomers and suitable catalysts for polymerization have been studied previously [4–8] and it was discovered that cyclic PBT oligomers can be polymerized to high M_W polymers using cyclic stannoxane catalysts in about 3 min at 190 °C. The polymerization of cyclic PBT oligomers with a catalyst is an athermal process because it is an entropically driven ring-expansion polymerization. This is as important as the high M_W of the resulting polyesters because the system will not thermally degrade thick sections or significantly raise mould temperatures. Only a small amount of heat is generated during the crystallization process.

Cyclic oligomers have many advantages. They have a low processing viscosity which can be as low as 17

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centipoise (water-like). They can be processed rapidly, since cyclic oligomers can be polymerized in as little as 20 s, or as long as 10 min or more, depending on the process requirements. There are no chemical emissions while processing and cyclic oligomers are relatively low-cost starting materials.

Cyclic polyester oligomers are ideal materials for a new generation of composite applications. Conventional engineering thermoplastics, such as PBT, often have competitive high temperature properties with thermosetting resins, yet they cannot be processed by traditional means into advanced composites because of their high viscosities. Cyclic oligomers have the low viscosity necessary for making composite binders via melt infusion; they are capable of rapid polymerization and crystallization at the processing temperature into a heat resistant and solvent resistant composite matrix. They also have sufficient integrity to support the stresses of composite applications and they are thermoplastic and thereby capable of being recycled through being reground, remelted and reprocessed into second generation material or depolymerized into cyclic oligomers. Replacement of thermosets by thermoplastics is a prime strategy of polymer life-cycle engineering [9]. Composites based on in situ polymerization from low-viscosity oligomers could overcome many of the processing problems of liquid resin composite molding techniques such as reinforced reaction injection moulding (RRIM) or resin transfer moulding (RTM) [10].

A second application of polymers from cyclic oligomers with enormous potential for novel structures and materials is in blends with other thermoplastics. These blends may be either miscible [11] or immiscible [12,13] and both types may have useful properties and structures inaccessible by other means [13]. The subject of this paper is the preparation of miscible PBT/poly(vinyl butyral) (PVB) blends by in situ polymerization of cyclic PBT oligomer in the presence of polyvinyl butyral.

PVB is an industrially important polymer widely used in laminated safety glass and surface treatments. It is prepared by reacting polyvinyl alcohol (PVA) with butyraldehyde in an acid medium [14]. Substantial amounts of unreacted vinyl alcohol units typically remain in the chain and so PVB is best regarded as a random copolymer of vinyl butyral and vinyl alcohol units. The vinyl alcohol unit is polar and hydrophilic and the vinyl butyral unit is hydrophobic. Random copolymers are able (and in fact very likely) to form miscible blends with other homopolymers because of intra-chain repulsion between different units in the copolymer [15,16]. For this reason PVB has been found to form compatible or miscible blends with a number of polymers. Systems which we have investigated include blends of PVB with poly(meythyl methacrylate) [17], with poly(3-hydroxybutyrate) [18] and the ternary crystalline system poly-(vinyl butyral)/(poly(vinyl alcohol)/nylon 6 [19].

In this study, as one of the potential applications of cyclic PBT oligomers, novel blends of PVB with PBT were prepared by in situ polymerization of cyclic PBT oligomers. Blends were also prepared by blending PVB and conventional linear PBT. The blends are characterized by a number of methods and comparisons made between blends based on linear and cyclic material. Finally some suggestions are offered as to the origin of the behaviour.

2. Experimental

2.1. Materials

Poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate), 18–20% hydroxy content (PVB), poly(1,4-butylene terephthalate), $M_v \sim 38,000$ (PBT) and antioxidant Irganox 1010 were procured from the Aldrich Chemical Company. The cyclic oligomers of PBT (c-PBT), with stannoxane catalyst were provided by the Cyclics Corporation.

