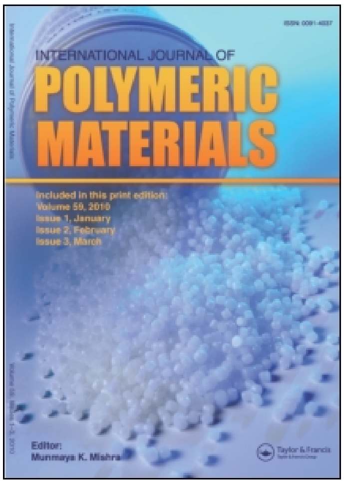

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Improvement of Mechanical Properties of Poly(butylene terephthalate)/Polyarylate Blends with Various Compositions via Zone Drawing-Zone Annealing

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Improvement of Mechanical Properties of Poly(butylene terephthalate)/Polyarylate Blends with Various Compositions *via* Zone Drawing-Zone Annealing

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Poly(butylene terephthalate)/polyarylate (PBT/PAr) blends of various compositions were subjected to a series of thermal and mechanical treatments. The evolution of the structure together with the static mechanical properties of produced fibers were investigated. It was found that zone drawing-zone annealing at 140 and 190°C markedly improves the blend mechanical properties: the Young modulus increases up to 5 times, the tensile strength–up to 10 times (compared to neat PBT) and up to 5 times (compared to neat PAr), the elongation at break drops 50–100 times with the rise of PAr content. The highest values of modulus and strength are obtained for blends containing between 10 and 35% (by wt) PAr. The observed improvement is explained by the substantial chain axis orientation and enhanced crystallization of PBT offered by the zone drawing-zone annealing process, as proven by wide angle X-ray diffraction and birefrigent tests. Finally, a conclusion is drawn that after the appropriate treatments the PBT/PAr blends represent microfibrillar reinforced composites, similarly to other polymer blends for which the same improvements in the mechanical properties are known to be due to the microfibrillar reinforcing effect. The PBT microfibrils are visualized by observations using scanning electron microscope.

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Keywords: Poly(butylene terephthalate)/polyarylate blend; Miscible blends; Microfibrillar reinforced composites; Young modulus; Tensile strength; Zone drawing-zone annealing

I. INTRODUCTION

Investigations of synergistic processing routes to obtain desired properties through blending have been the focus of intense research for several decades [1]. The morphology controls the physical properties and ultimately determines the commercial potential of the polymer blends. Particular interest is given to the miscible blends of one crystallizable and one amorphous component such as poly(butylene terephthalate)/polyarylate (PBT/PAr) blends [2–5] where PAr is completely non-crystalline, whereas PBT is semicrystalline. It is also shown that blends of PBT and PAr are miscible at all compositions in the melt or in the amorphous state [2] and once PBT crystallizes, separation of the PBT crystalline phase from the PBT/PAr amorphous phase may occur at slow cooling rates. In these blends, both PBT and PAr chains coexist as a single phase in the amorphous domains [2].

The efforts for improving the mechanical properties of the polymer blends resulted to the recent [6–8] development of a new type of composite materials based on polymer blends by applying appropriate processing routes. Since the reinforcing elements are the basic morphological entities of oriented polymers, the microfibrils, these new composites were called microfibrillar reinforced composites (MFC). MFC clearly differ, however, from the traditional composite systems. As far as the microfibrils are still not available as a separate component, the classical approach to composite preparation is inappropriate for MFC manufacturing.

MFC are prepared from polymer blends of immiscible partners. A second basic requirement to the partners is a difference in their melting points, T_m. The essential stages of MFC preparation are as follows: (i) blending, (ii) extrusion, (iii) drawing (with good orientation of all components), and (iv) annealing at constant strain above T_m of the lower-melting component and below T_m of the higher-melting one. During the drawing step, the blend components are oriented and microfibrils are created (fibrillization step). In the subsequent annealing process, at which melting of the lower-melting component occurs (isotropization step), it must be guaranteed that the oriented microfibrillar structure of the higher-melting component is preserved. It is important to note here that MFC are based on polymer blends but they should not be considered as "drawn blends" since the isotropization step results in the formation of an isotropic matrix reinforced by microfibrils of the higher-melting component, *i.e.*, one deals at the end with a typical composite material. The mechanical parameters of MFC (Young's modulus and tensile strength) are higher by 30–50% than the average values of the components and comparable to those of short glass fiber-reinforced polymer composites having the same matrix [9].

When MFC are prepared from blends of condensation polymers, as a result of chemical reactions (additional condensation and transreactions [10]), taking place at the fibril/matrix interface [11], a copolymer is formed which plays the role of a compatibilizer, *i.e.*, one deals with an *in-situ* compatibilization phenomenon [6–8, 12].

