Structural and mechanical studies of a blend of poly(butylene terephthalate) and poly(ether ester) based on poly(butylene terephthalate) and poly(ethylene glycol)

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Poly(butylene terephthalate) (PBT), poly(ether ester) (PEE) based on PBT and poly(ethylene glycol) (PEG) (PBT/PEG = 49/51 wt%) and their blend are extruded with quenching, drawn ×5 and annealed together with undrawn samples at 170, 180, 190 and 200°C for 6 h in vacuum. All samples are characterized by differential scanning calorimetry (d.s.c.), small-angle and wide-angle X-ray scattering, dynamic mechanical thermal analysis and static mechanical measurements. D.s.c. and X-ray results show the absence of complete cocrystallization of homo-PBT and PBT from PEE in the blend in accordance with other reports. The drawn blend annealed at 200°C reveals much higher (by 30°C) T_m than the PEE component (49/51). Also the mechanical properties of the blend are in between those of the components (homo-PBT and PEE 49/51) but improved compared to those of PEE with the same chemical composition (PEE 75/25). Both observations are explained by partial cocrystallization, i.e. formation of crystallites consisting of two populations of crystallites differing in their size, perfection, origin and time of appearance. The lack of complete cocrystallization and miscibility in this particular blend as well as in other cases with PEE containing less than 75 wt% PBT is explained by the insufficient length of PBT hard segments in PEE necessary for the formation of lamellar thickness typical of the crystallites of homo-PBT.

(Keywords: poly(butylene terephthalate); poly(ether ester); blend)

INTRODUCTION

Blending of polymers has become a basic approach for altering the properties of polymeric materials. The best example is the blending of thermoplastics with rubber-like polymers and copolymers in order to improve the impact behaviour. As polymer blends are multiphase systems, tending continuously to phase separation, the search for methods to suppress the incompatibility continues[1]. One of these methods is based on the generation of chemical bonds between the components of the blend[1]. This approach is particularly suitable for blends of condensation polymers where the reactive groups are inherently available, in contrast to polyolefins, which need additional creation of special reactive groups. Following this approach a new type of composites, microfibrillar reinforced composites (MFC), were recently obtained from blends of condensation polymers[2-5]. Owing to the additional condensation and trans-reactions typical of polycondensates[6,7], chemical bonds are created between the components after treatment at elevated temperatures (close to the melting points). MFC based on polyester/polyamide blends show a synergistic effect in their mechanical properties, which approach those of glass-fibre-reinforced composites having the same matrix[2,4,5].

Through blending of a crystallizable homopolymer with a copolymer containing blocks of the same homopolymer, one can expect that cocrystallization of the common component will provide a large amount of tie molecules linking between the two components. The main purpose of the present study is to explore this opportunity using a blend of poly(butylene terephthalate) (PBT) and a poly(ether ester) (PEE) thermoplastic elastomer, the latter being a copolymer of PBT hard segments and poly(ethylene glycol) (PEG) soft segments. This system is attractive not only because the two polymers have the same crystallizable component but also because the copolymer, being an elastomer, will strongly affect the mechanical properties of the blend. In addition to the cocrystallization effect, the system is distinguished by the potential possibility of chemical interaction (via mostly trans-reactions) between the two components.

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EXPERIMENTAL

PEEs were prepared on a semi-commercial scale[8] using PEG of molecular weight 1000 (PEG-1000) in various PBT/PEG-1000 weight ratios. For the preparation of the blend, both the homopolymer PBT and PEE were cooled in liquid nitrogen and finely ground. PBT was blended with PEE having the composition PBT/PEG-1000 = 49/51 wt% in a weight ratio PBT/PEE = 51/49. The blend obtained is designated further as Σ75/25 and is characterized by the same overall PBT content as another PEE sample containing 75 wt% only chemically bonded PBT and designated as 75/25. Films of the blend, PBT and the two PEEs were prepared according to the following procedure. A capillary rheometer, flushed with argon and heated to 250°C, was loaded with the dried powdered material. The melt obtained was kept in the rheometer for 5 min and then extruded through the capillary (diameter of 1 mm) on metal rolls rotating at 30 rpm. The rolls were immersed in a bath of liquid nitrogen. The films obtained were 3–4 mm wide and 100–150 μm thick depending on the extrusion rate and the force applied between the rolls.

These films were drawn × 4.8 at room temperature on a Zwick 1464 machine at a draw rate of 5 mm min^{-1} and then annealed under tension (with fixed ends) for 6 h at 170°C (sample 49/51) or at 170, 180, 190 and 200°C (samples PBT, Σ75/25 and 75/25) in a vacuum oven. The sample designations, composition and treatment are summarized in *Table 1*.

Mechanical tests in static mode were carried out at room temperature on the same Zwick machine equipped with an incremental extensometer using a crosshead speed of 5 mm min^{-1}. The Young's modulus (E), the tensile strength (σ) and the relative deformation at break (ε_b) were determined from the stress–strain curves. All values were averaged from three measurements. A dynamic mechanical thermal analyser in tensile mode at a frequency of 5 Hz and a heating rate of 10°C min^{-1} was used to test the samples.

Ni-filtered Cu K$_\alpha$ radiation was used in all X-ray experiments. Wide-angle X-ray scattering (WAXS) patterns were taken on a Siemens D500 diffractometer. The dimensions of the PBT crystallites in the respective directions were determined from the half-widths of the (0 1 0), (1 0 0) and ($\bar{1}$ 0 4) reflections using Scherrer's formula. Photographic patterns were obtained in transmission mode using a flat-film camera. Small-angle X-ray scattering (SAXS) measurements were carried out on a Kratky camera equipped with a high-temperature sample holder.

D.s.c. measurements were performed on a Shimadzu thermal analyser DSC-41 at a heating rate of 10°C min^{-1} in the range from 30 to 250°C in an argon atmosphere. Relatively small weights of 0.4 to 2 mg were used in order to decrease the heater-to-sample temperature difference.

