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Amorphous poly(ethylene terephthalate)/poly(butylene terephthalate) blends: miscibility and properties

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Poly(ethylene terephthalate) (PET)/poly(butylene terephthalate) (PBT) blends ($xPET/(1-x)$PBT) characterized by amorphous initial structure are prepared by ultraquenching of the melt between two metal rolls rotating in a liquid nitrogen bath. The thermal behaviour, miscibility, crystallization and mechanical properties of PET/PBT blends are investigated after three years of storage at −15°C. The physical properties of as-quenched samples change significantly after a long period of storage at low temperature. In contrast to the results for the as-quenched blends, a single glass transition temperature (T_g), intermediate between those of the pure components, is observed at each composition after a long period of low temperature relaxation. The dependence of T_g on the composition can be described by the Fox equation. On the basis of the thermal properties of PET/PBT blends, the conclusion drawn is that they are miscible in the amorphous state. Both components crystallize simultaneously at all compositions of the quenched blends. Each component forms its own crystal phase and the presence of the other component does not disturb, and even enhances, the crystallization process. The observed positive synergistic effect in mechanical properties of PET/PBT blends is related to their amorphous miscibility.

(Keywords: amorphous blends; miscibility; physical properties)

INTRODUCTION

Polymer blends are now of great scientific and industrial interest[1–5]. They are physical mixtures of structurally different polymers which adhere together through the action of secondary bond forces, with no covalent bonding between them[6]. In the search for new polymeric materials, blending of polymers is a method for obtaining new desirable property combinations without having to synthesize novel structures.

Besides factors affecting the supermolecular structure—processing history and crystallization—the mutual miscibility of components is of particular importance for the blends' final properties. On the other hand, in order to ensure high temperature and environmental resistance, the high performance thermoplastics are usually characterized by a certain degree of crystallinity. Therefore, it is of interest to understand the miscibility of polymer blends containing at least one component capable of crystallizing.

At first it was thought that compatible blends of crystallizable polymers would be very rare[7]. However, several semicrystalline/amorphous polymer systems that are miscible in the amorphous state have recently been reported[8–12]. Crystalline/crystalline polymer blends are less frequently investigated[13]. Several blends of poly(ethylene terephthalate) (PET)[14,15] and poly(butylene terephthalate) (PBT)[16,17] have been studied extensively. The increased interest results from practical implications.

Recently, amorphous blends of PET and PBT were obtained by ultraquenching of the melt between two metal rolls rotating in a liquid nitrogen bath[18]. Both calorimetric (differential scanning calorimetry, d.s.c.) and X-ray (wide-angle X-ray scattering, WAXS) studies indicate that immediately after preparation, the blends are amorphous regardless of the composition[19]. After quenching, further orientation of the amorphous blends and annealing with fixed ends (at constant length) lead to a significant improvement of the mechanical properties. The tensile strength and elasticity modulus are three to five times greater than those of conventionally obtained PET and PBT[20].

The aim of this paper is to investigate the miscibility, crystallization, thermal and mechanical properties of initially amorphous PET/PBT blends after a long period of storage at low temperature.

EXPERIMENTAL

Commercial PET and PBT (Dupont, USA) with molecular weights of about 25000 were ground at −193°C (liquid nitrogen) and dried for 24 h at 100°C in vacuum. A series of xPET/(1 − x)PBT blends (x = 1, 0.9, 0.8, 0.6, 0.5, 0.4, 0.2, 0.1 or 0 parts by weight) was obtained by the following procedure. A predetermined composition of PET and PBT was prepared as a dry polymer physical mixture, which was melted at 310°C and immediately extruded and ultraquenched between two metal rolls rotating in a liquid nitrogen bath[18]. Strips about 150 μm thick were formed while the rolls were drawing the material with a linear rate of about 30 cm s^{-1}. Both the melting and extrusion of polymer mixtures were finished in 30 s. Only the first portions of the produced material were used for further investigations in order to avoid chemical changes such as transesterification or degradation. Both n.m.r. and i.r. spectra (not shown) of physical mixtures of the pure components and corresponding extruded PET/PBT blends are identical. This indicates that mixing of these polymers is not accompanied by any specific chemical interactions and, under the chosen conditions, the presence of PET/PBT copolymers cannot be registered. Hence, the PET/PBT blends in this study are physical.

It was found that, within the range from 90 to 30°C, the cooling rate is about 400°C min^{-1} for PET[21]. The same ultraquenching technique was applied to obtain amorphous nylon-6[22] and a cooling rate of about 470°C min^{-1} was reported[23]. The essential step for vitrification of nylon-6 was the erasure of structural memory by melt annealing[24,25]. In the case of PET/PBT blends, the melt temperature was 310°C and annealing was not applied since these polymers are characterized by a lower rate of crystallization.

Immediately after they were obtained, the ultraquenched PET/PBT blends were studied by WAXS, d.s.c.[19] and mechanical testing[20]. In this study, the same blends are investigated after 3 years of storage in a freezer at −15°C.

