# Evaluation of polyesters and their blends with bisphenol-A-polycarbonate

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A new polyester, poly(2-ethyl-2-methylpropylene terephthalate) (PEMPT), as well as poly(1,5-pentylene terephthalate), poly(1,7-heptylene terephthalate) and poly(1,9-nonylene terephthalate), have been synthesized and characterized with respect to specific criteria including phase behaviour studies with bisphenol-A-polycarbonate (PC). Binary blends of the four polyesters with PC (50/50 wt%) all exhibit two amorphous phases when an inhibitor is present to prevent transreactions. When prepared without inhibitor, the same blends are single phase, indicating that transreaction has occurred between blend components. Additionally, thermal analysis shows that PEMPT is amorphous and has improved thermal stability compared to the other aliphatic–aromatic polyesters studied. These characteristics are attributed to ethyl–methyl substitution of the propylene group in PEMPT.

**(Keywords: polyesters; blends; phase behaviour)**

## *Introduction*

Numerous phase behaviour studies have been conducted on polyester and polyester/polycarbonate blends[1–38]. One unique aspect of these blends is their ability to undergo 'interchange reactions' or 'transreactions' between blend components. Interchange reactions lead to the formation of block/random copolymers. These block/random copolymers have a homogenizing effect on the blend, improving the degree of miscibility between components[1–8]. At the extreme, a two-phase blend can be transformed into a single-phase system due to these species. Conflicting reports on the degree of miscibility of poly(butylene terephthalate) (PBT)/bisphenol-A-polycarbonate (PC) and poly(ethylene terephthalate) (PET)/PC blends may in part be attributed to the lack of identification and quantitative measurement of interchange reaction in these systems[9–21]. The insolubility of PBT and PET to nearly all solvents commonly employed for spectroscopic examination inhibits the use of quantitative n.m.r. and i.r. analysis for this task. In cases where extensive transreaction has occurred, enhancing solubility, these techniques have been successfully employed to identify transreaction[22–25]. Decomposition reactions have also complicated the analysis of the transreacting blends, particularly in the PC/PET system[24–26]. Additionally, in blends where one or both components can crystallize, clear identification of the level of partial miscibility, as measured by the shifting of glass transition temperatures ($T_g$s) determined by thermal analysis, can be obscured by crystallization exotherms and endotherms[6,8,21,27]. Lack of clear knowledge of the shifts in miscibility combined with the inability to measure low levels of interchange reaction has made correlating phase-behaviour changes to the extent of interchange reaction difficult.

We wish to quantitatively examine the effect that interchange reaction has on the phase behaviour of polyester/PC blends. Initial candidates for this work are the industrially significant PBT/PC and PET/PC blends. However, from the above discussion, these blends are not ideally suited for these investigations. What is required is a model polyester that can replace PBT and PET in blends with PC. The ideal polyester should satisfy the following criteria: it should be structurally similar to PET and PBT, amorphous or slow to crystallize and soluble in common solvents; it should have a $T_g$ well separated from that of PC; it should be thermally stable at the temperatures required for exchange reaction; and it should form a two-phase blend with PC.

Based on these criteria, polyesters for initial screening can be selected. It is well known that aliphatic-terephthalate polyesters with an odd number of main-chain methylene groups (particularly those with five or more) have improved solubility and slower crystallization rates than their even-numbered counterparts[39]. They also have $T_g$s well separated from that of PC[23,40]. The three polyesters, poly(1,5-pentylene terephthalate) (PPT), poly(1,7-heptylene terephthalate) (PHT) and poly(1,9-nonylene terephthalate) (PNT), appear to meet the criteria and have been synthesized for study. In addition, a new polyester, poly(2-ethyl-2-methylpropylene terephthalate) (PEMPT), has been synthesized for study.

## *Experimental*

The diols, 1,5-pentanediol (Aldrich, 97%), 1,7-heptanediol (Aldrich, 95%), 1,9-nonanediol (Aldrich, 98%) and 2-ethyl-2-methyl-1,3-propanediol (EMPD) (Aldrich, 98%) for the synthesis of PPT, PHT, PNT, PEMPT, were vacuum distilled prior to polymerization. Due to its low purity level, PHT was dried over magnesium sulfate prior to distillation. Dimethyl terephthalate (DMT) (Aldrich, +99%) was purified by recrystallization from a chloroform/heptane (2/3 v/v)

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solution. With the benefits of being both a first and second stage catalyst and having the ability to minimize acid end-group formation, titanium(IV) isopropoxide (Aldrich) was selected as catalyst[41]. It was used as received.

