

Blends of Poly(ethylene Terephthalate) and a Polyarylate Before and After Transesterification

MASAO KIMURA,* GIDEON SALEE,† and ROGER S. PORTER,
*Materials Research Laboratory, Polymer Science and Engineering
Department, University of Massachusetts, Amherst, Massachusetts 01003*

Synopsis

Blends of poly(ethylene terephthalate) (PET) and a copolyester of bisphenol A-terephthaloyl-isophthaloyl (PAr) (2:1:1) have been studied both before and after transesterification. The physical blends exhibit phase separation in their amorphous states: a pure PET phase and a mixed PAr-rich phase. In spite of this phase separation, PET crystallinity in blends, normalized to PET fraction, surprisingly goes through a maximum at 25% PAr content. The transesterified copolymers are noncrystallizable and exhibit a single T_g between those of starting polymers, PET and PAr.

INTRODUCTION

Polyester blends have been studied both for industrial application and for academic interest. However, as polyesters readily transesterify near and above their melting points, interchange reactions commonly occur between constituents. This may occur during melt blending and in blend preparation procedures.¹⁻⁶ As the transesterification proceeds, blends convert first to block copolymers and finally to a random copolymer. This reaction concept is not new. However, the control of transesterification may provide a new method to prepare copolymers directly within processing equipment, both from miscible and from immiscible polymer blends.⁷ Such copolymers could have wider variation in microstructure than copolymers prepared directly from monomers.

In our previous paper,⁸ we have reported on the miscibility and transesterification of the miscible polyester blend pair, poly(butylene terephthalate) (PBT), and a polyarylate (PAr), a copolyester of bisphenol A-terephthaloyl-isophthaloyl (their molar ratios 2:1:1). In this paper, blends of poly(ethylene terephthalate) (PET) and this same polyarylate, before and after transesterification, have been examined. As PET is the most widely used of all polyesters, such polyester blends have been previously studied mainly from an industrial view.⁹⁻¹² On the other hand, neither properties of this binary physical blend, including miscibility, nor those of transesterified copolymer have been yet reported. We thus report here on interactions in the physical blends, on the transesterification process, and on the properties of transesterified copolymers.

A conclusion of this study is that physical blends of PET and PAr are phase-separated in their amorphous states involving a pure PET phase and a mixed phase rich in PAr. The transesterification reaction proceeds rapidly. The

* Nippon Steel Co., Inc., Kawasaki, Japan.

† Occidental Chemical Corp., Grand Island, NY 14302.

transesterified copolymers are noncrystallizable and exhibit a single glass transition temperature intermediate between the two starting polymers.

EXPERIMENTAL

Materials. The single PET sample used in this study was kindly provided by Goodyear Tire and Rubber Co., carrying the identification VFR5041 AS. Its intrinsic viscosity in trifluoroacetic acid was $[\eta] = 0.94$ dL/g at 30°C ($M_v = 81,000$). PAr was a copolyester of bisphenol A-terephthaloyl-isophthaloyl (their molar ratios 2:1:1), provided by Union Carbide Corp., under the trade name ARDEL-D100. Its intrinsic viscosity in tetrachloroethane-phenol 60:40 weight fraction solution was $[\eta] = 0.71$ dL/g. Equivalent results were obtained with a like PAr resin obtained from Occidental Chemical Corp., Grand Island, N.Y.

Blending of the two polyesters was carried out by the solution precipitation method detailed in our previous paper.⁸ The ratios of PAr and PET were 100/0, 75/25, 50/50, 25/75, and 0/100. The resultant precipitates were heated to dryness at 140°C for 2 days and subsequently used to examine the process of transesterification. As detailed later, this reaction was shown to have an induction time of ~15 min at 280°C. Therefore, films were made under the following conditions. The precipitate was put in a square mold between two metal sheets covered with aluminum foil and transferred to a hot-press held under pressure at 280°C for 4 min. After this, the film was removed from the press and quenched in ice water. A 5% NaOH aqueous solution was used to dissolve the aluminum foil from the film. The solution viscosity and thus the molecular weight did not change as the result of this brief caustic treatment. The film was subsequently washed and then dried at 50°C for 3 days in a vacuum oven. Finally, the film was kept in a vacuum desiccator prior to testing.