A Mettler TA 3000 system, equipped with a low temperature d.s.c. cell, was employed to study the thermal behaviour of the PET/PBT blends. Samples (~12 mg) were heated and reheated under nitrogen atmosphere at a rate of 20°C min^{-1} in the range from −100 to 300°C. After the first heating, samples were cooled in the d.s.c. apparatus at a rate of 130°C min^{-1} and then reheated at 20°C min^{-1}. The sample weight did not change after d.s.c. measurement. From the d.s.c. curves (first and second scans) the following parameters were evaluated: the glass transition temperature, T_g, recorded at the half-height of the corresponding heat capacity jump; the temperature interval of the T_g regions; the temperature of crystallization, T_c; the melting temperatures T_m of PET and PBT components; their melting enthalpies ΔH_m.

Tensile properties of the blends were measured at room temperature, employing an Instron testing machine. Specimens with a length of 5 cm were cut from the extruded strips and drawn at a cross-head speed of 0.5 cm min^{-1}. All reported results are the average of five runs.

RESULTS AND DISCUSSION

Glass transition temperatures of PET/PBT blends

All PET/PBT blends studied are transparent in the melt and when obtained in the amorphous state. Furthermore, they retain their transparency even after 3 years of storage in a freezer or at room temperature. The PET/PBT blends become opaque only after annealing, i.e. after crystallization of PET and PBT from the blends. Miscible blends are transparent; however, transparency itself is inadequate evidence for amorphous miscibility[6].

Both d.s.c. and WAXS studies[19] indicate that immediately after preparation the blends are amorphous, regardless of the composition. It should be noted that two T_gs were observed for the as-quenched PET/PBT blends. The activation energies determined from the dependence of each T_g of a 50PET/50PBT blend on the heating rate are approximately the same; they are equal to the mean activation energy for the overall crystallization, $E_c = 113$ kJ mol^{-1} (ref. 19).

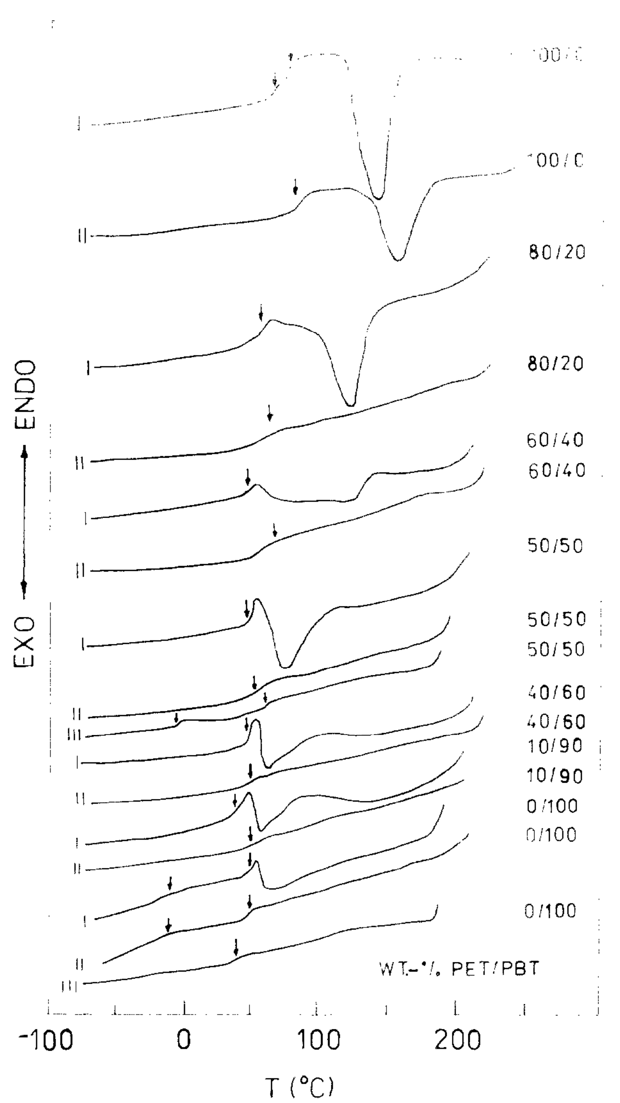

Figure 1 D.s.c. thermograms of PET/PBT blends: the blend composition (wt%) is given on each curve. I, First heating at 20°C min^{-1}; II, reheating (at same rate) after cooling at 130°C min^{-1}; III, third heating (20°C min^{-1}) after annealing for 2 h at 180°C. Arrows indicate the glass transition regions

The present study of the same blends after a long period of storage demonstrates the existence of a single T_g which is intermediate between the T_gs of pure PET and PBT. *Figure 1* shows d.s.c. thermograms (first and second scans) of PET, PBT and their blends with different compositions. Pure ultraquenched PET and PBT display two T_gs on their first d.s.c. traces. Usually, pure polymers are characterized by a single T_g but secondary transitions sometimes exist[26,27]. Both T_gs of pure PBT ($T_{g,1} = -20$°C and $T_{g,2} = 38.5$, *Figure 1*) are in good agreement with data reported for the T_gs of quenched amorphous PBT[26]. The T_g values obtained for pure PET are 60 and 75°C, respectively (*Figure 1*). During the second scan, pure PET displays a single T_g at 82°C while PBT again has two T_g transitions, $T_{g,1} = -20$°C and $T_{g,2} = 48$°C.

It has been reported[27] that double peaks in the specific heat capacity arise when a sample of atactic polystyrene is initially quenched at a rapid rate and then reheated at a slower rate. Such observations occur in all cases when the polymer sample is reheated immediately or very shortly after a rapid quench[27]. This behaviour has been predicted theoretically[27–30] and has been shown to result from the kinetics of the interactions of multiple retardation processes with the thermal history. It has been illustrated[27] on a polystyrene sample that annealing from 405 h at a temperature well below the T_g leads to the disappearance of the upper peak: only a single main peak appears after such treatment.