RESULTS

Figure 1 shows the thermograms of the blend annealed at two different temperatures as well as those of its components. Despite the fact that the two components of the PEE are crystallizable, a stable crystalline phase at temperatures above ambient temperature is observed only with PBT[9]. The melting temperature of the crystalline PBT in the homopolymer is between 225 and 229°C (curves a and b) depending on the annealing temperature, which is in accordance with literature

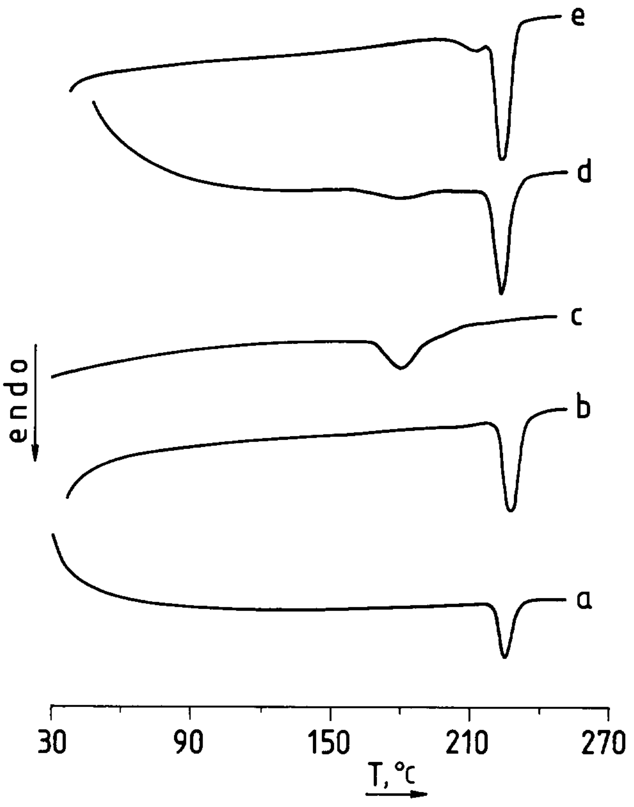

Figure 1 D.s.c. curves of drawn samples annealed at temperature T_a: (a) PBT, T_a = 170°C; (b) PBT, T_a = 200°C; (c) PEE 49/51, T_a = 170°C; (d) Σ75/25, T_a = 170°C; and (e) Σ75/25, T_a = 200°C

Table 1 Sample designations, composition and treatment conditions

Sample designation	Composition (weight ratios)	Treatment conditions		
		Drawing, λ	Annealing temperature, T_a (°C)	Annealing time, t_a (h)
PBT	PBT (100%)	4.8	170; 180; 190; 200	6
49/51	PEE (PBT/PEG = 49/51)	4.8	170	6
75/25	PEE (PBT/PEG = 75/25)	4.8	170; 180; 190; 200	6
Σ75/25	Blend of PBT/PEE = 51/49 (PEE of PBT/PEG = 49/51)	4.8	170; 180; 190; 200	6

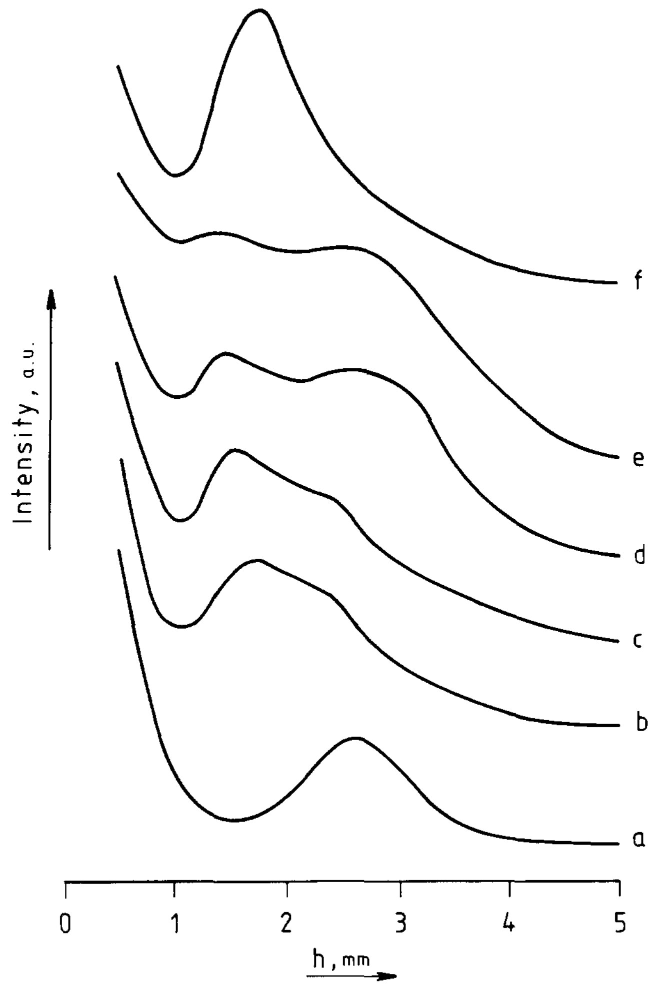

Figure 2 SAXS curves of drawn samples annealed at temperature T_a: (a) PBT, $T_a = 170$°C; (b)–(e) Σ75/25, $T_a = 170$, 180, 190 and 200°C respectively; (f) PEE 49/51, $T_a = 170$°C. The scattering angle 2θ (rad) is related to h (mm) as $2\theta = h/200$

data[10]. In the 49/51 copolymer the PBT crystals are smaller and less perfect, and melt at a lower temperature of 181°C (*Figure 1*, curve c), which is in accordance with the value reported previously[8]. The thermogram of the blend annealed at the lower temperature (170°C, curve d) reveals two melting peaks at 180 and 223°C, which agrees fairly well with the melting of the homopolymer PBT and PEE 49/51 annealed at the same temperature (170°C, curves a and c, respectively). It follows that the blend comprises two types of crystallites, i.e. more perfect ones, formed mostly by the homopolymer chains, and others, built up mainly of PBT blocks of the copolymer. These results indicate that the homo-PBT and the PBT blocks of PEE crystallize separately, i.e. no cocrystallization takes place. When the same blend is annealed at a higher temperature (above the melting point of PEE), a strong increase (by 30°C) of T_m of PEE 49/51 is observed while T_m of homo-PBT rises only by 5°C (*Figure 1*, curve e).

SAXS curves of the blend and its components annealed at different temperatures are shown in *Figure 2*. Curves a and f, corresponding to the components PBT and PEE 49/51 of the blend, reveal a well expressed long spacing that is characteristic of oriented and annealed samples. A maximum comprising two overlapping peaks positioned at different angles is present in the curves of the blend annealed at different temperatures (*Figure 2*, curves b–e). The observed tendency towards the appearance of two peaks can be considered as an additional indication of the coexistence of two types of PBT crystallites differing in their density and spatial arrangement. In order to prove this assumption, SAXS curves of the blend annealed at 200°C were taken at elevated temperature. The results are displayed in *Figure 3*.

At low temperatures (below 100°C) only one weak maximum is observed. With increase of the sample temperature T_s, a new maximum arises at a smaller angle. The intensity of both maxima increases with further increase of temperature up to $T_s = 180$°C, at which temperature the maximum at smaller angle disappears, as does the other one at $T_s = 230$°C. Having in mind the melting temperatures of the two components (*Figure 1*, curves d and e), it is easy to assign the maximum at smaller angle to PBT in PEE 49/51 and the other one to homo-PBT. This conclusion is supported also by the observation that the copolymers are distinguished by much larger long spacings (at the expense of amorphous regions) in comparison to the homopolymer, in accordance with previous findings[11].