Polymerization of the four polyesters followed the general two-stage polycondensation procedure commonly used for polyester synthesis[42]. A 100 ml trap tube served as the reactor. All polymerizations started by placing DMT (4–7 g, 0.021–0.036 mol) and the appropriate amount of diol (50 mol% excess) in the reactor. The tube was then sealed and flushed with nitrogen followed by submersion into the 200°C oil bath. When both components had melted and were thoroughly mixed (magnetic stirring), the nitrogen line was removed briefly and the appropriate amount of catalyst (0.001 g catalyst/1 g DMT) was injected into the mixture via a 10 $\mu$l syringe. First-stage reactions were conducted for 1.5 h at temperatures from 195 to 205°C. During the second stage of reaction, a heated vacuum line at 70°C connected the reactor tube outlet to a cold trap. The heated line was required to prevent diol from crystallizing in the tube outlet. Second-stage reactions were conducted under vacuum, 0.6–1.0 mmHg, at temperatures ranging from 247 to 253°C for 2 h. After cooling, the polyesters were removed from the reactor by dissolution into 75 ml of chloroform followed by filtration (25–50 $\mu$m fritted glass funnel) and recovery (dropwise precipitation into methanol). The polymers were washed with methanol and dried under vacuum for several days at 75°C.

The polycarbonate used for blend studies was obtained from the General Electric Company. It was reported to have a weight average molecular weight of 30 600 g mol$^{-1}$ and contained no additives. The $T_g$ was measured to be 149.3°C.

Blend preparation followed two techniques. One was a codissolution/precipitation procedure. Polyester (0.5 g) and polycarbonate (0.5 g) were dissolved in chloroform (5% w/v). After mixing, they were recovered by dropwise precipitation into methanol, washed with fresh methanol followed by vacuum drying at 70°C for 12 h. The other preparation method was a solution-casting technique. Polyester (0.5 g) and polycarbonate (0.5 g) were dissolved in chloroform (5% w/v). The chloroform contained a small amount of dioctadecyl phosphite (DNOP) such that it was in a theoretical 5/1 mol ratio of DNOP/Ti catalyst. DNOP is known to be a good transreaction inhibitor for the catalyst used in the polymerization of the polyesters[25,30]. After mixing, these solutions were cast into crystallization dishes and the solvent was removed by vacuum drying, at about 300 mmHg, at 50°C. After most of the solvent had been removed, these blends were dried under full vacuum for 12 h at 70°C. All polyesters and blends were stored in a vacuum desiccator prior to study.

A Perkin–Elmer DSC-4 with a System 4 Thermal Analysis Microprocessor Controller and a Thermal Analysis Data Station was used to determine the $T_g$s and crystallization data of the polyesters. A dry ice/ethanol slurry was used for subambient cooling. Indium was the calibration standard and baseline subtraction was used during the actual runs. Sample size was 6–8 mg and reported $T_g$s are midpoint values determined from a single heating run. The thermal programme was as follows: load samples at 20°C, heat at 100°C min$^{-1}$ to 200°C, quench to −40°C, scan at 20°C min$^{-1}$ to 200°C. The rapid quenching from 200 to −40°C mimicked the quench used during blend studies. Phase behaviour identification requires clear, distinguishable $T_g$s and the rapid quench should prevent or minimize crystallization of PPT, PHT and PNT. Thermogravimetric analysis (t.g.a.) was carried out in a Perkin–Elmer TGS-2 with the controller and data station described above. Nitrogen, at about 45 ml min$^{-1}$, was used as a purge gas. Calibration employed four ferromagnetic standards: alumel, nickel, nicoseat and perkalloy. All heating scans were conducted at 20°C min$^{-1}$ with a sample size of about 5 mg. The reported decomposition temperature, $T_d$, represents the temperature at which the maximum rate of weight loss occurred.

For polyester/PC blends, the phase behaviour was determined by the appearance of either one or two $T_g$s in a d.s.c. heating scan. Thermal analysis to determine $T_g$s was conducted in the differential scanning calorimeter described above. The thermal programme used for annealing and scanning is shown below.

*Annealing*: load at 50°C; heat at 100°C min$^{-1}$ to 280°C; quench to 240°C, hold 2 min; quench to −40°C.

*Scanning*: start temperature −38°C; scan at 20°C min$^{-1}$ to 202°C; quench to 50°C.

The thermal ramp to 280°C was required to melt PC crystals that formed in the solution-cast blends. No crystallization of the PC component was observed in the solution-precipitated blends. The identical temperature programme was followed for consistency.