As mentioned above, PET/PBT blends are characterized by two T_gs immediately after quenching[19]. It is seen from *Figure 1* that all PET/PBT blends exhibit a well defined single T_g after a long period of storage at a temperature well below their T_g. Under the same conditions, however, pure PET and PBT do not undergo processes leading to the appearance of a single peak.

On the other hand, the existence of a single T_g between those of the pure components in polymer blends is evidence for their miscibility[31]. It is well known that the Fox equation[32] adequately describes the T_g *versus* composition relation in various miscible blends[31]. This theoretical relation assumes random mixing at segmental level.

From the Fox equation,

$$1/T_g = (W_{PET}/T_{g,PET}) + (1 - W_{PET})/T_{g,PBT} \qquad (1)$$

the weight fraction of PET, W_{PET}, i.e. the PET/PBT ratio in the amorphous phase, can be calculated on the basis of experimental values of T_g, $T_{g,PET}$ and $T_{g,PBT}$. *Table 1* lists PET/PBT ratios in the amorphous regions calculated using T_gs for the first heating. The deviation of experimental ratio from the calculated ratio is relatively small.

Table 1 Experimental and calculated (equation (1)) data for the phase compositions in PET/PBT blends (first heating)

PET/PBT wt ratio in the blend	PET/PBT wt ratio in amorphous phase of blends (equation (1))
0/100	0/100
10/90	12/88
40/60	37/63
50/50	41/59
60/40	41/59
80/20	69/31
90/10	82/18
100/0	100/0

The T_g *versus* composition relationships of PET/PBT blends are given in *Figure 2*. Experimental data for the first and second runs are compared with corresponding T_g *versus* composition dependence according to equation (1). The T_gs from the first scan obey equation (1) satisfactorily, especially at $W_{PET} < 0.5$. The T_g values from the second scans also change regularly with composition, but the corresponding curve is above the former one.

It is worth noting that during cooling after the first scan, some crystallization occurs. This leads to an increase of T_g due to the immobilizing effect of crystals. Since PBT crystallizes faster[33], the lower the PET content the higher the crystallinity and T_g.

According to the single T_g criterion[31], the PET/PBT blends studied can be considered as miscible in their amorphous regions since they display, at each composition, a single T_g intermediate between those of the individual components. It should be noted that melting

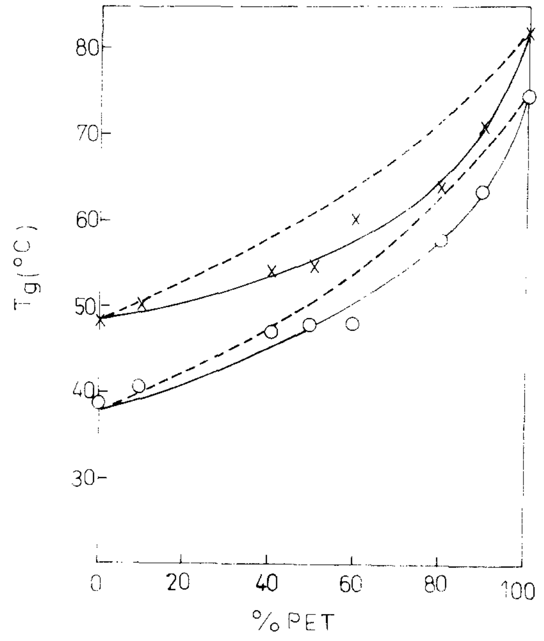

Figure 2 Glass transition temperature *versus* composition curves of the PET/PBT blends: ○, T_g determined from the first scan; ×, T_g determined from the second scan: , Fox equation

Table 2 D.s.c. data for intervals of the glass transition regions (°C) and for the melting temperatures of PBT and PET crystal phases in PET/PBT blends for the first (I) and second (II) scan

PET in blend (wt%)	Interval T_g(I)	Interval T_g(II)	T_m(PBT) (I)	T_m(PBT) (II)	T_m(PET) (I)	T_m(PET) (II)
0	14	11	228	228		
10	18	14	224	223	–	
40	16	18	222	220	253	249
50	20	38	220	216	254	247
60	16	58	220	216	254	248
80	11	48	218	212	255	250
90	14	12		–	256	255
100	13	12	–	–	262	262

and cooling of samples in the calorimeter does not lead to phase separation. During the second scan of the blends, a single T_g is always observed (*Figure 1*).

Further proof for the miscibility of components on the molecular level is the widening of the T_g regions[31]. In *Table 2* the temperature intervals of the T_g regions for the first and second scans of PET/PBT blends are given. One can see that the T_g intervals at heating and reheating of pure components and blends containing up to 10 wt% of the other component are nearly the same. Compositions with higher content of the other component (40–80%) show a considerable widening of the T_g regions at the second scan.

At the third scan of 50PET/50PBT blend, after annealing for 2 h at 180°C, two distinguishable T_gs appear (*Figure 1*). Possibly, a phase separation occurs as a result of such treatment.