As mentioned above, the PBT/PAr blend is a miscible one, as long as the two components are in the amorphous state; it converts into two-phase systems with the start of the PBT crystallization and at this stage one can apply the MFC concept for preparation of polymer–polymer composites from the initially miscible blends.

Polyarylate is among the polymers of interest for high temperature service, with a glass transition temperature $T_g = 185-190°C$. It is an amorphous aromatic polyester being a product of the reaction between bisphenol-A and an equimolar mixture of iso- and terephthalic acids. It has excellent mechanical and flammability properties and is inherently stable when exposed to ultraviolet radiation. However, it is very sensitive to common solvents. Thus, blending is a way to improve the properties of polyarylate [3], and a good candidate for blending is PBT [2–5].

Taking into account the commercial importance of the PBT/PAr blends, the main goal of this study is to investigate the opportunity for improvement of the mechanical properties profile of the blends *via* better orientation and crystallization routes, applying for example the zone drawing-zone annealing technique [13]. An additional challenge in this direction is the checking of possibilities for preparation of microfibrillar reinforced composites from miscible blends.

II. EXPERIMENTAL

PBT, tradename Celanex, is supplied by Celanese Corp. in pellet form. The melting point is 225°C. PAr, tradename Ardel DM100, is supplied by Amoco Corp. also as pellets and represents a copolyester of bisphenol-A and an equimolar mixture of terephthalic with isophthalic acids. PBT and PAr are dried carefully in a vacuum oven at 120°C for 24 hours before melt blending and subsequent extrusion.

The specifications of the extruder for the preparation of thin samples (fibers with diameter of 0.12–0.26 mm) are as follows: screw diameter 30 mm, L/D ratio 32.5 and capacity 30 kg h^{-1}. The rotation speed of the screws is kept constant at 100 rpm during blending.

All measurements are carried out on neat homopolymers PBT and PAr as well as on their blends prepared by melt blending using a Werner and Pfleiderer 30 mm twin screw extruder with the following PBT/PAr (wt%) compositions: 100/0, 90/10, 80/20, 65/35, 50/50, 25/75 and 0/100.

Zone drawing-zone annealing [13] was performed on the fibers by vertically moving a narrow (diameter of 2 mm) cylindrical heater attached to the crosshead of a Zwick tensile testing machine under various tensions. The temperature of the heater was measured by a thermocouple fixed on the 2 mm thick glass tube. The sample preparation conditions and their composition are given in Table I.

The wide-angle X-ray scattering (WAXS) film patterns on selected samples were obtained using a GE X-ray generator equipped with a

TABLE I Sample composition, designation and preparation conditions

Sample composition PBT/PAr (by wt)	*A Undrawn*	*B Zone drawn and zone annealed**	*C Zone drawn and zone annealed***
100/0	+	+	+
90/10	+	+	+
80/20	+	+	+
65/35	+	+	–
50/50	+	+	–
25/75	+	–	–
0/100	+	–	

*Zone drawn-zone annealed at 140°C, weight of 15 MPa with one passage of the heater followed by another passage at 75 MPa and 4 more passages at a weight of 150 MPa.

** Zone drawn-zone annealed at 190°C, weight of 15 MPa with one passage of the heater followed by another passage at 75 MPa and 4 more passages at a weight of 150 MPa.

copper target tube and Furnas small-angle X-rays – wide-angle X-ray scattering combination camera. The X-rays were monochromatized using a nickel filter. The exposure times were increased with the decrease in crystallinity of the samples.

The Young modulus, E, the stress at break, σ_b, and the strain at break, ε_b, of the undrawn and drawn fibers were measured in a static mode at room temperature and crosshead speed of 5 mm min^{-1} using a Zwick 1464 machine equipped with an incremental extensometer. For each sample at least 5 measurements were averaged.

For the morphological characterization of the samples, a Leica S 360 scanning electron microscope (SEM) with accelerating voltage of 15 kV was used. For observation of microfibrils, samples were prepared from the drawn neat PBT and its blends by breaking the fibers in liquid nitrogen. The fracture surface was coated with gold before analysis.

The birefringence (Δn) was measured by the spectrometric method [14] by means of a Shimadzu UV – 3101 PC scanning spectrophotometer. A single fiber was placed dry between crossed polarizers at 45° from the exctintion position and scanned between 400 nm and 700 nm. The wavelength values corresponding to the minimum intensity were used for the determination of the birefringence.

