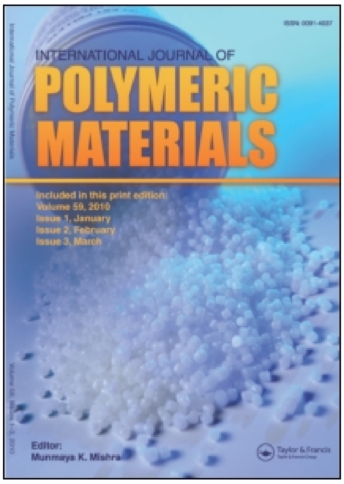

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Structure-property relationships of microfibrillar reinforced blends of linear polycondensates

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STRUCTURE–PROPERTY RELATIONSHIPS OF MICROFIBRILLAR REINFORCED BLENDS OF LINEAR POLYCONDENSATES

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Binary microfibrillar reinforced composites are obtained by melt-blending of poly (ethylene terephthalate) (PET) and polyamide 6 (PA6), as well as polyamide 66 (PA66) and PA6 (both 40/60 by wt) in the presence of a catalyst, followed by cold drawing of the bristle to about 3.5 times and annealing at 220 or 240°C. The blends are studied by X-ray diffraction, scanning electron microscopy (SEM), light microscopy and static mechanical testing. SEM and light microscopy reveal different blend morphologies due to differences in the miscibility of the homopolymers: the PA66/PA6 blend is morphologically more homogeneous, than the PET/PA6 blend. Annealing at 240°C results in preservation of the high orientation of PET and PA66 while the PA6 portions of the two blends are partially disoriented, much more for the PET/PA6 blend

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as concluded from the X-ray data. Annealing at 240°C suggest also transreactions leading to the in situ generation of block copolymers in addition to the generated ones during blend mixing in the extruder which improve the compatibility of the blend components. These physical and chemical changes affect the mechanical properties of the fibrillar reinforced blends and composites. The Young's moduli (E) and tensile strength (σ_t) of the drawn blends are 5–6 and 7–9 times higher than those of the as-extruded samples. Heat treatment at 220°C results in a slight (for PA66/PA6) and stronger (for PET/PA6 blend) decrease of the σ_t while E remains unchanged. A stronger decrease of E in both blends and of σ_t in PA66/PA6 sample has been observed after annealing at 240°C. Nevertheless, E and σ_t of the last samples are about 3 times higher than those for the neat PA6.

Keywords: PET/PA6 blends, PA66/PA6 blends, microfibrillar reinforced composites, mechanical properties

INTRODUCTION

For polymer blend performance of particular importance is the compatibility, *i.e.*, the properties of the interphase layer [1]. The chemical nature, molecular weight, composition and crystallizability, as well as processing conditions are other factors determining the final properties of the blends [2]. Since the vast majority of polymers are immiscible, there is a constant search for means of improving their compatibility.

Numerous studies of compatibility, morphology, crystallization and properties of blends based on semicrystalline and/or amorphous thermoplastic polycondensates have been published [3–22]. However, these studies are directed at elucidating structure-property relationships mainly in isotropic miscible or immiscible blends.

In a series of recent publications [23–27], we reported on a new type of reinforced polymer/polymer composite. These are formed by melt-blending of two or more immiscible thermoplastic polymers, followed by cold- or hot-drawing and annealing of the drawn blend. Upon drawing, the components of the blends are oriented and microfibrils are formed. The structure of the material is further developed by subsequent heat-treatment, and the temperature and duration of this processing step have been shown to significantly affect the structure and properties of the blend. If the heat-treatment temperature (T_a) is set below the melting points (T_m) of both components, the microfibrillar structure imparted by drawing is preserved and further improved as a result of physical processes, such as additional crystallization, minimization of defects in the crystalline regions and relaxation of residual stress in the amorphous regions. On the other hand, if T_a is set between the melting temperature of the two components, isotropization of the lower-melting polymer takes place, forming an isotropic, relaxed matrix, while the microfibrillar regions, involving the component with higher T_m, preserve their orientational and morphological characteristics. The resulting material is referred to as a microfibrillar reinforced composite (MFC) [23–26].