2.2. Mixing

Blends of PVB and cyclic PBT were prepared in situ by melt mixing PVB and cyclic PBT oligomer (with 0.5 mol% initiator and 0.2 wt% of Irganox 1010) at 190 °C for 6 min in an Atlas LMM Laboratory Mixing Molder. Samples were subsequently prepared for testing by melt compression at 190 °C for 4 min.

Melt-blending of conventional PBT with PVB took place in a twin-screw micro-compounder (DACA Instruments Model 20000A) at 235 °C for 6 min. This was followed by melt compression at 235 °C for 4 min.

2.3. Characterization

2.3.1. DSC
Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC-7 calibrated with indium. Experiments were run with samples ranging from 10 to 15 mg under dry nitrogen to prevent moisture and oxidative degradation. Samples were first equilibrated at -50 °C then heated to 250 °C. Both the linear and cyclic blends were obtained by annealing at 250 °C for 5 min and cooling at a rate of 20 °C/min to -50 °C.

2.3.2. DMTA
Dynamic mechanical thermal analysis (DMTA) used a Rheometrics Scientific IV in single cantilever mode bending with rectangular samples of dimensions 38 mm × 12 mm × 2 mm. A dynamic temperature scan was used from -50 to 150 °C at a heating rate of 5 °C/min and a frequency of 1 Hz.

2.3.3. Dielectric measurements
Measurements of the complex dielectric function were made with a Novocontrol BDC-S system composed of a frequency response analyzer (Solartron Schlumberger FRA

1260), a broad band dielectric converter and an active sample cell containing six reference capacitors from 25 to 1000 pF. Measurements were made over a frequency range from 1 to 100 Hz. The samples were kept between two gold-plated stainless steel plates of 20 mm diameter with a separation of 100 μm resulting in a sample capacitance of about 100 pF. Samples were gold plated to about 30 nm thickness on both sides prior to measurements. Care was taken so that the samples completely filled the capacitor cell. The sample temperature was varied from −50 to 150 °C.

2.3.4. FTIR

Fourier transform infra-red spectra were obtained on an IBM IR44 FTIR spectrometer. A total of 128 scans at a resolution of 1 cm^{-1} were signal averaged. Samples were dissolved in THF and cast into thin film on a Teflon sheet under a slow stream of nitrogen. The concentration of the solution used ranged from 2 to 6% (w/v). The thin films were dried at 60 °C for 3 days under vacuum before testing.

2.3.5. NMR

^{1}H NMR spectra were collected on a Bruker DPX300 spectrometer in THF-*d* solution with tetramethylsilane as an internal standard.

2.3.6. GPC

Gel permeation chromatography was performed using Polymer Laboratories high temperature GPC PL-220 equipped with a Watt high temperature light scattering detector containing a 690 nm diode laser. Experiments were performed at 150 °C in trichlorobenzene using a concentration of approximately 20 mg/ml for all polymer samples.

3. Results and discussion

3.1. DSC

Fig. 1 shows both the glass transition and melting behaviour of mechanical PVB/PBT blends over a temperature range of 0–250 °C using commercial samples of PBT. For unblended PBT (curve (a)) there an indication of a T_g at around 44 °C and a crystalline melting peak at 225 °C. In contrast, for unblended PVB (curve (f)), a T_g is indicated at around 78 °C. Over a range of PVB/PBT blend compositions (curves (b)–(e)) the T_g of PVB is still indicated though the magnitude of the peak decreases with decreasing PVB content. This suggests that the PVB remains phase separated regardless of composition range. The T_g of PBT does not appear clearly in the blends—however a crystalline melting peak is visible for all blend compositions. The position of the melting point does not change with composition, but the peak does split for some compositions, and this may be due to the two different types of crystallites present, as discussed by Miller [4]. These results suggest no
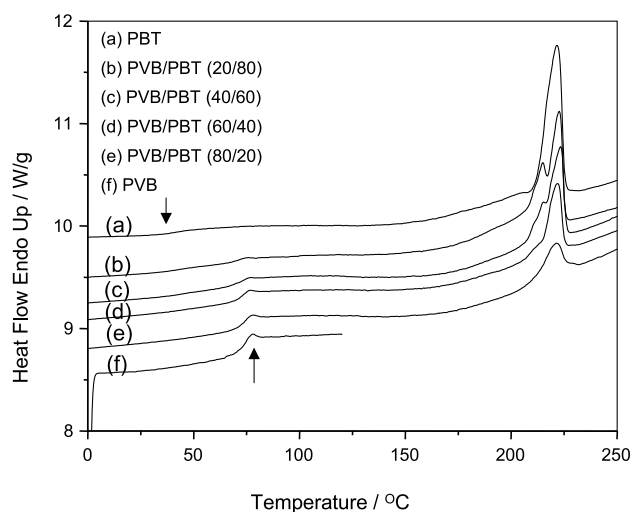