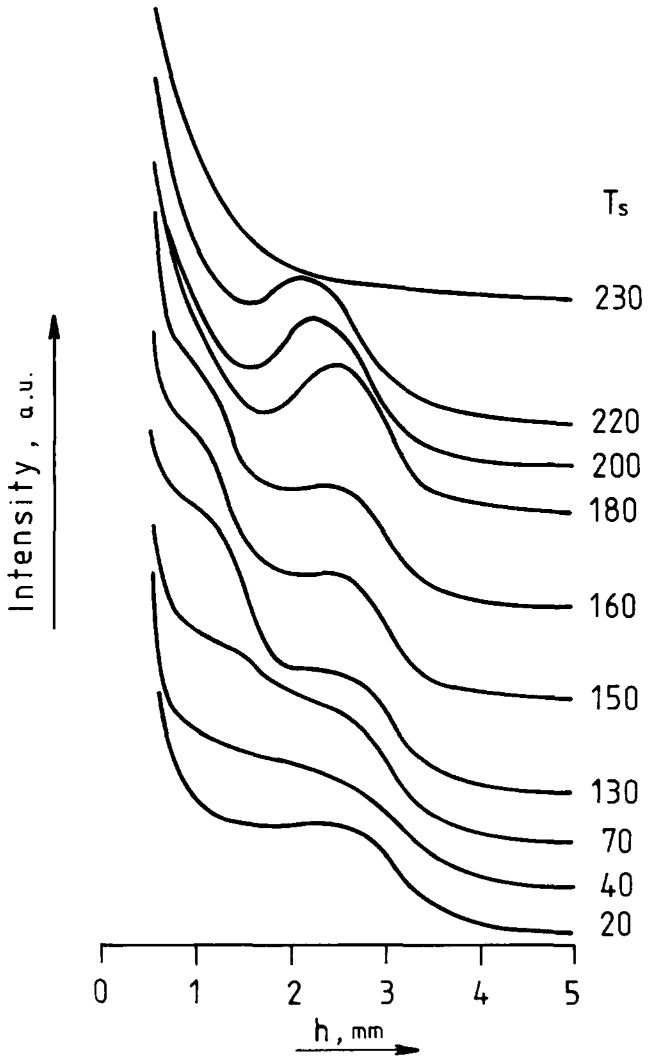

Figure 3 SAXS curves of a drawn sample Σ75/25 annealed at $T_a = 200$°C, taken at different temperatures T_s (°C) as indicated; h as in *Figure 2*

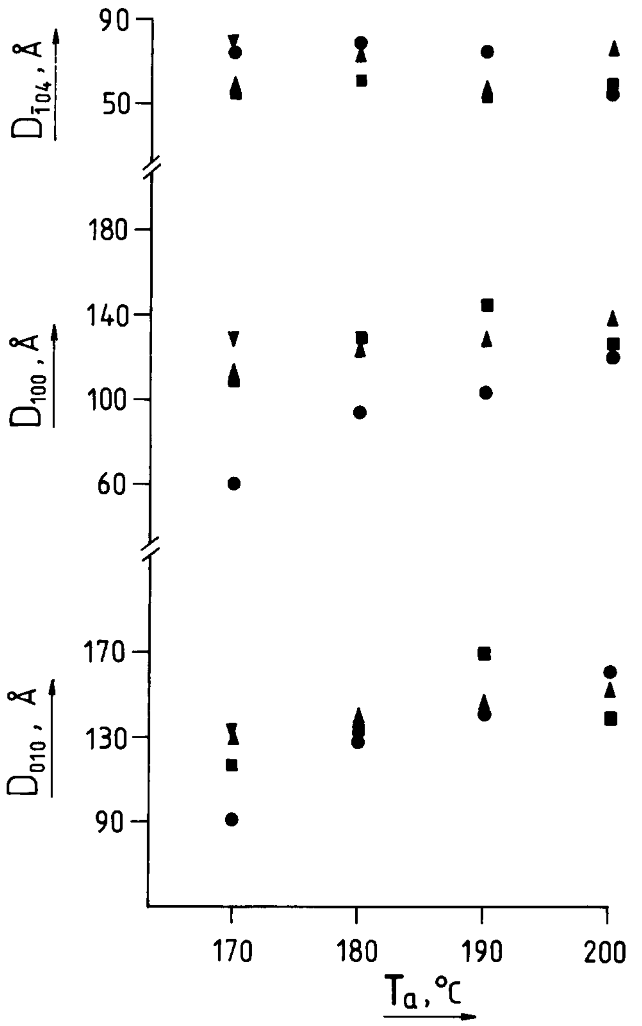

Figure 4 Dependence of the lateral size D_{010} and D_{100} and longitudinal size $D_{\bar{1}04}$ of the PBT crystallites on the annealing temperature T_a for drawn annealed samples as follows: (●) PBT, (▲) PEE 75/25, (▼) PEE 49/51 and (■) Σ75/25

Figure 4 shows the dependences of two lateral (D_{010} and D_{100}) and the longitudinal ($D_{\bar{1}04}$) dimension of the PBT crystallites in homo-PBT, in PEE 75/25 and in the blend (sample Σ75/25) on the annealing temperature T_a, measured at room temperature. Results for PEE 49/51 at 170°C are also shown in the figure for the sake of comparison. Since the standard deviation in the value of D_{010} and D_{100} is about 5–10 Å, an increase of these two magnitudes with increasing T_a can be seen for homo-PBT, PEE 75/25 and the blend. For the blend, both D_{010} and D_{100} decrease at the higher annealing temperature $T_a = 200$°C. The PBT crystallites arising from the PEE 49/51 melt during annealing at 200°C and subsequent cooling after the crystallization of homo-PBT. This observation is in agreement with the SAXS behaviour of this sample (*Figure 1e*).

The dimension along the orientation axis (lamellar thickness) $D_{\bar{1}04}$ is within the range of 55–75 Å for all three samples and seems to be insensitive to the annealing temperature. The standard deviation of this dimension is larger than in the case of D_{010} and D_{100} owing to the relatively low intensity of the ($\bar{1}$04) reflection in comparison to (0 1 0) and (1 0 0).

Figure 5 shows the dependence of Young's modulus E of the blend, of its components as well as of PEE 75/25 on the annealing temperature T_a. As expected, the PBT homopolymer reveals the highest E value while those of copolymers 75/25 and particularly 49/51 are much lower and depend in the same way on the annealing temperature. The Young's modulus of sample Σ75/25 takes an intermediate position between those of homo-PBT and sample 75/25. The ratio of the moduli of the blend Σ75/25 and of PEE 75/25 increases with the annealing temperature, and at $T_a = 200$°C its value exceeds 4.

The same figure also shows the dependence of the theoretical modulus E of the blend on T_a. For this purpose the blend is considered as a composite comprising highly oriented PBT fibrils with volume fraction V^{PBT} embedded in a PEE matrix with volume fraction V^{PEE} ($V^{PBT} + V^{PEE} = 1$). The modulus E of such a composite is calculated from the respective moduli of the fibrils (homo-PBT) and the matrix (PEE) as[12]:

$$E = E^{PBT}V^{PBT} + E^{PEE}V^{PEE} \qquad (1)$$

Since this formula is valid under the condition that the bonding between the fibrils and the matrix is perfect[12], the tendency of the experimental and theoretical curves to get closer with increasing T_a could be attributed to the improvement of this bonding.