In addition to physical changes, the thermal treatment of blends of condensation polymers might involve chemical changes, which, in turn, affect the compatibility of the components. In fact, exchange reactions between adjacent functional groups, generating *in situ* copolymers, are reported to be a possible method for compatibilizing condensation polymers [3–14, 28]. It should be noted that exchange reactions proceed considerably faster in the molten state [29]. The addition of an appropriate catalyst still further increases the conversion rate. Thus, for instance, Pillon and Utracki [6] report 5 to 23 percent conversion of the ester–amide interchange reaction in a poly(ethylene terephthalate)/polyamide 66 (PET/PA66) blend during a single pass (2–4 min) in an extruder at 300–310°C, catalyzed with 0.2% *p*-toluenesulphonic acid. Andresen and Zachmann [3] found a full conversion of transesterification in a PET/poly(ethylene-2,6-naphthalene dicarboxylate) blend during melt-pressing for 10 min at 280°C. Gattiglia *et al.* [8] have observed the formation of block copolymers after melt mixing a 75/25 by wt PA6/polycarbonate blend at 240°C for 45 min. Formation of segmented copolyamides due to transamidation has been observed during melt mixing of PA6 and poly(*m*-xylene adipamide) [9] as well as PA46 and PA6 [10]. Hours are required for the occurrence of such reactions in the solid state. Solid state reactions in linear polycondensates are particularly favored at high annealing temperatures and occur in the noncrystalline phases, which enjoy relatively higher mobility than the crystalline phases [30]. The *in situ* copolymers formed in this way affect some physical properties of the homopolymers (*e.g.*, crystallinity, morphology) as well as the chemical nature of the blend. The higher the degree of conversion, the stronger is this influence [23–25].

On the other hand, the supermolecular structure of the blends strongly depends on the homopolymers' chemical structures as well [2]. For this reason some differences in the morphology and behavior of blends with the same prehistory, but comprising completely immiscible (*e.g.*, PET/PA6) or partly miscible (*e.g.*, PA66/PA6) components could be expected.

The present study aims at a better understanding of the contribution of physical and chemical processes to the structure-property relationships in drawn PET/PA6 and PA66/PA6 blends subjected to isothermal annealing below and above the melting point of PA6. These polymers were chosen because of their great commercial importance for the large scale production of fibers, films, blends and composites [31, 32]. The blends studied here were prepared using extrusion parameters and catalyst that are very similar to those reported in [6], so that one can assume the occurrence of some degree of conversion, *i.e.*, the formation of PET-PA6 and PA66-PA6 block copolymers during melt blending.

EXPERIMENTAL

Materials and Sample Preparation

Commercial, engineering grade PET (Yambolen, Bulgaria), PA6 (Vidamid, Bulgaria) and PA66 (Ultramid, Germany) were dried in an oven at 120°C for 24 h and two blends, PET/PA6 and PA66/PA6, were prepared in the same weight ratio of 40/60, corresponding to volume ratios of 35/65 and 40/60, respectively. A catalytic amount of *p*-toluenesulfonic acid (0.35 wt%, referred to PA6) was added, followed by extrusion in a Brabander single screw (30 mm diameter) extruder at 15–20 rpm. The 2 mm thick extrudate was quenched in a water bath at 20°C. The temperature zones in the extruder were 285, 290, 295, 300 and at the die 310°C.

All blends were drawn at room temperature on a Zwick 1464 tensile tester at a strain rate of 50 mm min^{-1} to a draw ratio $\lambda = 3.5-3.6$ (diameter of about 1 mm) and then flushed with hot air (60–65°C) in order to remove internal stresses. Some of the drawn samples were then subjected to isothermal annealing with fixed ends at 220 or 240°C for 4 or 8 h in vacuum. The sample preparation conditions are given in Table 1.