The transesterified copolymers were prepared from physical blends by holding at 280°C for 16 h under vacuum. Films of the copolyesters were made in the same procedure as for their physical blends.

Annealing experiment was conducted at 200°C for 30 min in a vacuum oven.

Methods. A Perkin-Elmer DSC-2 Differential Scanning Calorimeter with a Data Station was used to evaluate phase behavior and transitions. The conditions were a heating rate of 10 K/min, with ca. 200 mg sample under a nitrogen atmosphere. For the study of the transesterification process, a Perkin-Elmer DSC-1B was used.

Dynamic mechanical measurements were carried out using a Rheovibron Viscoelastomer (Toyo Measuring Instrument Co., Ltd.), Model DDV-II-B, at 110 Hz. The heating rate was ca. 2°C/min. with temperature monitored by a thermocouple connected to a digital thermometer, Model 199, Omega Engineering, Inc.

Wide angle X-ray diffraction traces were recorded with a Siemens D-500 diffractometer, using Cu-K α radiation ($\lambda = 1.5198$ Å) with a Ni filter.

RESULTS AND DISCUSSION

Physical Blends

Figure 1 gives DSC curves of the several amorphous compositions prepared for the binary polyester system. The pure PAr shows a T_g at 460 K and no evi-

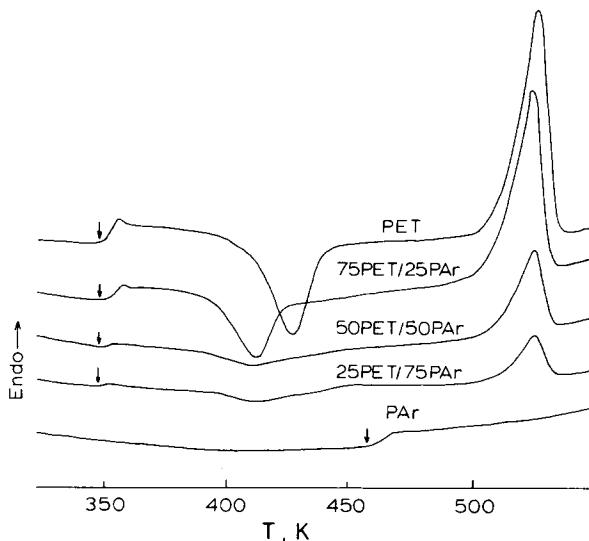


Fig. 1. DSC curves of the quenched binary polyester physical blends.

dence of crystallinity via a melting transition, even on heating to 650 K. The pure PAr film is transparent and indeed is not expected by composition to be crystallizable. The pure PET shows conventional transitions; a T_g at 343 K, a T_m at 527 K, preceded by a cold crystallization peak at 420 K.

A T_g was observed in blends at the same temperature as the T_g of the pure PET. No other T_g , i.e., none corresponding to that of the pure PAr or of partially mixed PAr with PET, was readily observable. The endothermic shift due to the T_g of PAr is likely obscured by the cold crystallization exothermic peak of PET. The only T_m observed in blends was identical with that of the pure PET; hence, crystals generated in blends are indistinguishable from crystals found in pure PET. Contrary to melting behavior, the cold crystallization mechanisms of PET in blends is found to be different from those of the pure PET. Cold crystallization in physical binary blends started and developed at lower temperatures than in pure PET. Because of this, some interaction between PET and PAr is inferred.

Annealing experiment was carried out on the binary blends to evaluate a T_g likely due to PAr. Annealing was performed at a slightly higher temperature (470 K) than the T_g of PAr (460 K) for 30 min. Figure 2 shows DSC curves of annealed binary blends and of the two corresponding pure polyester components. T_g 's of pure PET and PAr remained unaltered. As expected, blends exhibited two T_g 's: one at 350 K and another at 443 K. Evidently, the T_g at 350 K is due to the pure PET phase. The second T_g at 443 K may be assigned to a mixed amorphous phase rich in PAr. Moreover, the T_g for a pure PAr phase was not observed in the blends. Consequently, two amorphous phases likely coexisted in partially crystallized blends; a pure PET phase and a mixed PAr-rich phase. The T_m 's of the PET increased slightly, $\leq 2.5\%$, as the PAr content was increased. This may be due to crystal formation from a more mobile medium—correspondingly, the so-called premelting temperature goes through a minimum with PAr content. As to this premelting phenomenon, it is distinct and real (see Fig. 2). However, its origin may yet be controversial.¹³⁻¹⁵ Therefore, blends of $\sim 25\%$