Fig. 1. DSC thermogram of PVB/PBT blends (annealed at 250 °C for 5 min, cooled at 20 °C/min).

miscibility between PVB and PBT in conventional mechanical blends.

In contrast, the in-situ blends of c-PBT with PVB (Fig. 2) do not show a clear T_g for PVB in our annealed samples. There is also a broad transition in the melting region at approximately 225 °C rather than the distinct crystalline melting peak seen with PBT. This indicates that crystallinity is suppressed by the blending process. Taken together, these observations suggests miscibility of PVB with c-PBT leading to a one-phase system.

3.2. DMTA

Further evidence for miscibility in blends of cyclic PBT with PVB, in contrast to blends with conventional linear PBT, is shown by the DMTA curves of Figs. 3 and 4. These show the loss modulus E'' as a function of temperature for a series of different compositions. The blend with
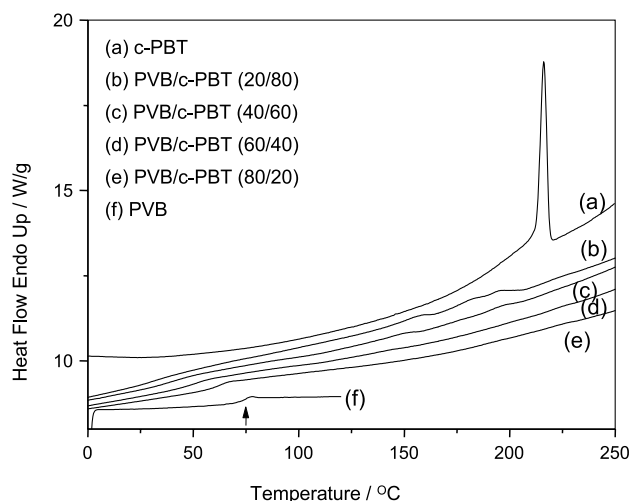

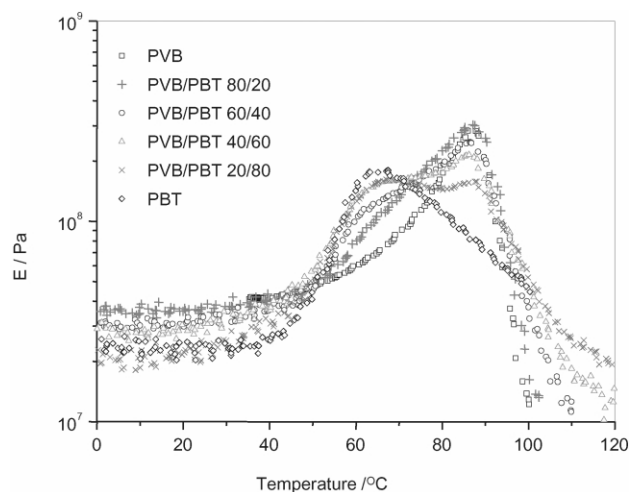Fig. 2. DSC thermogram of in situ PVB/c-PBT blends (annealed at 250 °C for 5 min, cooled at 20 °C/min).