There is also another proof of the existence of chemical bonding between the PBT fibrils and the PEE matrix.

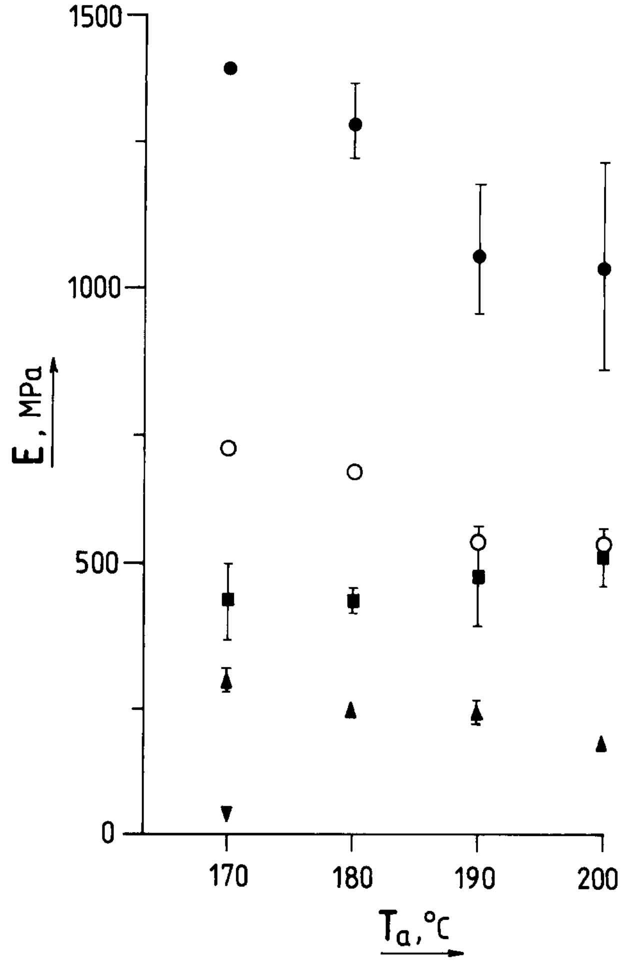

Figure 5 Dependence of the Young's modulus E on the annealing temperature T_a for drawn annealed samples as follows: (●) PBT, (▲) PEE 75/25, (▼) PEE 49/51, (■) Σ75/25 (all experimental); and (○) Σ75/25 (calculated)

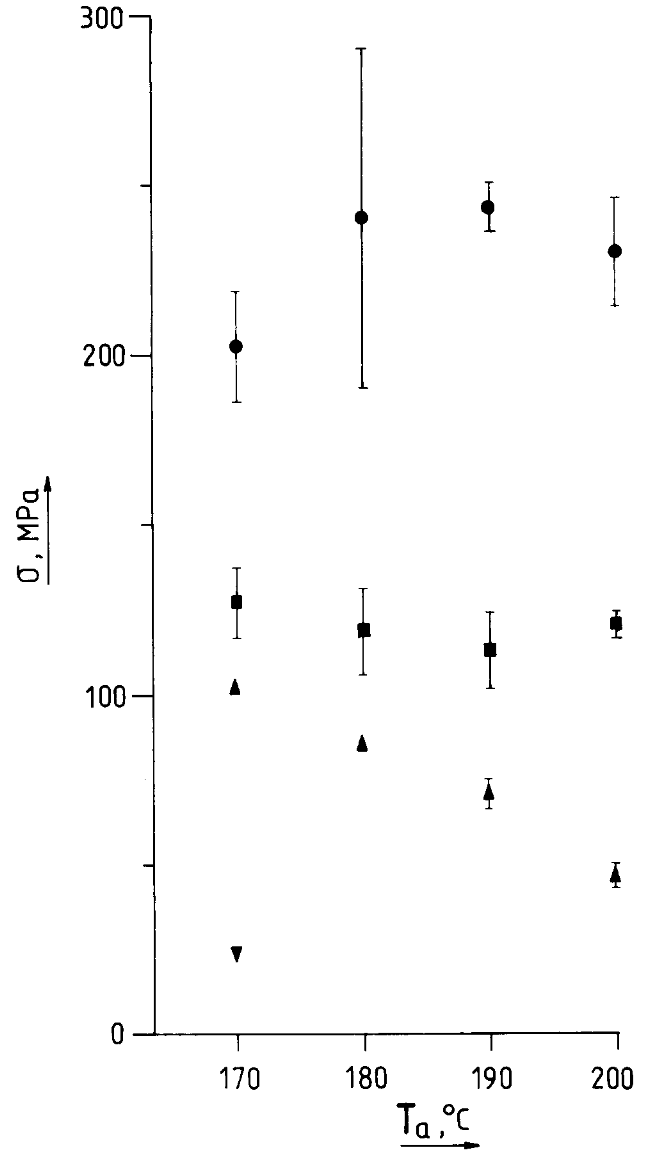

Figure 6 Dependence of the tensile strength σ on the annealing temperature T_a for drawn annealed samples as follows: (●) PBT, (▲) PEE 75/25, (▼) PEE 49/51 and (■) Σ75/25

The blend samples annealed at 170 and 180°C undergo strong defibrillization during breaking, which is not the case for the blend samples annealed at 190 and 200°C.

Figure 6 displays the dependence of the tensile strength σ on T_a. It is seen that σ of PBT changes insignificantly while the tensile strength of sample PEE 75/25 shows a two-fold decrease with increasing T_a and that of the blend remains constant. It should be noted that the σ vs. T_a dependence of the blend takes an intermediate position with respect to those of the other two samples, and at $T_a = 200°C$ the tensile strength of the blend is three times higher than that of the copolymer with the same chemical composition (PEE 75/25, *Figure 6*).

The relative elongation at break (ε_b) vs. T_a dependences for the same samples are shown in *Figure 7*. As could be expected, the copolymer 75/25 behaves as a typical elastomer; it is characterized by a high ε_b value, which increases strongly with the increase of T_a. The respective values for homo-PBT are relatively low (about 30%); those of the blend are of the same order of magnitude and are independent of T_a for both samples. *Figure 7* leads to the conclusion that the deformation behaviour of the blend is much closer to that of homo-PBT rather than to that of the copolymer with the same chemical composition or the copolymeric component (PEE 49/51).