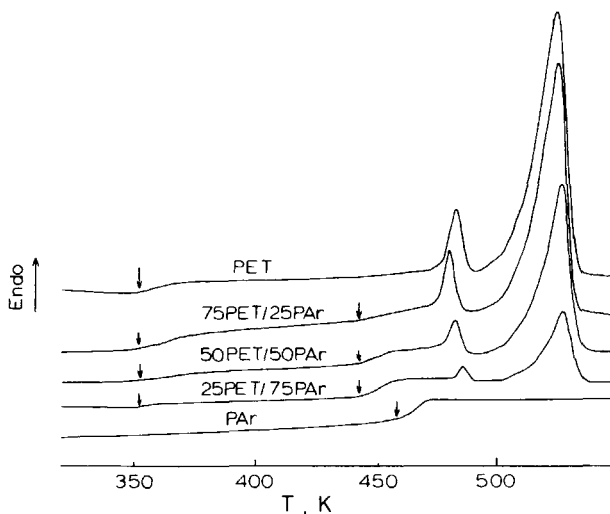


Fig. 2. DSC curves of the annealed blends.

PAr content may have the highest absolute PET crystallinity and certainly the highest normalized fraction.

Figure 3 shows the heat of PET fusion (ΔH_f), heat of cold crystallization (ΔH_c), and the heat of premelting (ΔH_{pm}), for both the initially amorphous blends and for the annealed blends, adjusted for the fractional PET content. Heats of fusion of PET obtained by DSC agreed well with those of other studies.¹⁶⁻¹⁸ Although the heat of fusion corresponds to crystallinity, that of 100% crystallized PET is still controversial.¹⁶⁻¹⁸ Therefore, in this study, the heat of fusion was not converted into crystallinity. The heat of fusion goes through a maximum at ca. 25% PAr as a function of concentration for both the series of amorphous and annealed blends.

For a phase-separated system, crystallization behavior of a component may

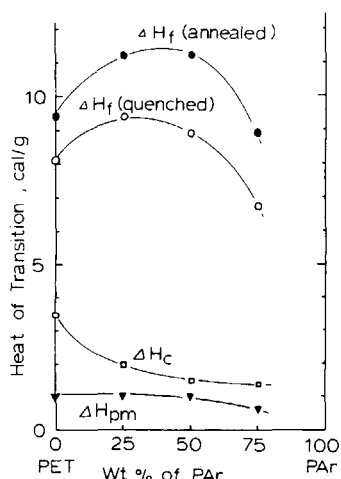


Fig. 3. Heat of fusion, heat of crystallization, and magnitude of glass transition of PET, normalized to its weight fraction.

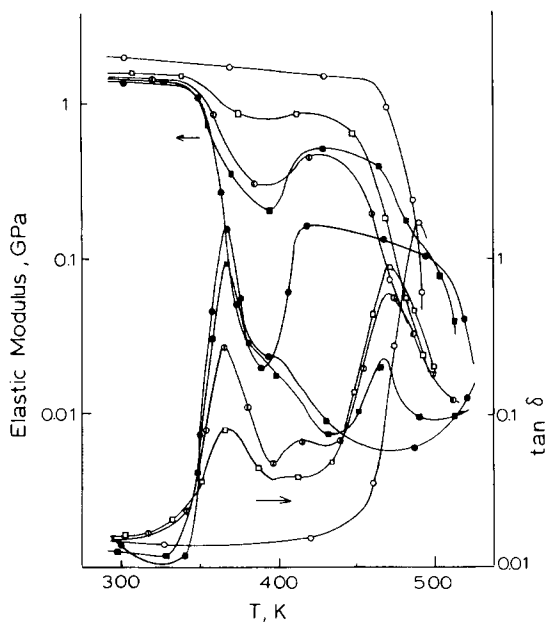


Fig. 4. Plots of elastic tensile modulus and $\tan \delta$ vs. temperature for quenched blends: (○) PAR; (□) 75% PAR; (⊙) 50% PAR; (■) 25% PAR; (●) PET.

be quite similar to that for the pure polymer.¹⁶ In this system, crystallization of PET may proceed in or near a mixed phase rich in PAR. According to crystallization kinetic theory,^{17,18} the rate of spherulitic growth is affected mainly by T_g , relative to other factors. However, the T_g 's of both the PET and the PAR-rich phases were independent of relative concentration for the range studied. Other parameters for the PET crystals, such as interfacial free energy of the chain-folded surface and the lateral interfacial free energy, may be smaller than those for pure PET crystallization. Terephthaloyl residue of PAR may decrease those parameters.