Fig. 3. Dynamic loss modulus (E'') of PVB/PBT blends at 1 Hz.

conventional PBT shows two peaks at temperatures characteristic of pure PBT and pure PVB. The position of each peak does not change with composition. It is found that mechanical blends of PVB/PBT exhibit relaxation peaks corresponding to PVB (at 68 °C) and PBT (around 88 °C) particularly in blends with a high PVB ratio. The relaxation peak corresponding to PBT appears as a small shoulder in blends of low PBT content (Fig. 3). These findings are in general similar to those obtained by DSC (Fig. 1). Unlike the macrophase-separated mechanical blends with two relaxation peaks, the in-situ blends of PVB/c-PBT exhibit a single relaxation peak (Fig. 4). The relaxation peak corresponding to c-PBT polymer in the in-situ blends is absent, suggesting a single-phase system. Unlike the PVB/PBT mechanical blend system, a systematic decrease in the relaxation temperature with the addition of c-PBT oligomers is noted (Fig. 4) in the in-situ blends. It is also noted that the loss modulus peaks in in-situ blends gradually decrease in height and finally broaden with increasing amounts of c-PBT polymer in the blend.
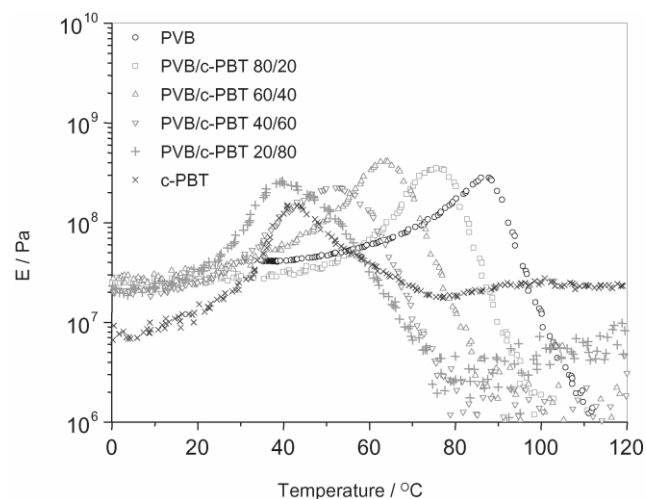
3.3. DETA

Fig. 5 shows dielectric tan E''/E' for PVB/PBT mechanical blends over a temperature range from room temperature to 100 °C and at a frequency of 50 Hz. The spectra show a broad relaxation peak at around 50–52 °C, which can be associated with PBT, and one around 78 °C corresponding to PVB. The peak positions remain largely unaltered with blend composition and in all cases there are two relaxation peaks, which again suggests immiscibility for PVB/PBT mechanical blends.

Fig. 6, for polymers made from c-PBT oligomers, shows a single relaxation peak for each in-situ blend. The relaxation peaks and temperatures appear to increase as the amount of PVB is increased. These results are further evidence that there is no phase separation for in-situ blends of PVB and c-PBT. The broad peak at higher concentrations of c-PBT in in-situ blends may indicate the compositional heterogeneity. These findings support those obtained by DMTA and DSC.

3.4. FTIR

Another source of information comes from FTIR after THF was used as a solvent followed by solution casting (Fig. 7). It is well-known that THF is a good solvent for PVB but not for PBT. The spectra for PVB-cPBT and for PVB-PBT are very similar. The lower curve for the mechanical blend of PVB and PBT is indicative purely of the behaviour of PVB since that is the only soluble phase. These curves differ from those in which c-PBT is the major component for the in-situ blends. If the blend of PVB-cPBT were immiscible, we would expect similar behaviour throughout to the lower curves in which only the PVB component is represented.