Figure 8 shows WAXS patterns of films of the blend annealed at 170°C (*Figure 8a*) and 200°C (*Figure 8b*). As seen in *Figure 8a*, the PBT crystallites are highly oriented, while concentric circles due to isotropic PBT are observed in *Figure 8b*, in addition to the arcs originating from highly oriented PBT crystallites. The PEE 49/51 weight fraction in the blend is about 1/2; the fraction of PBT in the 49/51 copolymer is also about 1/2, and approximately half of the PBT comonomer is crystalline. It follows that the weight fraction of randomly oriented crystallites in the blend amounts to only 1/8, and for this reason the circles corresponding to this isotropic fraction (*Figure 8b*) have much lower intensity. These two X-ray patterns visualize in the best way the isotropization step during MFC manufacturing. While annealing at 170°C (*Figure 8a*) results only in the improvement of the perfection of both types of oriented crystallites (originating from PEE and homo-PBT, as proven by d.s.c. and SAXS measurements, *Figures 1* and *3*, respectively), annealing at 200°C leads to melting of crystallites from PEE (with $T_m = 181°C$), which crystallize again during the subsequent cooling but not in the oriented state

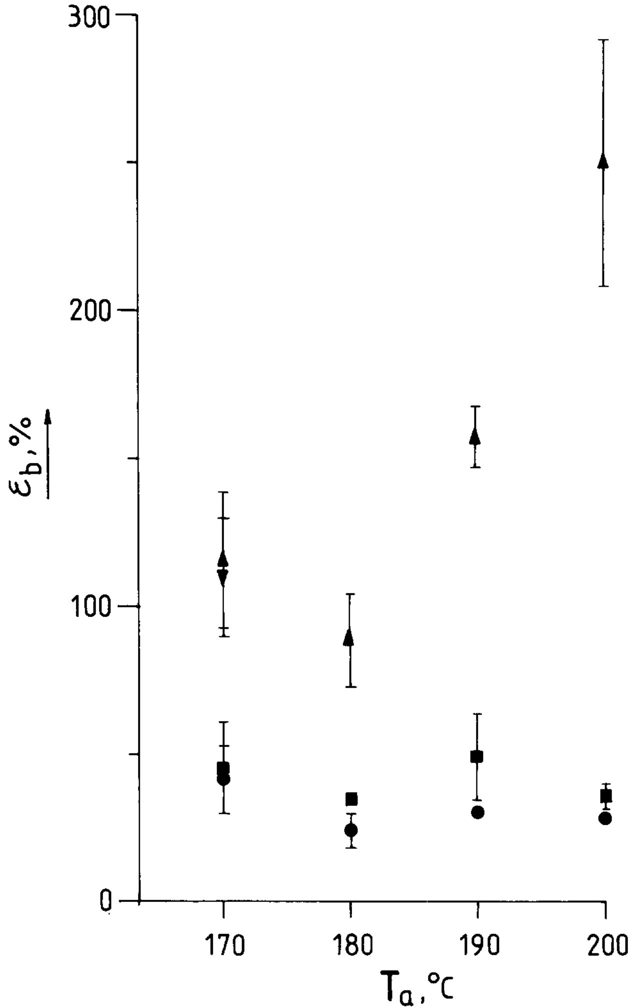

Figure 7 Dependence of the relative elongation at break ε_b on the annealing temperature T_a for drawn annealed samples. For the meaning of the symbols, see *Figure 6*

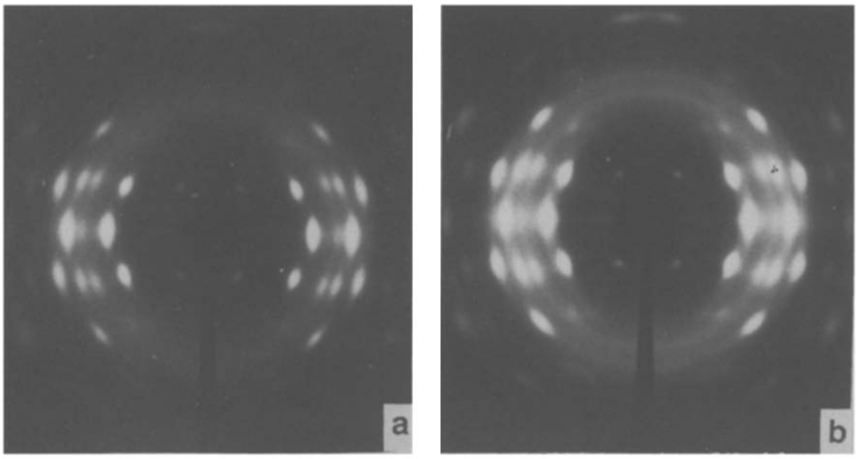

Figure 8 WAXS patterns of drawn samples of Σ75/25, annealed at (a) 170°C and (b) 200°C (taken at room temperature)