Figure 4 shows plots of E' , the real part of the dynamic tensile modulus, and the corresponding $\tan \delta$ vs. temperature for pure PET, pure PAR, and their binary blends. As PET crystallized during dynamic measurement, and with the location of its T_g affected by the level and nature of PET crystallinity, the E' values above T_g strongly, therefore, depend upon heating rate and applied tensile stress.

The pure PET showed several peaks in $\tan \delta$; a T_g at 92°C (365 K), a T_m at 230°C (503 K), and an unassigned peak at 130°C (403 K) that may be due to further crystallization. The pure PAR only showed, and clearly, a T_g at 220°C (493 K). For the blends, the loss peaks in the $\tan \delta$ curves showed interesting trends that did not appear in DSC measurement of quenched films. Each blend showed a peak at a temperature comparable to the T_g of PET, indicating the presence of an essentially pure PET phase. The magnitude of this peak decreased as the PET content was decreased, but its location remained at about the same temperature as that of pure PET. These results are consistent with the DSC measurements. However, each blend showed another peak at ca. 200°C; its temperature close to the T_g of pure PAR, but ca. 20°C lower, which corresponds to a maximum solubility of ~8% of PET in PAR. Its shape was also much wider

TABLE I
 PET Crystal Size Determined by X-Ray for Annealed Physical Blends of PAr and PET

PAr Content (Wt %)	Half-width 2θ (deg)	PET crystal size (Å)
0	2.36	110
25	2.54	98
50	2.58	95
75	2.61	92
100	—	—

than the pure PAr. Moreover, this peak became higher and wider with increasing PAr content. Therefore, this peak may be assigned to the T_g of an amorphous phase rich in PAr. The degree of miscibility appears to be relatively independent of PET content at >8% PAr. As a conclusion of the dynamic tensile tests, the binary systems all are concluded to have two amorphous phases; a pure PET phase and a likely mixed PAr rich phase.

Wide angle X-ray diffraction measurements were also carried out on both quenched and annealed binary blends. The quenched blends showed only an amorphous halo, i.e., without a diffraction peak due to crystals. Each component, PET and PAr, showed a similar diffraction strength and location, so no useful structure information was derived for quenched blends except to confirm that quenched films were amorphous.

The annealed blends showed amorphous halos for each PET and PAr plus crystal diffraction peaks for PET. Line width of the (100) diffraction peak at $2\theta = 26^\circ$ was estimated using the Hermans-Weidinger¹⁹ method to subtract the contribution from amorphous phase. From line width, the crystal sizes of PET in blends were calculated by Scherrer's equation.²⁰ The values are summarized in Table I.²¹⁻²³ This table shows that the PET crystal size in blends decreased from that of pure PET with increasing PAr content.

Transesterification Process

As reported previously, changes in melting and glass transition temperatures are useful indices of transesterification reaction.⁸ In this study, transesterification of 50% PAr-50% PBT precipitate was monitored by DSC. As the T_m of PET initially was 525 K, the reaction was carried out at 553 K (280°C) and for up to 16 h. Changes with time in the T_m , T_g , and T_c of PET are shown in Figure 5. T_m of PET began to decrease after 15 min and, eventually, disappeared after 60 min. The T_c started to increase after 10 min and disappeared after 60 min. In contrast, the T_g of PET appeared to increase after 10 min at 553 K and arrived at an equilibrium value at 10 h. These data suggest that randomization of the copolymers initially formed proceeds after 10 min with completion at least in 10 hr at 280°C.