X-ray Diffraction

Wide-angle X-ray scattering (WAXS) was carried out in a Warhus flat-film camera, using Ni-filtered Cu K_α radiation and a 4 cm specimen-to-film distance.

TABLE 1 Sample preparation conditions of PET/PA6 and PA66/PA6 (both 40/60 by wt) blends

Sample designation	*Draw ratio* (λ)	*Annealing in vacuum with fixed ends* T_a (°C)	t_a (h)
PET/PA6 blend			
A	as extruded	–	–
A-0	3.5	–	–
A-220-4	3.5	220	4
A-220-8	3.5	220	8
A-240-4	3.5	240	4
A-240-8	3.5	240	8
PA66/PA6 blend			
B	as extruded	–	–
B-0	3.6	–	–
B-220-4	3.6	220	4
B-220-8	3.6	220	8
B-240-4	3.6	240	4
B-240-8	3.6	240	8

Scanning Electron Microscopy

A JEOL JSM 5400 scanning electron microscope (SEM) with an accelerating voltage of 25 kV was used for the observation of the specimens. Specimens were prepared by peeling along the length of the drawn blends. Specimens for observation of microfibrils were prepared also from the drawn blends by extraction of PA6 with formic acid for 24 h. All specimens were then mounted and coated with gold before analysis.

Light Microscopy

The filaments were encapsulated with a resin between two thin plates of polypropylene and sectioned in the longitudinal direction with a Leitz 1401 microtome fitted with glass knife. The sections were immersed between glass slide and cover slip and viewed with a 100 × objective under an Olympus BH2 microscope using polarized and phase contrast techniques.

Mechanical Testing

Mechanical tests were carried out at room temperature, at a strain rate of $5\,\mathrm{mm\,min^{-1}}$ using an Instron 4201 tensile tester. The tensile Young's modulus (E), tensile strength (σ_t) and ultimate strain (ε_u) were determined from the load-extension curves. All values are averaged from five measurements.

RESULTS

X-ray Observations

Figure 1 presents WAXS flat-film patterns for as-drawn and heat-treated PET/PA6 and PA66/PA6 blends. Both as-drawn blends exhibit diffraction from imperfect but highly oriented PA crystals (the "fuzzy" spots on the equator). Because of its relatively slow crystallization rate, the PET has not crystallized during cooling of the extrudate. At 220°C crystallization of PET (the first, third and fifth equatorial reflections) is observed and some loss of orientation of the PA6 (the second and fourth equatorial reflections) is seen. Heat-treatment at 240°C has promoted a major disorientation of PA6, while preserving the orientation of PET (Fig. 1, blend PET/PA6).

For the PA66/PA6 blend, the equatorial diffraction of the two components overlaps and one cannot distinguish PA6 from PA66. Nevertheless, one sees no increase in disorientation of either material after annealing at 220°C and only a modest azimuthal broadening of the equatorial reflections after heat-treatment at 240°C (Fig. 1, blend PA66/PA6).