The calculated value for the polymer–polymer interaction parameter of Flory and Huggins[31] $\chi_{1,2}$ is 0.018, which is somewhat lower than the corresponding critical value of $\chi_{1,2}$, 0.020. Miscibility can be observed if $\chi_{1,2}$ is negative or very close to zero. It is known[34–36] that specific intermolecular interactions are favourable to mixing. It is likely that, besides the relatively low $\chi_{1,2}$ value, specific intermolecular interactions between PET and PBT macrochains contribute to the miscibility. The reported theoretical predictions of compatibility of PET and PBT blends, based on calculations of the heat of mixing, interaction parameter and free energy, also lead to the conclusion that the system behaves as a compatible polymer pair[37].

Crystallization behaviour of PET/PBT blends

On first heating, all PET/PBT blends exhibit only one crystallization peak. The higher the PET content in the blend, the higher the T_c and the better the exotherms are expressed. Possibly, richer PBT blends crystallize partially during preparation for d.s.c. measurements. The second scan does not show crystallization effects.

The crystallization process of pure PBT and all PET/PBT blends occurs immediately on exceeding T_g, while crystallization of pure PET starts at about 30°C above T_g (*Figure 1*). In spite of the fact that all the blends display only one crystallization exotherm, they exhibit the usual melting endotherms of the two polymers on their d.s.c. traces (*Figures 1* and *4*). Obviously, PET and PBT crystallize from their amorphous blend simultaneously, independent of the composition. This result is quite unusual since neither polymer forms isomorphic crystals.

In *Figure 3* the dependence of crystallization temperature T_c on the PET/PBT blend composition is given. T_c is determined as the start or as the maximum of the crystallization peak. In this way two T_c *versus* composition curves of similar shape are obtained. It is of interest to note that in both curves a certain decrease of T_c for the 10PET/90PBT blend is observed. Unexpectedly, blends containing up to 60% PET start to crystallize at a somewhat lower T_c than pure PBT (*Figures 3* and *1*). A sharp increase of T_c for the blends containing more than 60% PET is clearly expressed by both curves in *Figure 3*. This effect is due to the rise of T_g.

Evidently, the addition of PET to PBT matrix does not suppress, and is even favourable, for the crystallization

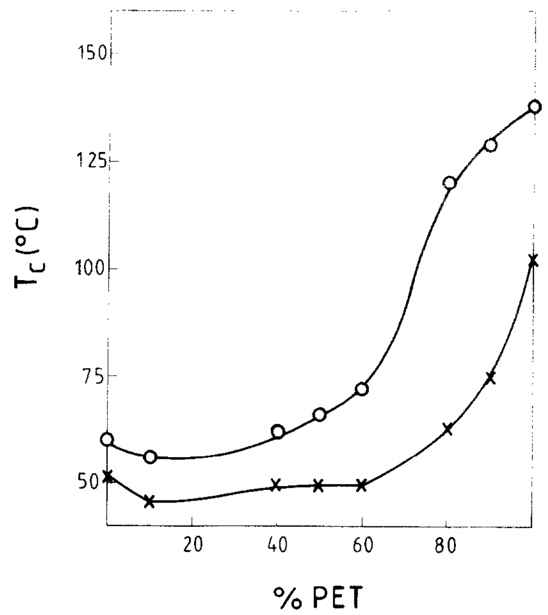

Figure 3 Dependence of crystallization temperature, T_c, on the composition of PET/PBT blends: ○, T_c determined from the maximum of crystallization peak; ×, T_c determined as the start of crystallization

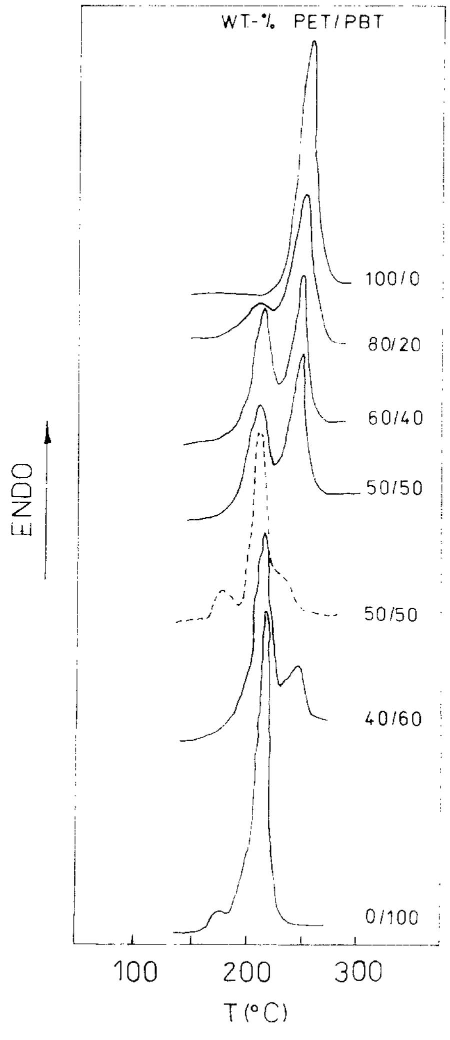

Figure 4 D.s.c. melting curves for the first heating (20°C min^{-1}) of PET/PBT blends with different compositions (wt%) given on each curve. The dashed line thermogram is for the third heating of 50PET/50PBT blend (after heating for 2 h at 180°C)

process. The addition of PBT to PET matrix also facilitates the crystallization process for at least two reasons. First, because of the higher rate of crystallization of PBT[33], its crystals can play the role of athermal nuclei for the crystallization of PET; and second, the addition of PBT decreases T_g and therefore enhances the crystallization. Hence, a conclusion can be drawn that blending of PET and PBT has a synergistic effect on the crystallization process.