There is no change in the peak intensity of the –OH (3610 cm^{-1} for ν_{-OH}) group of PVB in the PVB/PBT 60/40 blend compared with pure PVB. The absorbance at

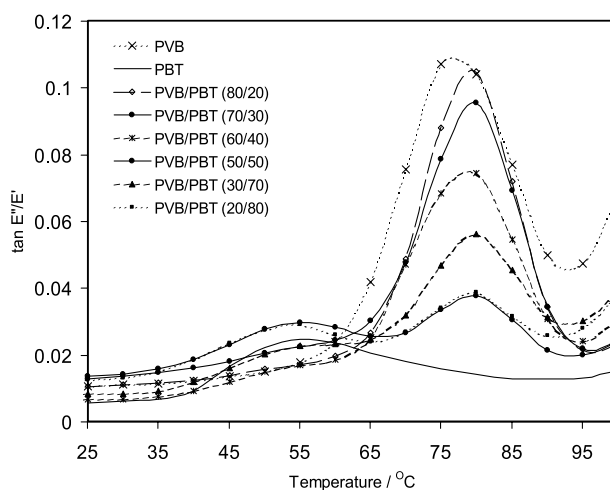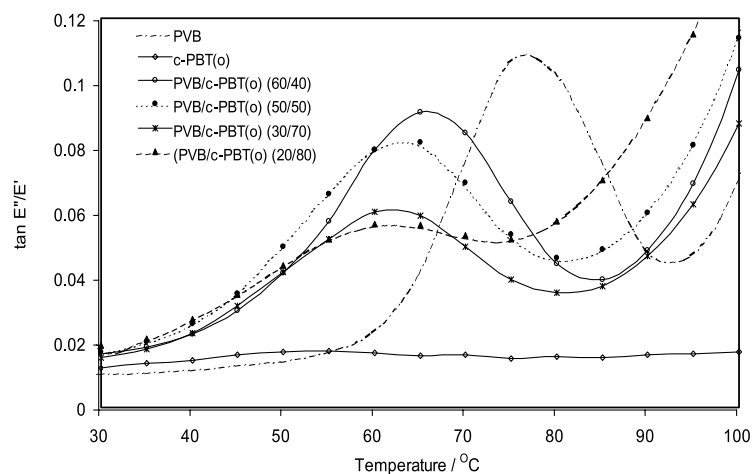Fig. 4. Dynamic loss modulus (E'') of in situ PVB/c-PBT blends at 1 Hz.

Fig. 5. Dielectric tan δ of PVB/PBT blends at 50 Hz.

Fig. 6. Dielectric tan δ of in situ PVB/c-PBT blends at 50 Hz.

1730 cm^{-1} is from the $\nu_{C=O}$ ester group of PBT. As the concentration of PBT is increased the absorbance at 1730 cm^{-1} also increases and it maintains the same trend in the in-situ blends also. However, the absorbance peak corresponding to the $-OH$ (ν_{-OH} at 3610 cm^{-1}) of PVB gradually decreases with increasing c-PBT in the in-situ blend. This reduction suggests a chemical reaction such as grafting of c-PBT to PVB through the -OH group by transesterification (Fig. 10) leading to a graft copolymer and hence miscibility of c-PBT and PVB.

3.5. NMR

The NMR results (Fig. 8) are again from solution studies using deuterated THF as a solvent. THF is a good solvent for PVB but not for PBT. Again one would expect the behaviour of PVB alone to be exhibited by immiscible blends since only the PVB is present in the solvent. Fig. 8