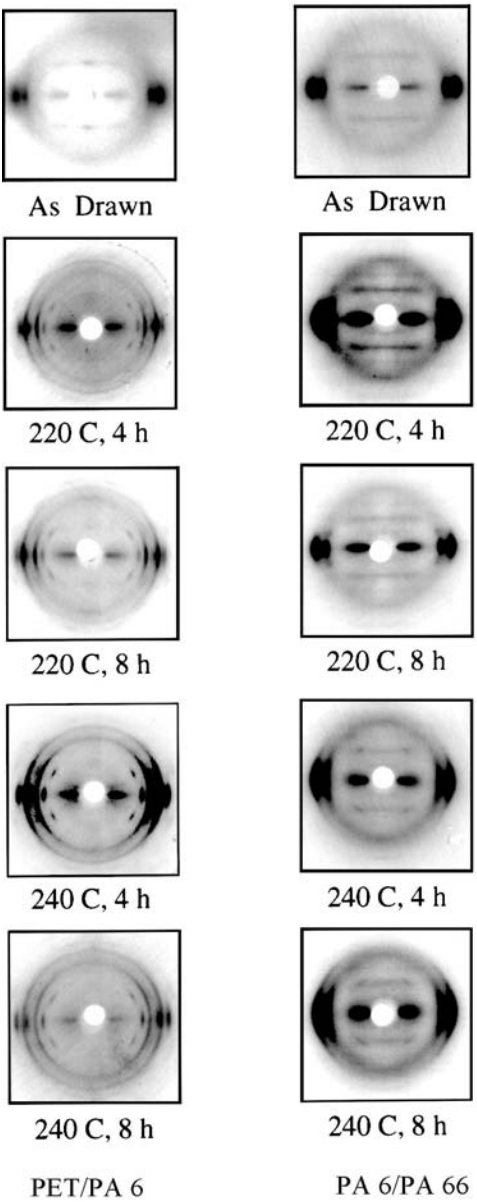

FIGURE 1 WAXS transmission patterns of as-drawn and annealed at different temperatures PET/PA6 and PA66/PA6 (both 40/60 by wt) blends; the treatment conditions are given in the figure.

Morphology

Scanning electron micrographs with various magnifications of peeled surfaces of as-drawn PET/PA6 and PA66/PA6 blends are shown in Figure 2. It is seen that both blends have a skin-core structure. The skin thickness amounts to about 15 – 20 µm. Due to the higher weight and volume percentage of PA6 in the overall blends, this is also the major component in the skin. This is, however, the only similarity of the two blends; Figure 2 shows their different morphologies. Two clearly distinguished phases are observed with the PET/PA6 sample: PET fibrils with diameters of about 1 – 2 µm, oriented in the draw direction, are inserted in a continuous, oriented PA6 phase. The morphological detail of the fibrillized PET phase is better visualized in the micrograph of the sample in which PA6 has been extracted with formic acid (Fig. 2, sample PET fibrils). Separate PET fibrils (0.5 – 1 µm diameter) as well as bundles of them are clearly seen. From the letter it is concluded that a thin layer of PA6 and/or of a copolymer is present between the separate fibrils, forming the PET bundles in the blend.

To the same conclusion lead the observations with light microscope as can be concluded from Figure 3 where three samples are shown using different observation techniques but the same magnification. While the micrograph of the as-extruded (non-drawn, non-annealed) PET/PA6 sample (40/60 by wt) (Fig. 3a) clearly show presence of almost completely round particles with diameters of couple of microns dispersed in the dominating PA6 matrix, the other samples, being drawn and annealed at 240°C (Figs. 3b – d) are distinguished by typical fibrilar morphology. This means that the PET microfibrils created during the cold drawing (Fig. 2, sample PET fibrils) are preserved during the subsequent heat treatment at 240°C when the other component of the blend (PA6) is in a molten state and non-isothermally crystallizes during the subsequent cooling down. What is more, the light microscopic observation support the conclusion based on the WAXS data (Fig. 1, blend PET/PA6, 240°C, 4 and 8 h) that disorientation of PA6 is in a more advanced stage after annealing for 8 h in comparison to the case of 4 h. This can be seen from Figures 3b and d taken by means of phase contrast technique and reflecting the situation after annealing at 240°C for 4 and 8 h, respectively. In the first case (Fig. 3b) the PET microfibrils are surrounded by the similarly oriented PA6 matrix in contrast to the second case (Fig. 3d) where they are rarely distributed in a more or less isotropic matrix after annealing for 8 h. In favor of this conclusion is the micrograph of the sample annealed at 240°C for 8 h made in polarized light. One can see a clear difference between the highly oriented bright PET microfibrils and the disoriented dark PA6 matrix arising from the increased difference in the birefrigerence between the two blend components after the isotropization of PA6. In fact, at this stage of treatment (240°C, 8 h) one deals with a more or