For a thermodynamically miscible blend, the addition of an amorphous to a semicrystalline polymer has a dramatic effect on the crystallization behaviour of the latter[38-40]. It has been shown that the total level of crystallinity in the blends decreases exponentially as the concentration of the amorphous polymer increases[39]. On the contrary, the present study demonstrates that the crystallization of a quenched PET/PBT blend is not hindered but even enhanced if compared to pure components.

Melting behaviour of PET/PBT blends

Figure 4 shows d.s.c. melting curves during the first heating of PET/PBT blends with different compositions. Pure PET has one melting maximum. Pure PBT displays one main melting peak with a small shoulder at 185°C. Melting of 10PET/90PBT and 90PET/10PBT blends is also characterized by a single endotherm (not shown in *Figure 4*). Most likely, a 10% content of the dispersed component in the matrix of the other component is not enough to form its own crystal phase, although it is sufficient to affect the glass transition and crystallization process of the matrix (*Figures 2* and *3*).

All other blend compositions have double melting peaks. The higher the content of one component, the higher the corresponding maximum. D.s.c. melting curves on reheating (not given) display the same shape as those shown in *Figure 4*. However, the curve of the 50PET/50PBT blend annealed at 180°C is rather different (dashed line in *Figure 4*).

Table 2 lists the melting temperatures T_m (peak maxima) of PBT and PET components for the first and second heating of blends. It should be noted that the second scans always display lower melting temperatures than the first scans.

From *Figure 4* and *Table 2* one can see that the T_m of each component decreases with increasing content of the other component. The melting point depression in PET/PBT blends is better expressed in *Figure 5*, which shows T_m (PET) and T_m (PBT) *versus* blend composition dependence. Even a small amount of the other component leads to a significant decrease of T_m.

Generally, the T_m depression of a crystalline polymer in its blends results from morphological, kinetic and thermodynamic effects. Many authors[39,41-44] have reported detectable differences between the melting behaviour of a pure semicrystalline polymer and that of its blend. Almost invariably, the observable T_m of the semicrystalline homopolymer is depressed in the miscible blends[38]. Melting point depression for both crystalline components, PET and PBT, is also reported[45] when the blends crystallize from the melt at 185°C.

As mentioned above, PET/PBT copolymer formation was not observed in this study under the chosen conditions. The PET/PBT blends remain in the molten state for only a few seconds, while for complete chemical non-catalysed ester exchange reactions, several hours are needed[14,16]. Nevertheless, during a d.s.c. scan some transesterification is taking place. Possibly for this reason, on reheating an additional T_m depression is registered (*Table 2*).

The effects observed, however, are not related only to copolymer formation. The rate of ester exchange reactions is proportional to the concentration of components and the role of transesterification should be maximal for the 50/50 blend. On the contrary, small

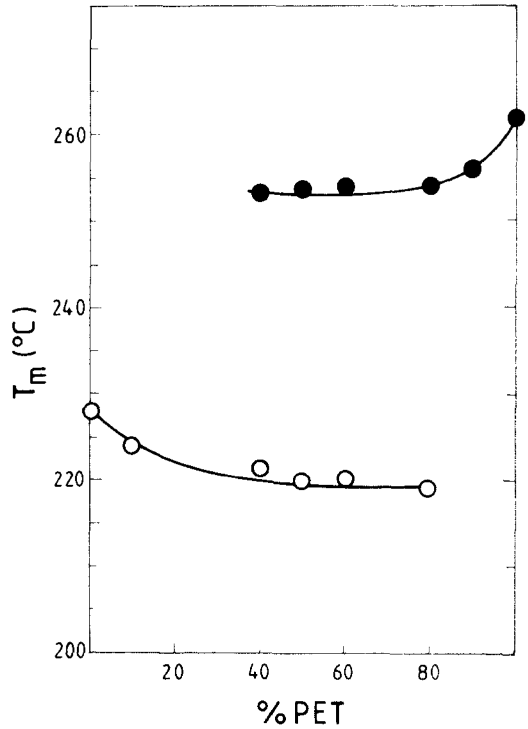

Figure 5 Dependence of melting temperature T_m of PET (●) and PBT (○) on the blend composition

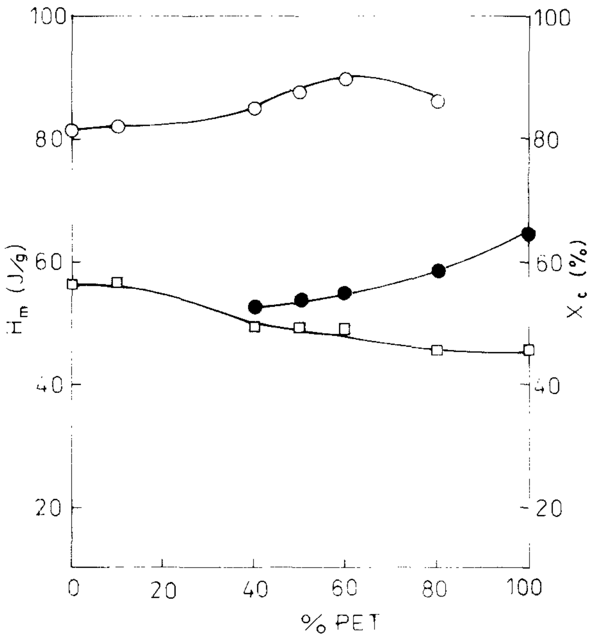

Figure 6 Fractional melting enthalpies, ΔH_m, of PET (●) and PBT (○), and total degree of crystallinity, X_c, of PET/PBT blends (□) *versus* blend composition

amounts of one component have a considerable effect on the T_m of the major component, and this effect tends to level off with further increase of concentration of the first polymer (*Figure 5*).