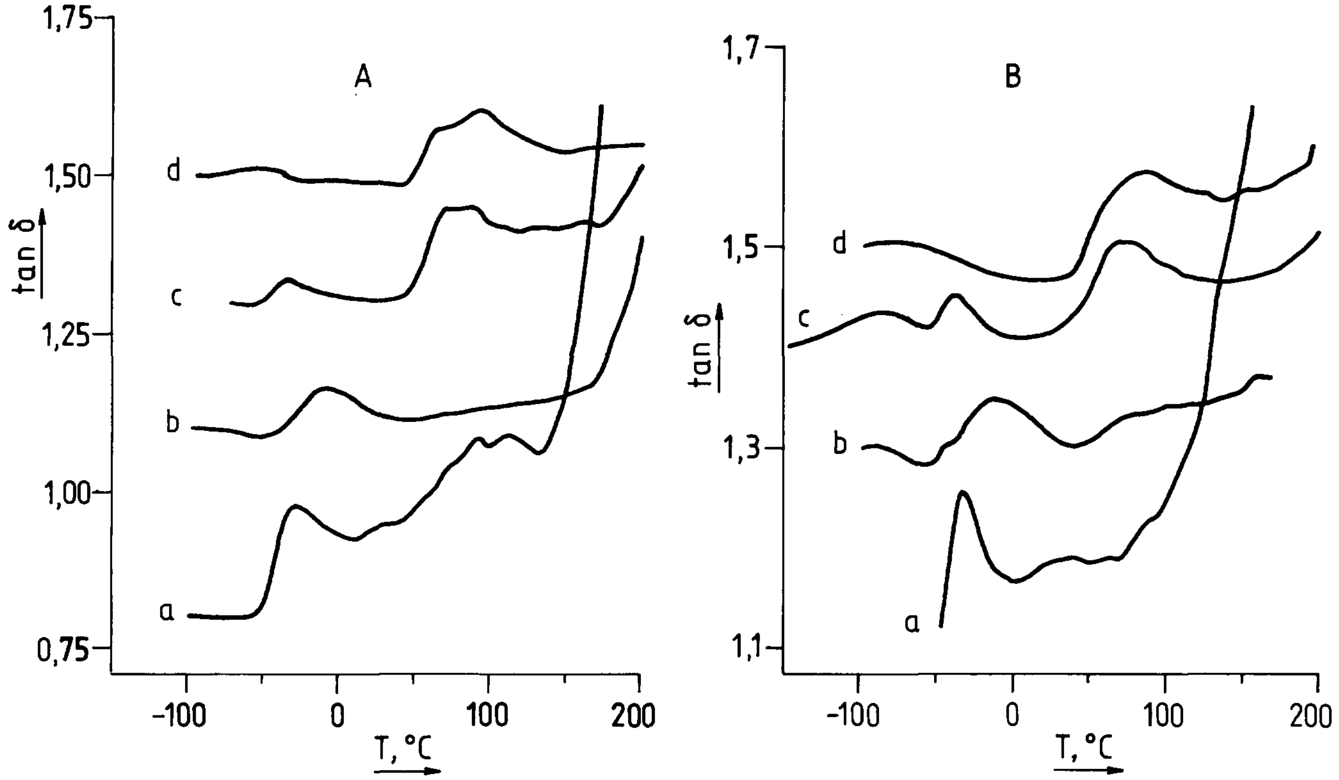

Figure 9 D.m.t.a. curves (tan δ vs. temperature T) of (A) unannealed undrawn and (B) unannealed drawn samples of (a) PEE 49/51, (b) PEE 75/25, (c) blend Σ75/25 and (d) PBT

(*Figure 8b*). Actually the coexistence of PBT reflections in the shape of arcs (from homo-PBT) and circles (from PEE 49/51, *Figure 8b*) indicates again the presence of two types of PBT crystallites.

The results of the dynamic mechanical measurements of the blend, of its components as well as of sample PEE 75/25, in both drawn and isotropic states, are shown in *Figures 9* and *10*. One can see that the drawn samples PBT, Σ75/25 and PEE 75/25 reveal a low-temperature maximum (at about −100°C, *Figure 9B*). The curve of the drawn blend taken from −150°C (*Figure 9B*) shows that this maximum in the other samples originates from the PBT component and represents the γ relaxation of this polymer[13]. For PBT the γ relaxation has been attributed to the local-mode motions of the ester group in non-crystalline regions, while the γ transition of the copolymers is believed to be a combination of the local motions of tetramethylene oxide units of the soft segment (for the case of PEE with such soft segments) and the γ relaxation of the uncrystallized hard segments[14]. The next maximum observed at about −50°C appears in all samples, except for homo-PBT (*Figure 9*), and for this reason it should be assigned to the β relaxation of PEG, which is associated with cooperative (T_g-like) motion in the amorphous phase. The value of $T_g = -50°C$ is typical of PEE 49/51[8], and in the present case it is observed with PEE 49/51 and with the blend containing the same PEE.

The PEE characterized by a lower PEG content (75/25) reveals a much higher T_g^{PEG} value (−18°C) compared to those of the blend Σ75/25 and of PEE 49/51, in both the

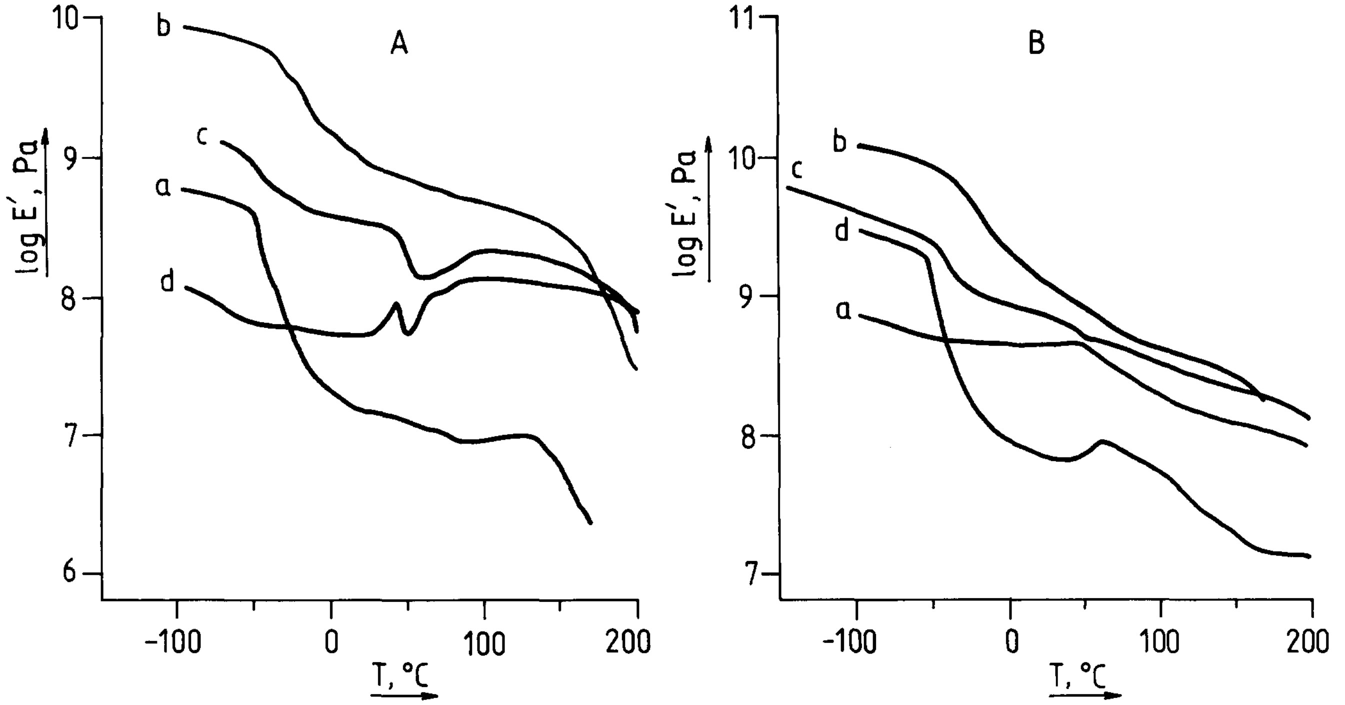

Figure 10 D.m.t.a. curves (tensile modulus E' vs. temperature T) of (A) unannealed undrawn and (B) unannealed drawn samples, indicated as in *Figure 9*

drawn and the isotropic states (*Figure 9*), whereas the blend exhibits the same T_g as its component PEE 49/51. It can be concluded that blending, i.e. introduction of homo-PBT, does not affect the glass transition temperature of the soft segments — it is the same as that of PEE 49/51.

The last relaxation peak positioned at about 70°C, which is again a β relaxation, is related to the glass transition of PBT $(T_g^{PBT})^{13}$. For this reason it is best resolved for the homo-PBT sample and for the drawn and undrawn blend.