III. RESULTS AND DISCUSSION

III.1. Chemical Interactions in PBT/PAr Blends

In addition to the isotropization step in the manufacturing of MFC, during short thermal treatment, chemical reactions (additional condensation and transreactions [10]) in the melt and in the solid state take place at the interface of condensation polymers [11], resulting in the formation of a copolymeric interphase playing the role of a self-compatibilizer [6–8, 12] as stated above. At longer thermal treatment, the interphase grows and involves all of the isotropic (molten) component and the amorphous portion of the fibrillized one in block copolymers and later in random ones. These chemical interactions and transformations in the sequential order of copolymers are proved by DSC, WAXS, DMTA, IR, SEM and NMR analyses [8, 10, 15].

In addition to the repeatedly reported randomization of a molten block copolycondensate, driven by entropic forces, a regeneration of blocks, driven by crystallization forces, *i.e.*, a crystallization-induced sequential reordering is demonstrated. Both, the randomization and block regeneration strongly depend on temperature, transesterification catalyst, blend composition and miscibility of blend components [11]. What is more, regeneration of blocks in a molten random copolycondensate, driven by miscibility forces has been observed for the first time [11]. The miscibility-induced sequential reordering takes place when a random copolycondensate of immiscible partners is melt-blended with a homopolymer, which is miscible with one of the first two components [11].

The described chemical interactions result in a total change of the chemical composition of MFC, the initial homopolymeric matrix being now replaced by a new, copolymeric one. By an appropriate combination of treatment conditions, it is possible to explore the physical and more particularly, the chemical interactions at the interfaces and in the interphases in order to establish a controllable manner for the obtaining of polymer–polymer composites. Experiments, performed on a semi-commercial scale using a specially added catalyst for the transreaction between poly(ethylene terephthalate) (PET) and polyamide 6 (PA6), led to very promising results [16].

Independently, by means of a blend of PA6 with functionalized polypropylene (PP), it was recently demonstrated [17] that transreactions occur within the first few minutes after melting during processing (extrusion by means of twin-screw extruder).

It seems noteworthy that the above mentioned miscibility-induced sequential reordering was observed using the miscible PBT and PAr partners in molten state together with another third, unmiscible component [11, 18]. This means that the potential for chemical interactions between PBT and PAr is well documented [11, 18]. The question of interest for the present case is to what extent these interactions can take place under the conditions of zone drawing-zone annealing applied, and more specifically, at temperatures of 140 and 190°C.

Taking into account the important facts that (i) the thermal treatment in this case is very local and effective for short times (a few seconds), and (ii) the lower temperature used (140°C) is hardly high enough for the occurrence of transreactions or additional condensation [19], one can expect that in this particular case no significant chemical interactions between the components can take place.

The possibilities for chemical interaction between PBT and PAr at the higher temperature (190°C) for zone drawing-zone annealing are much favorable mostly because the temperature conditions are better (at the both treatment temperatures, 140 and 190°C, the PBT/PAr blends are far above their T_g). The T_g of the two blends under consideration (90/10 and 80/20), according to the dynamic mechanical thermal analysis (DMTA) are 54 and 65°C, respectively, (Tab. II, [20]). A support in favor of the assumption that chemical interactions between PBT and PAr can take place to some extent can be found in the comparizon of the mechanical properties (tensile modulus E and the tensile strength σ_b) of the samples with the composition (80/20) and treated at 140 and 190°C (Tab. II). In the second case E and σ_b are by 10% higher (Tab. II). Obviously, this slight increase can be explained by the improved adhesion between the PBT microfibrils and the surrounding amorphous matrix comprizing both, the PAr and the amorphous PBT, due to the chemical interactions between the two phases. Even slight chemical interactions, as in the present case, can have a compatibilizing effect with positive influence on the mechanical properties profile.

III.2. Improvement of the Static Mechanical Properties by Zone Drawing-Zone Annealing of PBT/PAr Blends with Various Compositions

Two sets of PBT/PAr samples, both with high chain orientation and with increased crystalline perfection were obtained by applying the zone drawing-zone annealing technique at 140°C (sample B, Tab. I) and at 190°C (sample C, Tab. I) from the "as extruded" material (samples A in Tab. I).