Crystallinity of PET/PBT blends

The fractional degree of crystallinity of each component in the blend was calculated by measuring the areas under the melting peaks. After graphical separation of peaks, the ΔH_m values were calculated for each component and normalized for fractional content. *Figure 6* displays the dependence of melting enthalpies ΔH_m of PET and PBT components on the blend composition. In the same figure, the total degree of crystallinity (including both phases), X_c, *versus* composition of PET/PBT blends is also shown. X_c is calculated as the sum of degrees of crystallinity of the pure components:

$$X_c = X'_c W_{PET} + X''_c (1 - W_{PET}) \qquad (2)$$

where X'_c and X''_c are the degrees of crystallinity of PET and PBT, respectively, and W_{PET} is the weight fraction of PET; the values used for enthalpies at equilibrium melting temperatures are 140 J g^{-1} for PET[46] and 144.5 J g^{-1} for PBT[47].

Figure 6 shows that melting enthalpies of PET and PBT in the blends do not differ significantly from the corresponding values for pure polymers. Surprisingly, ΔH_m of PBT even increases when it is blended with PET. This interesting result correlates with the reported decrease of temperature of cold crystallization of blends (*Figure 3*). The increase of PET content is related to some increase of the melting enthalpy of its phase. The total degree of crystallinity of PET/PBT blends changes gradually between the corresponding values of pure components (*Figure 6*). Obviously, each polymer crystallizes individually and contributes to the total crystallinity.

It has been reported[13] that a strong mutual disturbance prevents spherulitic morphology from developing in other crystalline/crystalline polymer blends. The total degree of crystallinity drops for polypropylene and polybutene-1 blends. The total crystallinity attained is lower than the linearly added contributions of the compounds. The presence of two components in the system hinders the crystallization processes of both phases[13].

PET and PBT not only crystallize simultaneously but the crystallization of each pure component is even enhanced by the presence of the other. The fractional degree of crystallinity of both polymers in their blends is high, and close to the typical maximal values. It is quite unusual that the degree of crystallinity of PBT even increases in blends with PET (*Figure 6*). The values of the melting enthalpies of PET blended with PBT are higher than reported[15] values for pure PET crystallized for 17 h at temperatures up to 240°C. It should be noted that PET/PBT blends are not thermally treated. Once more, one can assume that a synergistic effect in the crystallization of PET/PBT blends exists.

Microscopic observations[45] indicate individual spherulitic crystallization of both species of PET/PBT blends at low degrees of supercooling. It has been noted that the minor component is excluded within the spherulites of the major component and may subsequently crystallize in this location.

It should be pointed out here that the crystallization of ultraquenched PET/PBT blends at first heating takes place at rather high degrees of supercooling (*Figure 1*), i.e. at relatively low rates. Nevertheless, the normalized melting enthalpies for both components and the total degree of crystallinity of blends have high values (*Figure 6*). Hence, the crystallization process is not disturbed. This result is in agreement with other reported data. The WAXS study of PBT blends[19] demonstrated that the crystallite structure of individual components in blends is as perfect as the structure of pure substances. PBT can crystallize when its miscible blend is annealed above the single T_g of the blend, excluding the second polymer from PBT crystals.

It is interesting to note that the highest values of melting enthalpies were obtained at the first heating of ultraquenched PET, PBT and their blends. Reheated samples, which crystallize during cooling and then at the second heating, have ΔH_m values that are lower by 25%. This result is consistent with our reported data for high performance PET/PBT blends through ultraquenching[20].

Mechanical properties of PET/PBT blends

Due to the amorphous miscibility and ability to reach high total crystallinity, the ultraquenched PET/PBT blends are characterized by good mechanical properties. It was found[20] that as quenched 50PET/50PBT blend exhibits relative elongation at break $\varepsilon = 400\%$, while pure ultraquenched PET strips are brittle. The isotropic ultraquenched 50PET/50PBT blend has a tensile strength three to four times higher than that of pure conventionally quenched PET or PBT. After subsequent drawing and annealing, the ultraquenched blend has an elasticity modulus that is double that of PET and five times higher than that of PBT, and almost doubly lower elongation at break[20].

Various factors of both a chemical and physical nature can affect this system, and they should be taken into account. The polymer pair is transesterifiable[45,48] and the presence of copolymer improves the compatibility of the system[49]. However, conventionally quenched PET/PBT blends[50] exhibit poor improvement in the mechanical properties as compared to the ultraquenched blends studied. On the other hand, copolymer formation was not registered. Hence, in this case the main reason for the better performance of physical ultraquenched PET/PBT blends should be related to their structure.

As already mentioned, annealing of initially amorphous PET/PBT blends is related to coincident crystallization, forming two separate crystal phases of both compounds. After crystallization, the amorphous phase remains miscible (exhibiting a single T_g, *Figure 2*, upper curve). The interphase adhesion between PET and PBT crystals, on the one hand, and the miscible amorphous phase, on the other, should provide good mechanical properties of blends.