Summarizing these results of the dynamic mechanical measurements, one can conclude that, in the drawn and undrawn thermally untreated blend of PBT and PEE 49/51, two well defined amorphous phases are present. The first one originates from the soft segments (PEG) of the copolymer (with $T_g^{PEG} = -50°C$) and the second one represents amorphous PBT belonging to homo-PBT and to the PBT hard segments of the copolymer (with $T_g^{PBT} = 70°C$). As amorphous PBT has almost the same T_g regardless of its origin, the present measurements do not answer the question whether the amorphous PBT phase is spatially separated in accordance with its origin, as the crystalline phase does, demonstrated by the other measurements discussed above.

Another peculiarity in the mechanical behaviour of the blend in comparison to its components, homo-PBT and PEE 49/51, is related to the storage modulus E' measured in dynamic mode. The results for undrawn and drawn samples are plotted in *Figures 10A* and *10B*, respectively. One can see that the highest values in the entire temperature range (-100 up to 150°C) are obtained with the copolymer PEE 75/25 followed by the blend. Homo-PBT exhibits E' lower than that of both the copolymer PEE 75/25 and the blend. It should be stressed here that just the opposite is observed with the Young's modulus E measured in static mode (*Figure 5*), where homo-PBT reveals the highest values, PEE 75/25 the lowest, and the blend being again in between. The moduli of the copolymer PEE 49/51 remain relatively low regardless of the mode of measurement — static or dynamic.

Comparing the data of *Figure 5* and *Figure 10*, the conclusion can be drawn that by blending of thermoplastic and elastomeric polymers a significant improvement of the mechanical behaviour in dynamic mode can be achieved. While the static modulus E of the blend is about half the value for homo-PBT (*Figure 5*), the modulus measured in dynamic mode (*Figure 10*) at 25°C is much higher for both undrawn (*Figure 10A*) and drawn samples (*Figure 10B*).

In order to estimate the extent of elastic deformation of the blend, cyclic mechanical tests were performed with a stepwise increase of the deformation of 5, 10, 15%, etc., till sample breaking. The hysteresis curves obtained are shown in *Figures 11A* and *11B* for $T_a = 170$ and 200°C, respectively. It is seen that the residual plastic deformation strongly increases with the progress of the overall relative deformation. After the tenth cycle (overall deformation of 50%), the sample annealed at 200°C (*Figure 11B*) reveals smaller residual (plastic) deformation than that annealed at 170°C (*Figure 11A*, 18% against 26%), whereas the elastic deformation for $T_a = 200°C$ is 1.3 times larger than for $T_a = 170°C$.

DISCUSSION

The results of thermal analysis and X-ray scattering experiments strongly suggest that the PBT and PEE 49/51 are not capable of cocrystallization at least when blended approximately 1:1 by weight. This conclusion is in accordance with the results of a very recent[15] thorough study on miscibility and cocrystallization of homo-PBT with PEE containing tetramethylene oxide as soft segments. In this study Gallagher *et al.* concluded that the amorphous-phase behaviour of blends varies from completely immiscible to miscible when the PBT content in PEE changes from 75 to 91 wt%. Cocrystallization was observed in the miscible blends under all crystallization conditions[15].

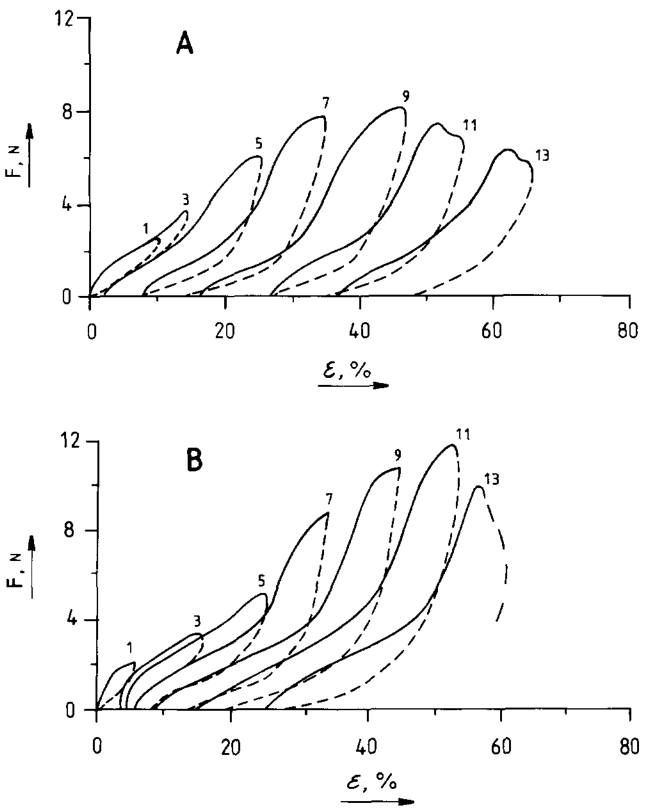

Figure 11 Stress–strain hysteresis curves of drawn samples of the blend Σ75/25, annealed at (A) 170°C and (B) 200°C. The curves are taken using loading (——)/unloading (– – –) cycles with 5% strain step. The numbers above the curves refer to the number of the cycle (only the curves corresponding to the odd cycles are drawn)

Special attention should be given to the observation that the blend annealed above the $T_m = 181$°C of the copolymer ($T_a = 200$°C) for 6 h shows a rather high melting point of the crystallites, arising from PEE (30°C higher than the annealed at $T_a = 170$°C blended or neat copolymer), while T_m of the homo-PBT changes slightly (5°C). Such behaviour is reported by Gallagher *et al.*[15] but only for PEE containing 65 wt% and more PBT. In order to understand the melting behaviour of PEE in the blend, one has to take into account two facts. First, previous investigations on PEE with different PBT/PEG ratios led to the conclusion that the thermal treatment of PEE results in dephasing of the two types of segments, i.e. annealing at 200°C causes the formation of a chemically more uniform PBT melt in the molten PEE ($T_m = 181$°C). Secondly, at the same temperature ($T_a = 200$°C) the crystallites of homo-PBT are not molten ($T_m = 225$°C) and play the role of nucleation agents for the subsequent crystallization of the PBT hard segments during cooling. Actually in the present case one deals with some sort of 'epitaxial' growth as noted by Gallagher *et al.*[15]. Only by the effect of the pre-existing crystallites of homo-PBT can one explain the unusual high melting temperature of PEE in the blend whose present T_m has not been reported for the copolymer.