The dependence of the static tensile modulus E on the composition of untreated samples (samples A, Tab. I) and of those zone drawn-zone annealed at two different temperatures (samples B and C, Tab. I) is shown in Figure 1a. It can be seen that the undrawn and unannealed samples are characterized by the same E values regardless of blend

TABLE II Static mechanical properties (E, σ_b, ε_b), thickness (d), birefringence (Δn), and glass transition temperature T_g of the PBT/PAr blends for various compositions and treatments

Sample composition	*A*					*B*					*C*					T_g(°C) *from*
PBT/PAr (by wt)	E (*GPa*)	σ_b (*MPa*)	ε_b (%)	d (*mm*)	$\Delta n \cdot 10^4$	E (*GPa*)	σ_b (*MPa*)	ε_b (%)	d (*mm*)	$\Delta n \cdot 10^4$	E (*GPa*)	σ_b (*MPa*)	ε_b (%)	d (*mm*)	$\Delta n \cdot 10^4$	*tan* δ *of drawn at* 25°C *fibers* [20]
100/0	1.65	94	985	–	–	6.6	626	18	0.065	19.6	5.5	552	18	0.065	19.4	53.1
90/10	1.70	90	940	0.15	14.14	11.8	1044	14	0.064	17.9	10.8	987	15	0.066	17.9	54.2
80/20	1.74	86	810	0.24	11.1	9.4	785	12	0.075	17.1	10.2	876	13	0.072	14.7	64.8
65/35	1.74	88	470	0.12	7.5	13.6	906	7	0.056	16.5	–	–	–	–	–	83.9
50/50	1.81	66	150	0.11	–	7.3	538	8	–	–	–	–	–	–	–	114.4
25/75	1.18	79	118	0.26	5.9	–	–	–	–	–	–	–	–	–	–	–
0/100	1.77	188	81	0.13	0.2	–	–	–	–	–	–	–	–	–	–	193.0

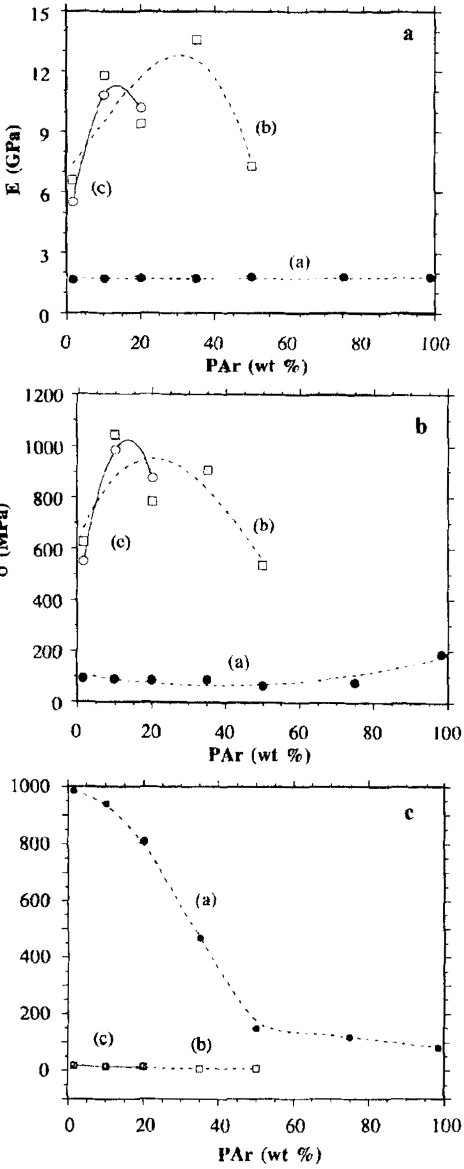

FIGURE 1 Dependence of the static mechanical properties measured at room temperature on the composition for PBT/PAr blends (neat PBT and PAr are also included): a – Young's modulus E: (a), (●) – undrawn, unannealed samples; (b), (□) – zone drawn-zone annealed at 140°C samples; (c), (O) – zone drawn-zone annealed at 190°C samples; b – tensile strength σ_b: (a), (●) – undrawn, unannealed samples; (b), (□) – zone drawn-zone annealed at 140°C samples; (c), (O) – zone drawn-zone annealed at 190°C samples; c – relative elongation at break ε_b: (a), (●) – undrawn, unannealed samples; (b), (□) – zone drawn-zone annealed at 140°C samples; (c), (O) – zone drawn-zone annealed at 190°C samples. In all figures a, b and c, the best fitting lines are drawn for experimental points for clarity.

composition (Fig. 1a, curve (a)). This value being around 1.75 GPa is almost equal to those of the neat components, the PBT and PAr (Tab. II, samples A). Zone drawing-zone annealing results in a significant increase in E (Fig. 1a, curves (b) and (c)). A value of $E = 13.6$ GPa, *i.e.*, a 7 fold increase relative to the untreated samples is reached at the blend composition PBT/PAr = 65/35 (by wt) (Tab. II, sample B).