It is well known that mechanical properties of pure polymers change drastically after ageing. Such effects were observed for PET[51]. It was of interest to investigate how the long period of storage at low temperature of ultraquenched PET/PBT blends affects their mechanical properties. Tensile tests on stored blends demonstrated that elongation appeared to be the most sensitive characteristic. In contrast to the as-quenched samples[20], pure stored PBT and PET/PBT blends fracture without neck formation, while pure PET breaks after necking.

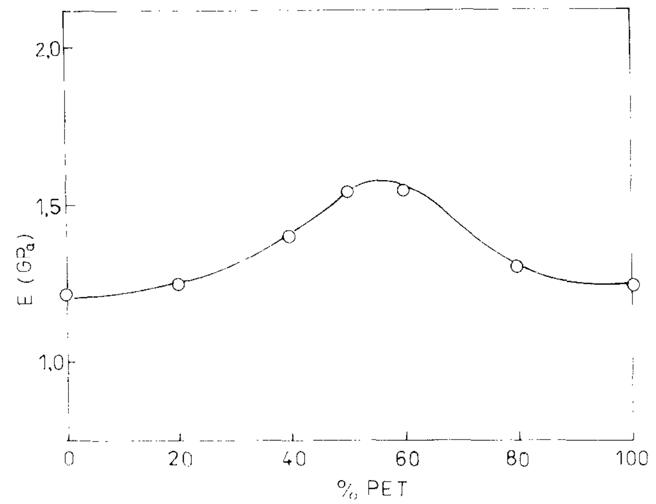

Figure 7 Elasticity modulus, *E versus* composition of PET/PBT blends

The elasticity moduli of blends increase from 20 to 50% after storage and display maximal values in the intermediate composition range (*Figure 7*).

Incompatible blends exhibit very poor mechanical properties, while compatibility is related to mechanical properties proportional to the composition[6,52]. The blends studied even display positive synergism in their mechanical properties, which can be considered as evidence for their amorphous miscibility[31]. Obviously, ultraquenched PET/PBT blends preserve this miscibility after 3 years of storage at low temperature, i.e. phase separation does not occur during storage.

As for other PBT blends[16], the observed miscibility can be explained by intermolecular π-electron interaction between the terephthalate residues of PET and PBT macromolecules. The tetramethylene glycol units of PBT provide flexibility to facilitate terephthalate interactions[16]. Such specific interactions can overcome the dispersion forces and contribute to mixing. Even if the mixing is thermodynamically unfavourable, the phase separation can be kinetically hindered due to the strong interactions[43]. Even if interactions are not sufficient to achieve negative heat of mixing to satisfy the thermodynamic criterion for miscibility, another feature of the system studied should be taken into account. By rapid quenching, the homogeneous structure of the melt becomes frozen. The molecular motion is strongly restricted and the phase separation is additionally kinetically hindered. As a result, melt blended and quenched PET/PBT blends do not undergo phase transitions and separation, even after 3 years of storage. It was recently demonstrated for amorphous polyamide-6 that the initial amorphous structure is more favourable for orientation than the semicrystalline structure and provides good mechanical properties[53].

Although the stored ultraquenched PET/PBT blends remain miscible, their thermal and mechanical properties are changed. The properties of ultraquenched pure PET and PBT are also different after storage. This can be explained by taking into account that the ultraquenched polymers are highly non-equilibrium systems. They are far from configuration equilibrium and slowly relax to the 'ideal' metastable amorphous state with minimum energy. This process is homogeneous, in contrast to the heterogeneous process of crystallization[54]. It is likely that, during the storage of ultraquenched polymers and blends, a low temperature relaxation takes place. Crystallization under such conditions is excluded but, nevertheless, the relaxation leads to a significant change in properties. This fact is known for the glassy metals[54] but, to the best of our knowledge, it is observed for the first time for polymer blends.

CONCLUSION

Physical blends of PET and PBT are found to be miscible in all compositions in the amorphous state. While the melt-blended and as-quenched PET/PBT blends are characterized by two T_gs[19], after a long period of storage at low temperature a single T_g is observed, intermediate between those of the pure components. As-quenched blends are highly non-equilibrium systems. During the long period of storage at low temperature, PET/PBT blends undergo low-temperature relaxation resulting in a change of structure, thermal and mechanical properties.

PET and PBT crystallize coincidentally on exceeding T_g. Each component crystallizes separately and its crystallization is not disturbed and is even enhanced by the presence of the other component, i.e. a synergistic effect in the crystallization of PET/PBT blends is observed. The semicrystalline blends are still miscible in the amorphous regions. On heating, all blends exhibit a double melting peak and well expressed melting point depression. The observed synergistic effect in mechanical properties is consistent with miscibility in the amorphous phase of these physical blends.

In agreement with our results for amorphous polyamide-6[53], the conclusion has been drawn that reported good mechanical properties are facilitated by the miscibility, as well as the initial homogeneous amorphous structure of ultraquenched blends.