shows the ^{1}H-NMR spectra of in situ PVB/c-PBT blends of various compositions together with the spectrum for pure PVB. Several new peaks can be seen in the spectra of in situ polymerized PVB/c-PBT blends in comparison with that for pure PVB i.e. peaks at 8.09 due to aromatic protons, and 4.41 and 1.95 ppm assigned to methylenes and ester groups, respectively. A signal at 3.70 ppm assigned to methylene of 1,4-butadiol in the PBT chain and a multiplet between 1.7 and 1.9 ppm due to methylene in β and γ are also present. This indicates that PBT is present in the blend solution. Also it can be seen that the ratio of integrals at 0.88 ppm due to the methyl protons of the butyral group of PVB, and 8.0 ppm representing the aromatic protons of the PBT molecule is correlated with composition. It decreases with increasing PVB in the in situ blends. This supports the hypothesis of a miscible system in which there is a link between the PVB and c-PBT chains.
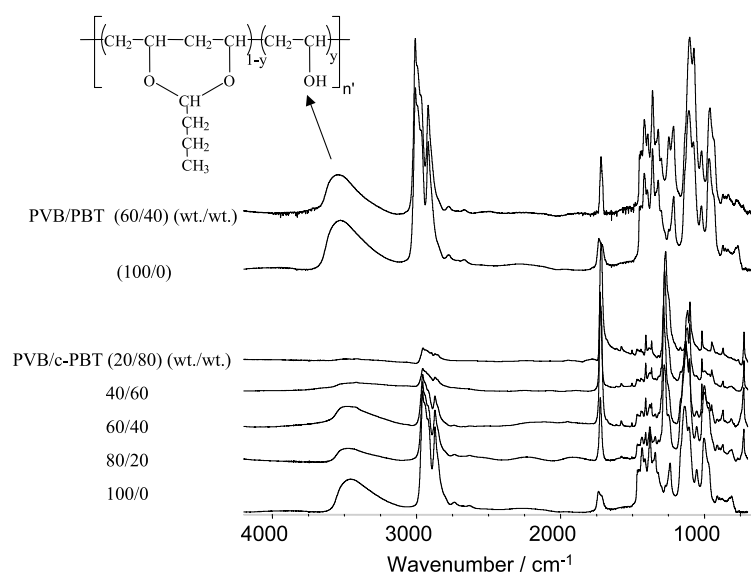

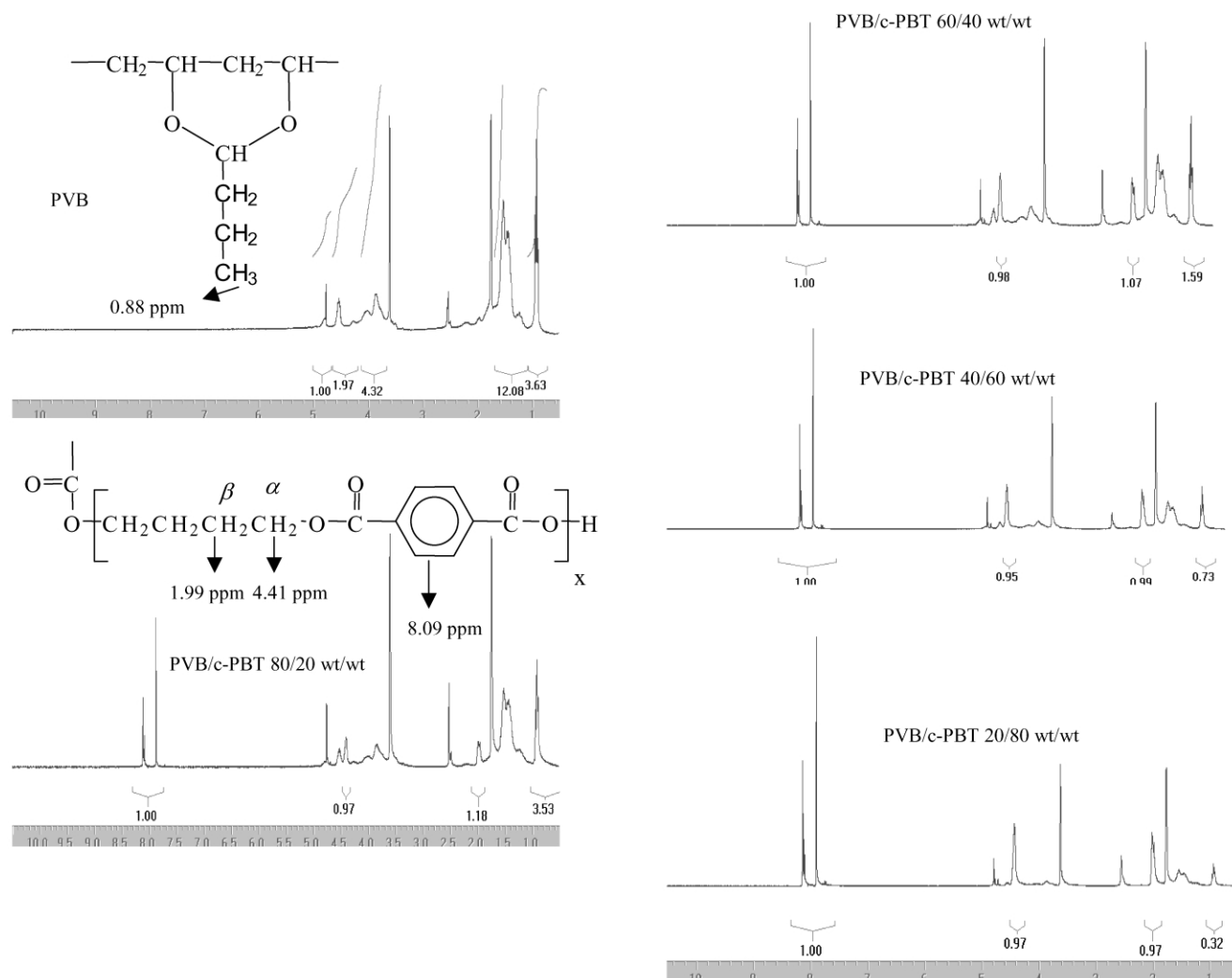Fig. 7. FTIR of in situ PVB/c-PBT and PVB/PBT blends.