Rather similar behavior was observed for the tensile strength, σ_b, as shown in Figure 1b. Again the undrawn and unannealed samples are distinguished by an almost constant σ_b value of around 85 MPa (except for the neat PAr, for which $\sigma_b = 188$ MPa) (Fig. 1b, curve (a)). Zone drawing-zone annealing leads also to a marked increase in σ_b. The tensile strength exhibits its maximum (1044 MPa, Tab. II) value at the composition PBT/PAr = 90/10 (by wt) (Fig. 1b, curve (b)). This corresponds to an almost 10 fold improvement over the undrawn neat PBT and of about 5 fold one as compared with PAr (Tab. II, samples A and B).

From the curves for E and σ_b (Fig. 1a and 1b, respectively) an important observation can be made. The temperature at which the zone drawing-zone annealing is carried out does not play the most significant role for the improvement of mechanical properties (E and σ_b) since the difference between the maximum values of E and σ_b for the two treatment temperatures, 140 and 190°C, are not that great (between 10 and 20%, curves (b) and (c) in Fig. 1a and 1b). The drastic improvement in the mechanical properties (E and σ_b) is related mostly with the blend composition and orientation (Fig. 1a and 1b, curves (b) and (c)). Provided all the samples are preoriented, as in the cases of samples B and C (Tab. I), one can easily see the strong effect of composition on E and σ_b. In both cases, the introduction of only 10 wt% of PAr to PBT results in a double increase in E (Fig. 1a, curves (b) and (c)) and in σ_b (Fig. 1b, curves (b) and (c), Tab. II) values. While the further increase of the PAr component in the blend does not improve the σ_b value, the static modulus E reaches its maximum at the PAr content of 35 wt%.

One could explain this strong effect of PAr content by the progressive increase of the T_g values with the rise of the PAr amount in the blend (from 50°C for neat PBT to 110°C for 50/50 blend as shown on the same blends by DMTA (Tab. II, [20])). Obviously, this factor is not sufficient for the explanation of the observed improvement in mechanical properties because a similar increase in T_g is found also for the undrawn blends (from 40°C for the neat PBT to 90°C for the 50/50 blend [20]) and in the same time with negligible effect on the E values (from 1.60 GPa for the neat PBT to 1.80 GPa for 50/50 undrawn blend [20]). It seems also important that in addition to the increased T_g values for explaining the drastic improvement of the mechanical properties, one has to account for the orientation and enhanced crystallization of PBT, particularly at the higher (190°C) treatment temperature.

The contribution of the orientation to the improvement of the mechanical property profile can be judged from Figure 2 where birefringence Δn of PBT/PAr samples with various mechanical and thermal history is presented.

Curve (a) in Figure 2 illustrates the effect of blend composition on Δn since this series of samples represents PBT/PAr blends that have not been subjected to drawing or annealing. One can see the strong increase of Δn only due to the increasing fraction of PBT in the blend.

The drawn samples (Fig. 2, curves (b) and (c)) demonstrate the same composition dependence but also the contribution of the orientation

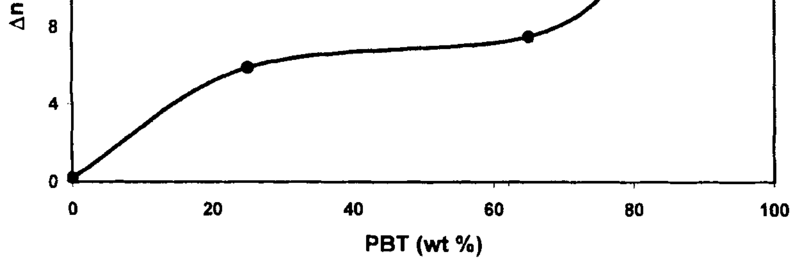

FIGURE 2 Dependence of birefringence Δn on composition of PBT/PAr blends for samples with various mechanical and thermal prehistory: (a) – undrawn, unannealed; (b) and (c) – zone drawn-zone annealed at 140°C (b) and 190°C (c).

to the higher values of mechanical properties. What is striking in this two curves (Fig. 2, curves (b) and (c)) reflecting the zone drawing-zone annealing at 140 and 190°C, respectively, is the strong decrease in Δn for $T_a = 190°C$ when the PAr amount increases up to 20 wt% in comparizon to the sample with the same composition but annealed at $T_a = 140°C$.

The only probable explanation for the observed decrease of Δn (Fig. 2, curve (c)) are the more intensive relaxation processes in the amorphous PBT/PAr phase resulting in the decrease of orientation. To the disorientation contributes also the partial melting of small and/or imperfect crystallites of PBT as well as the partial disorientation of the remaining crystallites imbedded in the relaxing amorphous phase. Such an isotropization tendency at $T_a = 190°C$ has another important sequences which will be discussed in the subsequent subsection.