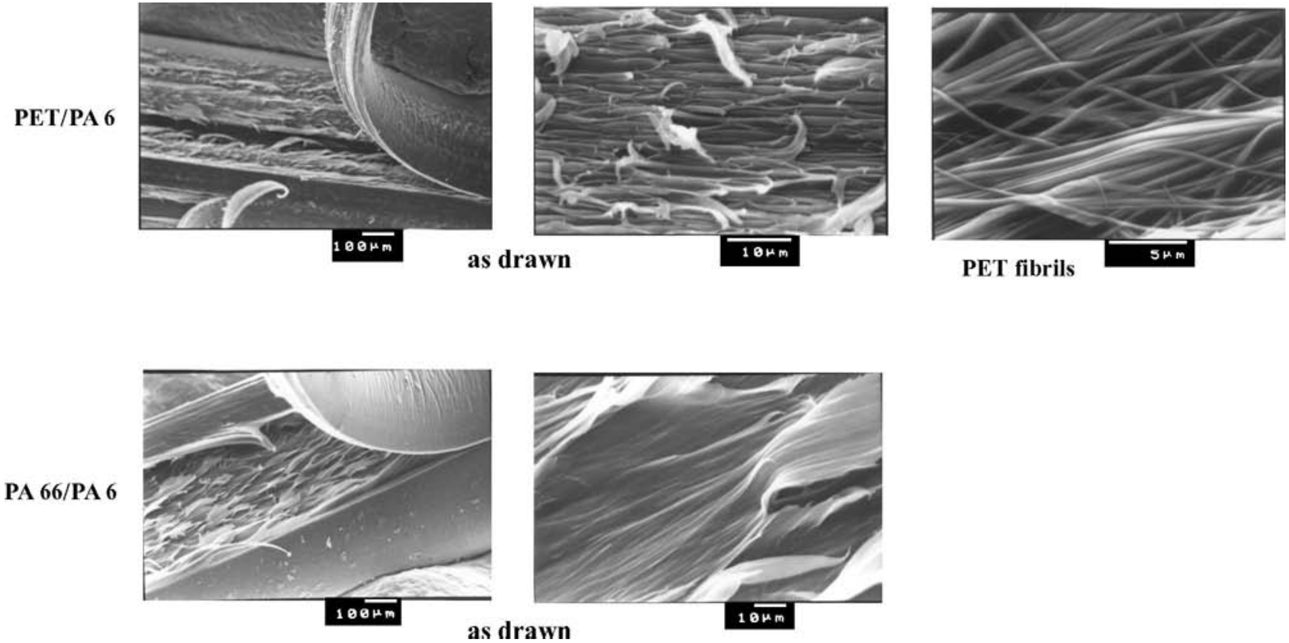

FIGURE 2 SEM micrographs of as-drawn PET/PA6 and PA66/PA6 (both 40/60 by wt) blends. Specimens obtained by peeling or by extraction of PA6 from the drawn PET/PA6 blend (PET fibrils).