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REFERENCES

1 Heikens, D., Hoen, N., Barentsen, W., Piet, P. and Ladan, H. *J. Polym. Sci., Polym. Symp.* 1978, **62**, 309
2 Runt, J. P. and Rim, P. B. *Macromolecules* 1982, **15**, 1018
3 Chik, S. C. and Smith, T. G. *J. Appl. Polym. Sci.* 1984, **29**, 1781, 1797
4 Woo, E. M., Barlow, J. W. and Paul, D. R. *Polymer* 1985, **26**, 763
5 Fernandes, A. C., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1986, **32**, 5357
6 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Compositions' Plenum, New York, 1976
7 Bohn, L. *Rubber Chem. Technol.* 1968, **41**, 495
8 Alfonso, G. C., Turturro, A., Pizzoli, M., Scandola, M. and Geccorulli, G. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 1195
9 Imken, R. L., Paul, D. R. and Barlow, J. W. *Polym. Eng. Sci.* 1976, **16**, 593
10 Morra, B. S. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 2243
11 Galin, M. *Makromol. Chem.* 1987, **188**, 1391
12 Briber, R. M. and Khoury, F. *Polymer* 1987, **28**, 38
13 Siegmann, A. *J. Appl. Polym. Sci.* 1979, **24**, 2333
14 Pillon, L. Z. and Utracki, L. A. *Polym. Eng. Sci.* 1984, **24**, 1300
15 Pillon, L. Z. and Lara, J. *Polym. Eng. Sci.* 1987, **27**, 984

16 Kimura, M. and Porter, R. 1983, **21**, 367
17 Robeson, L. M. *J. Polym. Sci., Polym. Lett. Edn* 1978, **16**, 261
18 Avramova, N., Avramov, I., Fakirov, S. and Schultz, J. M. US Patent 4915885, 1990
19 Avramov, I. and Avramova, N. *J. Macromol. Sci.-Phys.* 1991, **B30**(4), 335
20 Avramova, N., Fakirov, S. and Avramov, I. *Angew. Makromol. Chem.* 1992, **199**, 129
21 Avramov, I., Avramova, N. and Fakirov, S. *J. Polym. Sci., Polym. Phys.* 1989, **27**, 2419
22 Avramova, N., Avramov, I., Fakirov, S. and Schultz, J. M. Bulgarian Authorship Certificate No. 45124, C 08 L 67 08, 1987
23 Avramov, I., Avramova, N. and Fakirov, S. *Makromol. Chem., Rapid Commun.* 1990, **11**, 135
24 Avramova, N., Fakirov, S. and Avramov, I. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 311
25 Avramova, N. and Fakirov, S. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 761
26 Cheng, S. Z. D., Pan, R. and Wunderlich, B. *Makromol. Chem.* 1988, **189**, 2443
27 Ruddy, M. and Hutchinson, J. M. *Polym. Commun.* 1988, **29**, 132
28 Ramos, A. R., Hutchinson, J. M. and Kovacs, A. J. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 1655
29 Hutchinson, J. M. and Kovacs, A. J. *J. Polym. Eng. Sci.* 1984, **24**, 1087
30 Hutchinson, J. M. *Lect. Notes Phys.* 1987, **277**, 172
31 Paul, D. R. and Newman, S. (Eds) 'Polymer Blends', Academic Press, New York, 1978
32 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **2**, 123
33 Pratt, C. F. and Hobbs, S. Y. *Polymer* 1976, **15**, 12
34 Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 18[illegible]
35 Patterson, D. and Robard, A. *Macromolecules* 1978, **11**, 690
36 Ma, D.-Z. and Prud'homme, R. E. *Polymer* 1990, **31**, 917
37 Mishra, S. P. and Deopura, B. L. *Polym. Commun.* 1985, **26**, 5
38 Rostami, S. *Polymer* 1990, **31**, 899
39 Ullman, W. and Wendorff, J. H. *Compos. Sci. Technol.* 1985, **23**, 97
40 Cimmino, S., Martuscelli, E., Silvestre, C., Canetti, M., de Lalla, C. and Seves, A. *J. Polym. Sci., Polym. Phys.* 1989, **27**, 1781
41 Flory, P. J. 'Principles of Polymer Chemistry' Cornell University Press, Ithaca, NY, 1953
42 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 909
43 Kwei, T. K. and Frisch, H. L. *Macromolecules* 1978, **11**, 1267
44 Blundell, D. J. *Polymer* 1987, **28**, 2248
45 Stein, R. S., Khambatta, F. B., Warner, F. P., Russell, T., Escala, A. and Balizer, E. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 313
46 Wunderlich, B. *Polym. Eng. Sci.* 1978, **18**, 431
47 Marusii, N. J., Tkachuk, B. W. and Pavlov, W. I. *Vysokomol. Soed. A* 1981, **23**, 1091
48 Kotliar, A. M. *J. Polym. Sci., Macromol. Rev.* 1981, **16**, 367
49 Gaylord, N. G. *Adv. Chem. Ser.* 1975, **142**, 76
50 Wong, A. H. DE 2912610, 1979; *Chem. Abstr.* 1979, **91**, 212338v
51 Avramova, N., Fakirov, S. and Schultz, J. M. *J. Appl. Polym. Sci.* 1986, **31**, 1631
52 Krause, S. *J. Macromol. Sci., Rev. Macromol. Chem.* 1972, **7**, 251
53 Avramova, N. *Polym. Polym. Compos.* 1993, **1**, 261
54 Köster, U. and Herold, U. in 'Glassy Metals' Vol. I (Eds H.-J. Güntherodt and H. Beck), Springer-Verlag, Berlin, 1981