Quite similar situation – a significant drop in Δn as result of temperature increase – was recently [21] reported for drawn PET films. This observation is explained by chain relaxation in amorphous areas and partial melting of PET crystallites [21].

So, the observed improvement in mechanical properties (E and σ_b) can be attributed mostly to the molecular orientation and enhanced crystallization during the zone drawing-zone annealing carried out at temperatures above T_g of the blends. It is generally accepted that this process can be used for imparting molecular orientation and obtaining a more perfect physical structure [13]. This property is also supported by the present observations.

Finally, in Figure 1c, the dependence of the elongation at break, ε_b, for the same samples A, B and C (Tab. I) is plotted. Undrawn and thermally untreated neat PBT as well as PBT-rich blends (PBT/PAr up to 80/20 by wt) (samples A, Tab. I) show very high extensibility (between 800 and 1000%) (Fig. 1c, curve (a)). The decrease of the PBT content leads to a decrease of the elongation at break, reaching $\varepsilon_b = 118\%$ (almost an order of magnitude) for the blend composition PBT/PAr = 25/75 (Fig. 1c, curve (a)). On the other hand, the zone drawn-zone annealed samples (samples B and C, Tab. I) show very low deformation at break ε_b (between 7 and 18%) (Fig. 1c, curves (b) and (c), Tab. II).

So, the blend composition is found to drastically influence the maximum drawability of the blend. This has been also concluded from the behavior of the thicker (diameter 0.62–0.80 mm) undrawn and thermally untreated samples [20]. For instance, the neat thicker bristle of PBT can be drawn at room temperature up to 5 times while blend containing 10% (by wt) of PAr – only 3.5 times; the rise of PAr content up to 20 and 35% (by wt) results in a further drop in λ-values – 3 and 2.5, respectively, for the same series of bristles [20].

The strong negative effect of the PAr content on the drawing ability helps one to explain the finding that the best mechanical characteristics of the blends are obtained with the samples containing no more than 30–35 wt% PAr. Possibly, for the same reason a blend containing more than 20 wt% PAr can not be zone drawn at 190°C because it breaks (Tab. II, sample C, Fig. 1a and 1b, curve (c)).

In summary, from the comparison of the results of static mechanical tests for zone drawn-zone annealed samples and untreated ones (Tab. II), one can conclude that (i) for the untreated samples the blend composition has a slight effect on the tensile strength and almost no influence on static modulus, contrasting to the effect on the elongation at break in the entire range of compositions; (ii) a drastic improvement in the mechanical properties is observed after zone drawing-zone annealing: E increases up to 7 times, σ_b – up to 10 times (compared to the untreated PBT) and 6 (for E) and 5 times (for σ_b) (compared to the untreated PAr), and ε_b decreases by a factor of 50 – 100; (iii) the highest values are obtained for the blends containing between 10 and 35% (by wt) PAr (Tab. II).

III.3. Structure Development In Zone Drawn-Zone Annealed Fibers of PBT/PAr Blends

An attempt was undertaken to characterize to some extent the structure development during thermal and mechanical treatment of the blends by means of WAXS, SEM and birefringence measurements.

The WAXS film patterns of zone drawn-zone annealed fibers containing 0 to 50 wt% PAr are shown in Figure 3a and 3b for fibers treated at 140°C and 190°C, respectively. It should be noted that all the selected samples are rather crystalline with high degree of orientation. But the main conclusion from all of these patterns (Fig. 3a and 3b) is that the chains in the crystalline regions of the PBT phase are oriented along the draw direction, *i.e.*, the fiber axis (FA).