Other thermodynamic quantities such as heat of fusion, heat of cold crystallization, and variation of specific heat through T_g , also demonstrate the progression toward randomization. Figure 6 shows these changes with transesterification for the ΔH_f and ΔH_c of PET. The ΔH_f dropped just as the T_m . The ΔH_c decreases slightly from the beginning of transesterification, although T_c

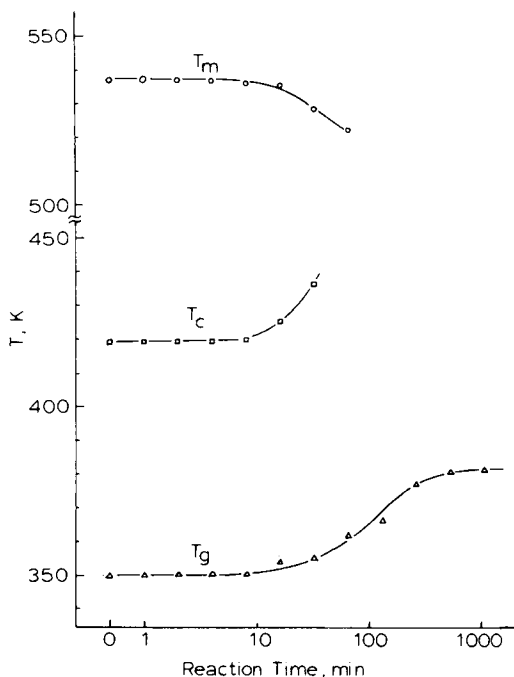


Fig. 5. Changes of PET melting point, cold crystallization, and glass transition temperatures during transesterification.

remained constant for 10 min. Changes in specific heat occurred predominantly in midreaction.

At temperatures for the molten state, degradation as well as transesterification may occur. However, Mazur studied transesterification of this pair, by high performance liquid chromatography (HPLC). He did not observe degradation at reaction conditions similar to ours.¹² Moreover, as transesterification proceeded, T_g of PET went up; therefore, degradation would not be severe even if

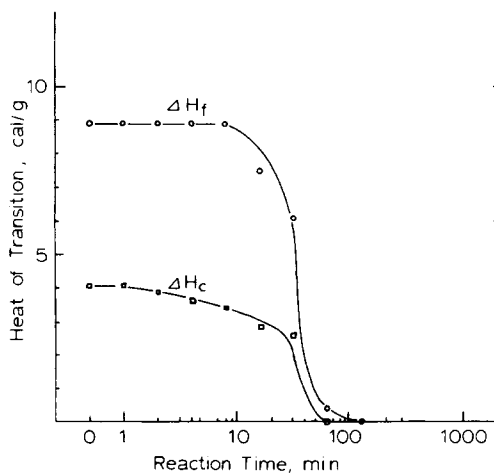


Fig. 6. Changes in heat of fusion and T_g during transesterification.

it occurred. However, some chain shortening cannot be ruled out even as T_g increases. The overriding effect may be the insertion of the rigid PAr units in PET.

Transesterified Blends

Figure 7 shows the DSC curves of the transesterified binary blends, believed to be completely randomized. Each reacted blend showed a single T_g between the T_g 's of the two pure, original polyester constituents. The T_g of these copolymers was a little lower than a linear interpolation between the limits for the pure polyesters: 362 K for 25% PAr (linear interpolation gives 374 K), 381 K for 50% PAr (399 K) and 406 K for 75% PAr (424 K). Transesterified blends did not show any trace of PET melting nor cold crystallization even after annealing at 450 K for 6 h. Wide angle X-ray diffraction measurements of annealed and transesterified blends were concordant with DSC results, showing no PET crystallinity.

Dynamic mechanical tests in tension were carried out to study the change in mechanical properties due to transesterification (see Fig. 8). Each curve showed a glass transition effect, typical of amorphous polymers. The elastic moduli of transesterified blends were almost the same as that of the original physical blends. The T_g 's of transesterified blends, by the dynamic mechanical method, were ca. $\sim 30^\circ\text{C}$ higher than those observed by DSC method, also comparable to observations on the physical blends.