Fig. 8. NMR of in situ PVB/c-PBT blends.

3.6. GPC

High temperature GPC results, using a common solvent (1,2,3 trichlorobenzene) for PVB and PBT, also support miscibility. Fig. 9 shows the viscosity curve of various in situ PVB/c-PBT blends. The viscosity curve clearly indicates that there is copolymer formation in the in situ catalytic polymerization of c-PBT with PVB. The major shift in the elution volume for the in-situ blends indicates that the original homoploymers of PVB have been modified by the c-PBT oligomers. Moreover, the increase in viscosity shown in Fig. 9 also indicates that there might be branching during the in situ polymeriz-ation in the presence of catalyst. Table 1 also suggests branching with increasing amounts of c-PBT oligomers. Although the PDI data are not consistent throughout, they do suggest that PDI increases as the proportion of c-PBT increases in the blends. The weight-average molecular weight (obtained from light scattering data) appears to lie in between the values for the homo-polymers in all except the 60/40 blend. One of the

reasons for low molecular weights might be the formation of a branched copolymer instead of a linear one. The weight-average molecular weight, obtained by light scattering is based on measurements of the radius of gyration of the hydrodynamic volume of the polymer, which is always lower in branched polymers.

In order for miscibility to occur, it is clear that there must be some chemical interaction between c-PBT and PVB, which results in a one-phase system. It is suggested from the above results that the hydroxyl group from the PVB

Table 1
GPC data of in situ PVB/c-PBT blends

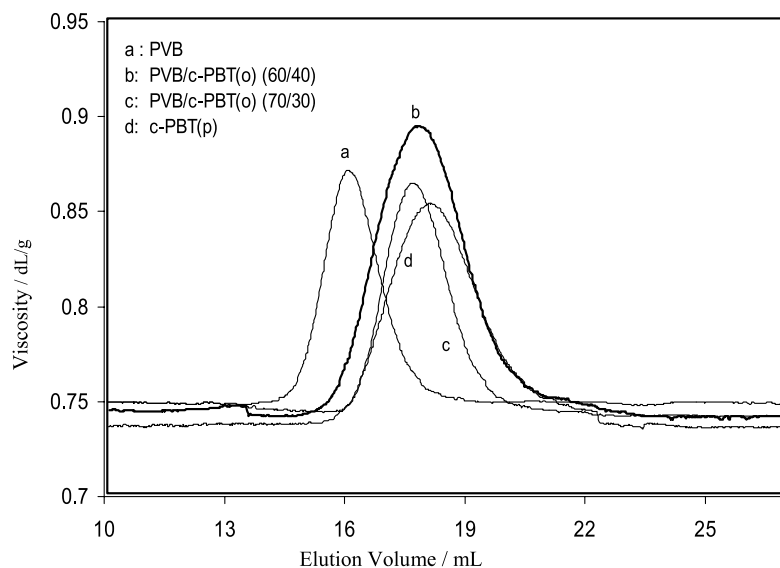| PVB (wt%)	M_W ($\times 10^5$ g/mol)	M_Z ($\times 10^5$ g/mol)	PDI (M_W/M_n)
100	1.45	2.73	1.2
70	0.28	0.91	1.8
60	5.32	2.37	1.6
30	0.22	2.23	2.2
20	0.67	5.84	1.9
0	0.87	3.08	1.5