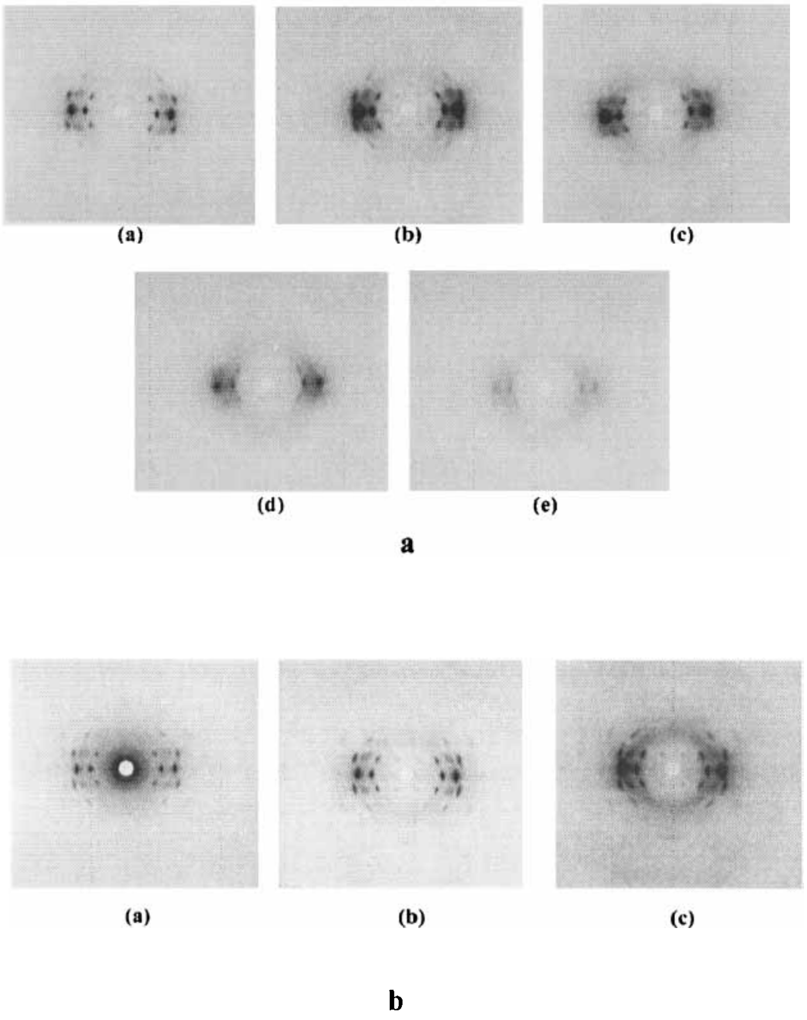

FIGURE 3 Selected WAXS film patterns of zone drawn-zone annealed PBT/PAr fibers at treatment temperatures: a – 140°C with various PBT/PAr blend composition (by wt): (a) – 100/0; (b) – 90/10; (c) – 80/20; (d) – 65/35 and (e) – 50/50; b – treatment temperature 190°C and composition (by wt) as follows: (a) – 100/0; (b) – 90/10 and (c) – 80/20.

What is remarkable in these data, is that even the fibers containing as much as 50% noncrystallizable polyarylate show significant levels of orientation in their PBT crystalline phases (Fig. 3a, pattern (e)). This indicates a very high efficiency of transmission of forces to the polymer chains during the zone drawing-zone annealing process resulting in such high chain axis orientations in the stretch direction.

This high orientation of PBT crystals is due to the peculiarities of the orientation technique used – drawing at elevated temperatures where the thermal treatment is located on a very small area (less than 1 mm). What is of particular importance in this case is that the orientation takes place at temperatures well above T_g of the neat PBT and more ($T_a = 190°C$) or less ($T_a = 140°C$) close to T_g of the neat PAr. What is more in this case is the fact that the two treatment temperatures are significantly above the T_g values of the blends used being around 65–85°C (Tab. II, [20]). Under these conditions, the amorphous PBT chains are very flexible and the produced orientation enhances significantly the crystallization.

Unfortunately, the X-ray technique does not offer almost any information about the completely amorphous PAr. If one assumes that such orientation is lacking, the zone drawn-zone annealed blend samples should have a polymer–polymer composite structure. In other words, the more or less isotropic PAr matrix is reinforced by PBT crystallites, possibly organized in microfibrils with chain axes in FA direction. Such a system, when the isotropic polymeric matrix is reinforced by microfibrils of the other blend component, represents, as a matter of fact, a microfibrillar reinforced composite. These MFC are known and well characterized and the found improvement in their mechanical properties (E and σ_b) [6–9] is of the same order of magnitude as in the present case.

A more careful inspection of the X-ray patterns in Figure 3a and 3b gives some indications supporting the above statement about formation of MFC structure during the thermal treatment at $T_a = 190°C$. If one compares patterns (c) from Figure 3b and 3a, where samples with the same composition (PBT/PAr = 80/20) are zone drawn-zone annealed at 190 and 140°C, respectively, one can see that in addition to the good orientation of the PBT crystallites, a slight amorphous hallo can be detected (as compared with the patterns of the neat PBT, patterns (a) in Fig. 3a and 3b). What is more, the hallo of the sample zone annealed at lower temperature ($T_a = 140°C$) is not isotropic, contrasting to that of the sample zone annealed at $T_a = 190°C$ (pattern (c) of Fig. 3b). This difference in the intensity distribution of the amorphous hallo can be interpreted as a result of relaxation, *i.e.*, isotropization of amorphous chains at higher temperature.