### *Results and discussion*

*Table 1* summarizes the d.s.c. and t.g.a. data of the polyesters. The $T_g$s of PPT, PHT and PNT agree with those reported by Smith *et al.*[40]. It is observed that the three polyesters with linear, aliphatic sequences were all able to crystallize to some extent, even with the rapid quench. Some of this crystallization occurred during the actual heating scan once the temperature was above the polyester $T_g$. In general, the reported melting temperatures, which are peak temperatures, are slightly lower than those reported by Smith *et al.*[40]. However, during the current experiment, the goal is to minimize the crystallization. No attempt was made to enhance the amount of crystallization obtained or to improve crystal perfection. All three linear aliphatic polyesters crystallized to some extent under these minimizing conditions. However, PEMPT exhibited a $T_g$ at 63°C and had no identifiable crystallization endotherm over the temperature range scanned. Random incorporation of the ethyl–methyl substituted propylene group in the polymer backbone produces an atactic polyester with a corresponding amorphous structure. The lack of crystallinity is also probably responsible for the improved

**Table 1** Thermal analysis data of PPT, PHT, PNT and PEMPT

| Polyester | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_f$ (cal g$^{-1}$) | $T_d$[a] (°C) |
|---|---|---|---|---|
| PPT | 14 | 129 | 7.5 | 421 |
| PHT | 4 | 88, 95 | 0.3 | 422 |
| PNT | −1 | 90, 96 | 10.9 | 422 |
| PEMPT | 63 | – | – | 461 |

[a] Temperature of the maximum rate of decomposition

solubility of PEMPT in chloroform compared to polyesters such as PET and PBT.

The t.g.a. data of *Table 1* show marked differences in the maximum rate of decomposition, $T_d$, between the linear aliphatic polyesters and PEMPT. Comparing the $T_d$ of PEMPT to that of PPT, PHT and PNT, a 40°C increase is observed. The removal of the $\beta$-hydrogens in PEMPT eliminates a common mechanism of decomposition of esters similar to the Chugaev reaction[43,44]. This mechanism involves the formation of a cyclic intermediate incorporating the $\beta$-hydrogens and the carbonyl, followed by decomposition to acid and alkene end groups. The stability of esters has been shown to decrease as the number of $\beta$-hydrogens increases[45]. Thus, the replacement of the $\beta$-hydrogens in PEMPT by ethyl–methyl substitution produces a more thermally stable polyester. With the thermal characterization completed, the remaining criterion to be evaluated is the phase behaviour of the polyesters with PC.

*Table 2* identifies the phase behaviour of the four blends with respect to the two preparation methods. Blends that were cast and stabilized with DNOP all exhibit two-phase behaviour. The $T_g$s of the PC-rich phase are shifted considerably lower, implying some level of miscibility of PEMPT in this phase. The $T_g$s of the polyester-rich phase are nearly identical to the pure component values. In contrast, blends that had been prepared by codissolution/precipitation show single-phase behaviour. The $T_g$s fall between the two pure component values, being somewhat biased towards the lower $T_g$ polymer. The most interesting result is the contrast in the observed phase behaviour between the two preparation techniques. In DNOP-stabilized samples, transreaction appears to be inhibited, allowing the identification of the two-phase nature of these blends. In the non-stabilized blends it appears that enough reaction occurs during the short annealing time in the differential scanning calorimeter to create a miscible, single-phase blend. Behaviour of this type has previously been reported in a PC/PBT blend; however, the annealing time was considerably longer and the annealing temperature higher[31].

One additional point to be discussed is the ability of PPT, PHT and PNT to crystallize in the blend system. The d.s.c. heating scans of the PPT/PC, PHT/PC and PNT/PC blends all showed small crystallization peaks in the temperature region associated with the $T_g$. The appearance of these crystallization endotherms very near the $T_g$s makes precise determination of the $T_g$s more difficult. The PEMPT/PC blend exhibits no crystallization endotherm and two very distinct $T_g$s are observed.

**Table 2** Phase behaviour of polyester/PC 50/50 wt% blends

| | Preparation technique | |
|---|---|---|
| Blend | Cast; DNOP-stabilized | Solution precipitation; non-stabilized |
| PPT/PC | Partially miscible<br>$T_{g1}=16°C$, $T_{g2}=103°C$ | Miscible<br>$T_g=63°C$ |
| PHT/PC | Partially miscible<br>$T_{g1}=3°C$, $T_{g2}=107°C$ | Miscible<br>$T_g=56°C$ |
| PNT/PC | Partially miscible<br>$T_{g1}=-4°C$, $T_{g2}=100°C$ | Miscible<br>$T_g=41°C$ |
| PEMPT/PC | Partially miscible<br>$T_{g1}=60°C$, $T_{g2}=117°C$ | Miscible<br>$T_g=94°C$ |

## *Conclusions*

PEMPT is an amorphous polyester with a $T_g$ of 63°C, well removed from that of PC (149°C). It is soluble in a common solvent that facilitates blend preparation. Replacement of the $\beta$-hydrogens in PEMPT produces a polyester that has improved thermal stability compared to its linear aliphatic–aromatic counterparts. Finally, PEMPT/PC blends form two amorphous phases and the present studies indicate that transreaction occurs in non-DNOP-stabilized blends. These properties make PEMPT ideally suited for quantitative phase behaviour and transreaction studies with polymers such as PC.

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