Fig. 9. Viscosity vs. elution volume of PVB/c-PBT blends.

interacts with a carbonyl group in phthalate from the c-PBT to produce a graft copolymer as shown in Fig. 10. This mechanism is consistent with the results and would explain the observed miscibility behaviour of c-PBT with PVB.

4. Conclusions

Cyclic oligomers of PBT have successfully been polymerized in situ, and blended with PVB in the presence of a stannoxane initiator. These blends have been characterised by a large variety of complementary techniques. They were compared with blends prepared from conventional, linear PBT blended with PVB.

Results from all these techniques show significant differences between blends with cyclic and conventional PBT and indicate clearly that c-PBT-PVB blends are miscible whereas conventional PBT-PVB blends are immiscible. A mechanism of graft copolymer formation, consistent with the observed behaviour, is suggested.
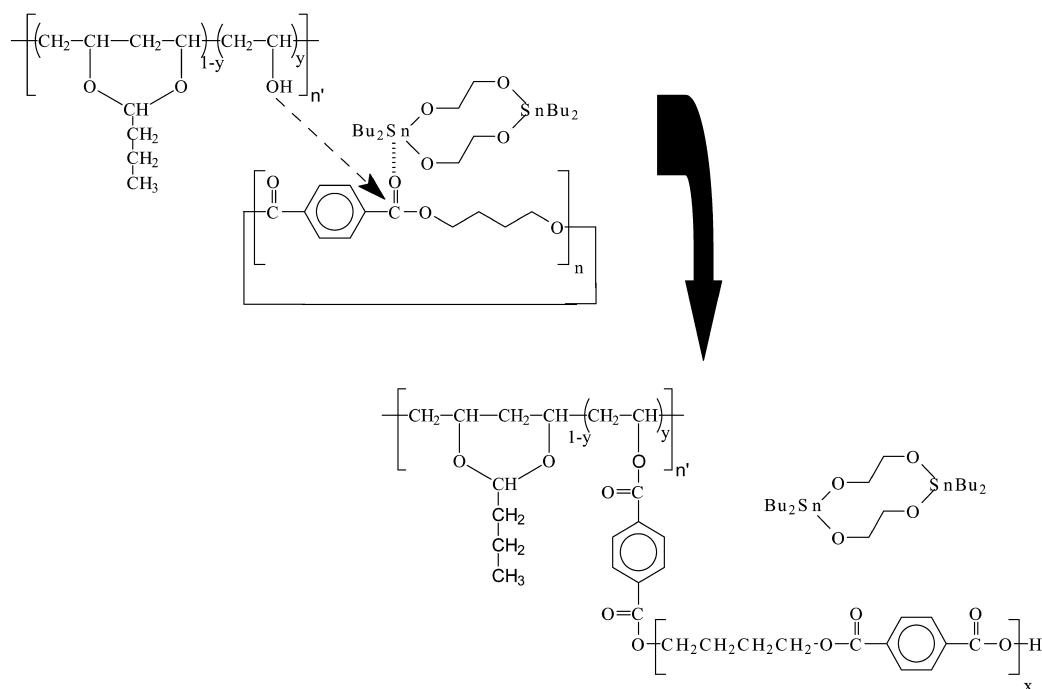

Fig. 10. Formation of graft copolymer of PVB-PBT.

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