This 'epitaxial' growth of PBT crystallites from PEE on homo-PBT crystallites can be considered as partial cocrystallization, i.e. formation of continuous crystals consisting of two spatially not separated crystallographically identical populations of crystallites, differing in their size, perfection, origin and time of appearance, as shown schematically in *Figure 12*. Obviously the epitaxial effect of the homo-PBT crystallites contributes to the perfection of the PBT crystallites arising from the copolymer as concluded from their T_m, but this effect is not enough to overcome the peculiarities of the copolymer (e.g. short PBT segments diluted by PEG) in order to produce crystallites of the same perfection as those of homo-PBT (*Figure 12B*). Only by these peculiarities of PEE can one

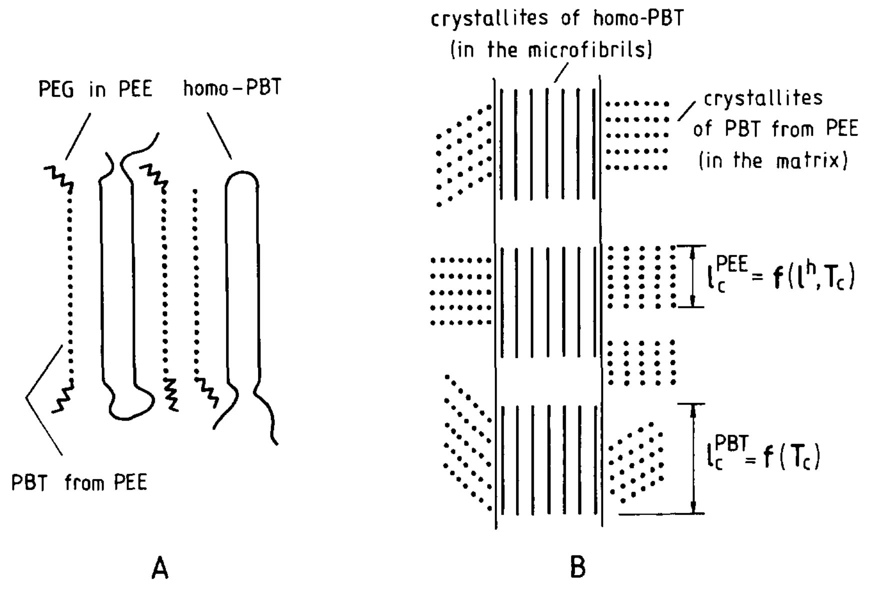

Figure 12 Schematic representation of the two types of cocrystallization of homo-PBT and PEE with different PBT content in microfibrillar reinforced composites: (A) complete cocrystallization (PBT in PEE is 75–91 wt%)[15]; (B) partial cocrystallization (PBT in PEE is below 75 wt%, in present case 50 wt%). l_c = lamella thickness, T_c = crystallization temperature, l^h = length of the hard segments (PBT) in PEE

understand the finding of Gallagher *et al.*[15] that a complete cocrystallization, i.e. formation of uniform crystallites with simultaneous participation of PBT from both the homopolymer and the copolymer, is observed only with PEE containing 75–91 wt% PBI (*Figure 12A*). Such PEEs are distinguished by long enough hard segments (longer than 170 Å[11]). PEEs that do not cocrystallize (typical ones contain 50 and 65 wt% PBT)[15] have an average hard-segment length of 50 Å and longer, which is not enough for the formation of the thermodynamically required lamellar thickness as shown in our previous study[11] and also by Gallagher *et al.*[15] (*Figure 12*).

Although in the present case we do not observe complete cocrystallization, the partial one contributes substantially to overcoming the immiscibility of homo-PBT and PEE and thus improves the adhesion between the matrix (PEE) and the reinforcing macrofibrils (PBT). Actually, the isotropic crystallization of PEE after annealing at 200°C occurs on the surface of highly oriented crystalline microfibrils (*Figure 12B*). Only by this improved adhesion can we explain the improved mechanical integrity of the MFC based on PBT and PEE after annealing at 200°C, unlike the MFC that is annealed at lower temperatures. This conclusion is supported also by the observed tendency for merging of the measured and calculated Young's modulus with increase of the annealing temperature (*Figure 5*).

It is hard to expect the formation of new chemical linkages between homo-PBT (fibrils) and the PEE copolymer (matrix) because of the low temperature of thermal treatment ($T_a = 180$–$200°C$), which is insufficient for the occurrence of trans-reactions[6,7]. Even thermal treatment at higher temperature (250°C) during sample preparation does not result in any significant trans-esterification reactions, for the following reasons. Recently, Huo *et al.*[16] studied the possibility of trans-reaction occurring at 250°C in the miscible PBT/polyarylate blend using the d.s.c. technique. They found that for times shorter than 10 min the sample has not undergone any significant trans-esterification. This result is consistent with the previous report by Kimura *et al.*[17], indicating that the trans-esterification reaction is severe only after holding the same blend at 250°C for more than 100 min. In the present case the probability of occurrence of trans-reactions is much smaller, not only because the annealing time is too short (5 min) but also because our blend is immiscible and the annealing at 250°C is a 'static one', i.e. stirring is not applied.

The advantages offered by the MFC[2–5], as well as earlier[18] and present observations with respect to improvement of mechanical properties of blends of PBT and PEE, make it possible to design polymer blends and to control their properties.

Cocrystallization, even the partial one, seems to be an attractive approach to overcoming incompatibility in polymer blends, and it can be applied to both condensation polymers and polyolefins having a common crystallizable component. Experiments with other blend ratios and blending conditions are in progress.

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REFERENCES

1 Utracki, L. A. 'Polymer Alloys and Blends', Hanser, Munich, 1989

2 Evstatiev, M. and Fakirov, S. *Polymer* 1992, **33**, 877

3 Fakirov, S. and Evstatiev, M. in 'The Interfacial Interactions in Polymeric Composites' (Ed. G. Akovali), Kluwer Academic, Dordrecht, 1993, p. 417

4 Fakirov, S., Evstatiev, M. and Schultz, J. M. *Polymer* 1993, **34**, 4669

5 Fakirov, S., Evstatiev, M. and Petrovich, S. *Macromolecules* 1993, **26**, 5219

6 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953

7 Fakirov, S. in 'Solid State Behavior of Linear Polyesters and Polyamides' (Eds. J. Schultz and S. Fakirov), Prentice-Hall, Englewood Cliffs, NJ, 1990, p. 1

8 Fakirov, S. and Gogeva, T. *Makromol. Chem.* 1990, **191**, 603

9 Apostolov, A. A. and Fakirov, S. *Bulg. J. Phys.* 1989, **16**, 4

10 Privalko, V. P. 'Handbook on Physical Chemistry of Polymers', Naukova Dumka, Kiev, 1984, Vol. 2, p. 177 (in Russian)

11 Fakirov, S., Apostolov, A. A. and Fakirov, C. *Int. J. Polym. Mater.* 1992, **18**, 51

12 Hull, D. 'An Introduction to Composite Materials', Cambridge University Press, Cambridge, 1981, p. 83

13 Wahrmund, D. C., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1979, **22**, 2155

14 Lilaonitkul, A. and Cooper, S. L. *Macromolecules* 1979, **12**, 1146

15 Gallagher, K. P., Zhang, X., Runt, J. P., Huynh-ba, G. and Lin, J. S *Macromolecules* 1993, **26**, 588

16 Huo, P. P., Cebe, P. and Capel, M. *Macromolecules* 1993, **26**, 4275

17 Kimura, M., Porter, R. S. and Salee, G. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 367

18 Brown, M. *Rubber Ind.* 1975, **9**, 102