Obviously, the amorphous phase in this case does not contain only a neat PAr but comprises also the amorphous fraction of PBT, which is completely miscible with that of PAr. One can assume further, that the intensity of the amorphous hallo in pattern (c) of Figure 3b is arizing mostly from the PAr but not from the amorphous PBT fraction because such a hallo is not observed in the pattern from the sample treated at the same temperature but with lower PAr content (90/10) (Fig. 3b, pattern (b)), as well as for the neat PBT (patterns (a), Fig. 3a and 3b).

Additional support in favor of the assumption for existence of well defined microfibrils in the PBT/PAr system was found in the microscopic analysis.

In Figure 4 are shown SEM micrographs at two magnifications, around 2 000x (Fig. 4(a) and (b)) and around 10 000x (Fig. 4(c) and (d)) for zone drawn-zone annealed at $T_a = 140°C$ neat PBT and a

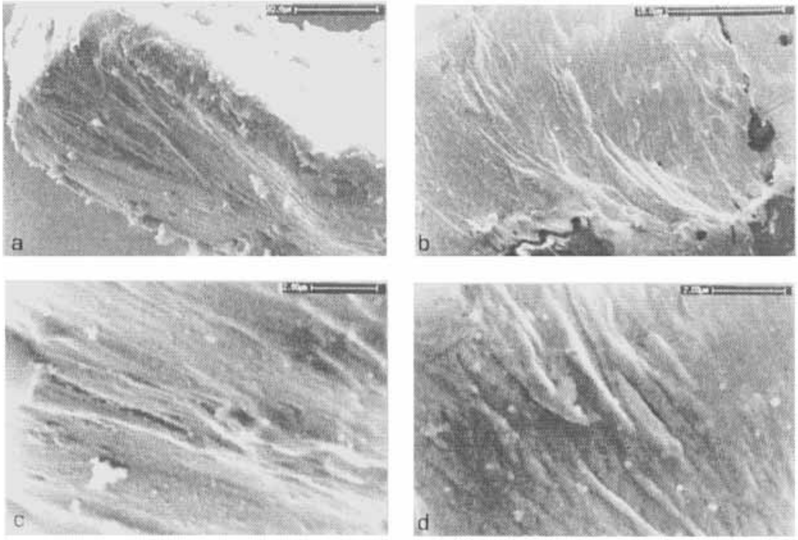

FIGURE 4 Selected SEM micrographs of zone drawn-zone annealed fibers of neat PBT ((a) and (c)) and of PBT/PAr blend (80/20 wt%) ((b) and (d)) taken in two different magnifactions: (a) and (b) – around 2 000x; (c) and (d) – around 10 000x.

80/20 PBT/PAr blend. The pictures are taken from the fracture surface obtained in liquid nitrogen.

Rather well expressed fibrillar structure on the surface parallel to FA as well as on the cross-section of the neat PBT treated at 140°C can be seen (Fig. 4(a)). The actual dimensions of the microfibrils can be better observed at the higher magnification (Fig. 4(c)). What is important, almost the same morphological entities can be seen on the fibers from the blend PBT/PAr = 80/20 wt% (Figs. 4(b) and (d)).

The data of WAXS analysis and, more specifically, those of SEM observations as well as the birefringence measurements demonstrate that one deals with a system being very close to the typical MFC where the isotropic polymer matrix is reinforced by fibrillar structures arising from the other blend component.

It seems important to note at this point that the blend PBT/PAr is the first MFC system where the matrix is a non-crystallizable polymer and the final composite-like structure is achieved starting from a blend of miscible components.

IV. CONCLUSIONS

The following conclusions are drawn from the present study:

1. A drastic improvement in the mechanical properties of the PBT/PAr blends is achieved by applying zone drawing-zone annealing technique: referring to the undrawn and thermally untreated blends and neat components, the tensile modulus E increases by a factor of 7, the tensile strength σ_b – up to one order of magnitude. Compared to the mechanical characteristics of the drawn unannealed neat PBT these improvements are two-fold. The strain at break ε_b for the zone drawn-zone annealed samples drops more than 50 times when the PBT/PAr blends contain 25–35 wt% PAr. The obtained improvements in the properties are partly due to the very high orientation of PBT chains in crystalline phases, as concluded from the WAXS and birefringence measurements.
2. The system studied can be considered as a microfibrillar reinforced composite after the simultaneous performance of the mechanical and thermal treatment, as reported for other polymer blends for

which the same microfibrillar reinforcing effect is observed. In addition, the reinforcing PBT microfibrils are visualized by SEM observation and the isotropisation tendency of amorphous matrix is proven by the drop in the birefringence at higher treatment temperature.

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