CONCLUSIONS

Physical blends of poly(ethylene terephthalate) (PET) and a polyarylate (PAr) show two amorphous phases; an essentially pure PET phase and likely a mixed phase rich in PAr. This conclusion is based on the dual glass transitions observed

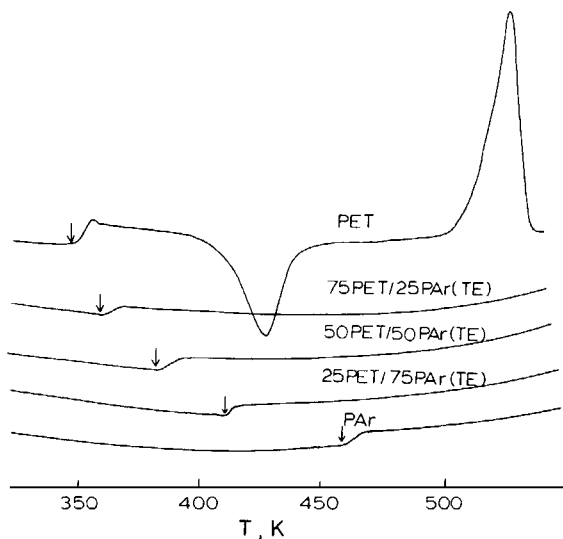


Fig. 7. DSC curves of transesterified (TE) blends.

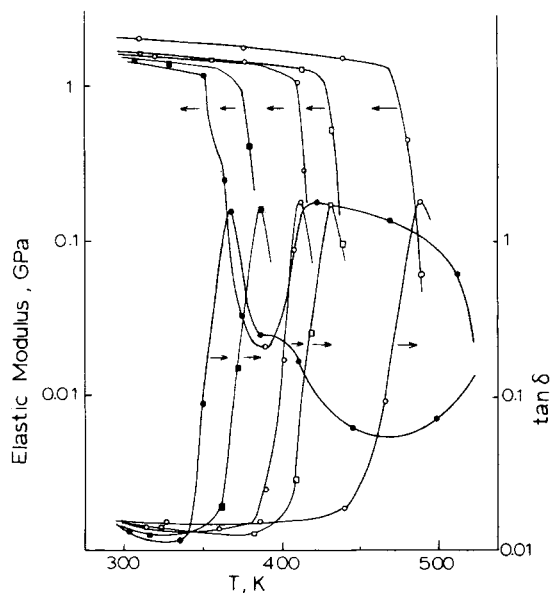


Fig. 8. Plots of elastic tensile modulus and $\tan \delta$ vs. temperature for transesterified blends: (O) PAr; (□) 75% PAr; (⊙) 50% PAr; (■) 25% PAr; (●) PET.

both in DSC measurement of annealed blends and in dynamic mechanical test of quenched blend films. One of the T_g 's corresponds to that measured for pure PET; the other is close to the T_g of the pure PAr, but is ca. 20°C lower. This second T_g is not sensitively affected by blends composition for >8% PET.

Even though some fraction of amorphous PET may compatibilize with the PAr, the melting point of the crystalline PET is not depressed. From DSC measurements, PET crystallinity in blend, normalized by its weight fraction, is found to go through a maximum near 25% PAr content. Wide angle X-ray diffraction measurements suggest that sizes of PET crystals decrease systematically with increased PAr content. Therefore, the number of PET crystallites would also be the largest near 25% PAr. As the crystallization behavior of two-phase systems may differ only slightly from the pure PET, crystallization in this PAr and PET binary system may proceed mainly in the proposed mixed phase rich in PAr or, at least, in an interface region between two amorphous phases. The specific mechanism is unknown. Both kinetics and thermodynamics are likely involved. The PAr could decrease the lateral interfacial free energy and/or interfacial free energy of the chain-folded surface, because of the facts that the melting point depression did not occur and that the T_g of the crystalline PET component remained constant in physical blends.

In contrast, during transesterification, changes in transition, heat, and temperature monitor the randomization. As the T_c of PET is lower than the T_g of PAr, molecular mobility in the amorphous phase of copolymers near T_c would decrease transesterification. Such a decrease in mobility would lead to an elevation of T_c and a lowering of ΔH_c . In contrast, the T_m of PET is higher than T_g of PAr. Therefore, copolymers can melt ever more readily as randomness proceeds.

The transesterified blends are noncrystallizable. They exhibit a single T_g

between T_g 's of the two pure polyester constituents and a little lower than a linearly interpolated value. The elastic tensile modulus of randomized copolymers are comparable to that of the corresponding initial physical binary blends of polyesters.

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