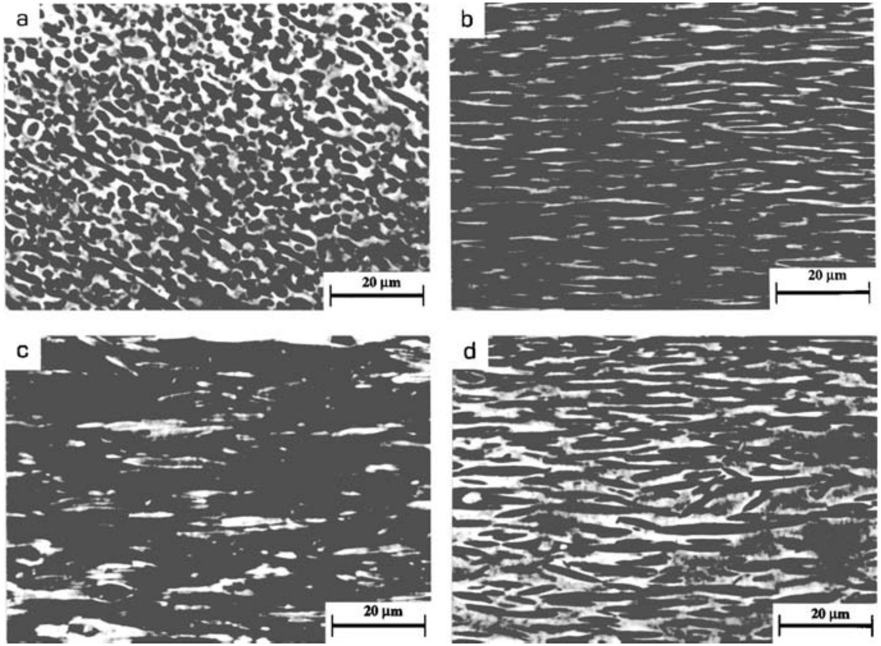

FIGURE 3 Light microscopic micrographs from PET/PA6 (40/60 by wt) blend subjected to various treatments: (a) as-extruded (sample A, Table 1) taken by phase contrast technique; (b) drawn and annealed at 240°C for 4 h (sample A-240 – 4, Table 1) taken by means of phase contrast technique; (c) drawn and annealed at 240°C for 8 h (sample A-240 – 8, Table 1) taken using polarized light; (d) drawn and annealed at 240°C for 8 h (sample A-240 – 8, Table 1) taken by means of phase contrast technique.

less isotropic matrix (PA6) reinforced by PET microfibrils clearly observed in Figures 2 and 3 *i.e.*, with a microfibrillar reinforced composite.

The as-drawn PA66/PA6 blend has a layer-like structure and, unlike the case of PET, clearly expressed separate fibrils are not observed (Fig. 2, blend PA66/PA6). Nevertheless, fiber-like entities oriented in the draw direction can be distinguished, their diameter being smaller than that of the PET fibrils. This morphological characteristics of the PA66/PA6 blend stems from the good compatibility of the two partners in amorphous state [12].

Mechanical Properties

Static mechanical properties of as-extruded, as-drawn and annealed PET/PA6 and PA66/PA6 blends are shown in Figure 4 and Table 2. The tensile moduli of the as-drawn blends are 4.5 to 6 times higher than those of the as-extruded samples in accordance with the expectation (Fig. 4a, Tab. 2). This holds also for the values of the tensile strength σ_t, where the respective difference is even greater, *i.e.*, 7–9 times (Fig. 4b, Tab. 2). It should be noted, however, that while σ_t of the as-drawn PET/PA6 blend (Tab. 2, sample A-0) is almost identical to the tensile strength of the same blend with

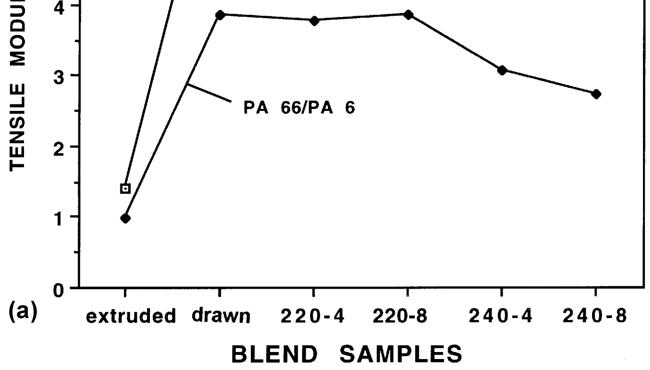

FIGURE 4 Static mechanical properties of as-extruded, as-drawn and annealed at 220 and 240°C PET/PA6 and PA66/PA6 blends: (a) tensile modulus; (b) tensile strength, and (c) ultimate strain.

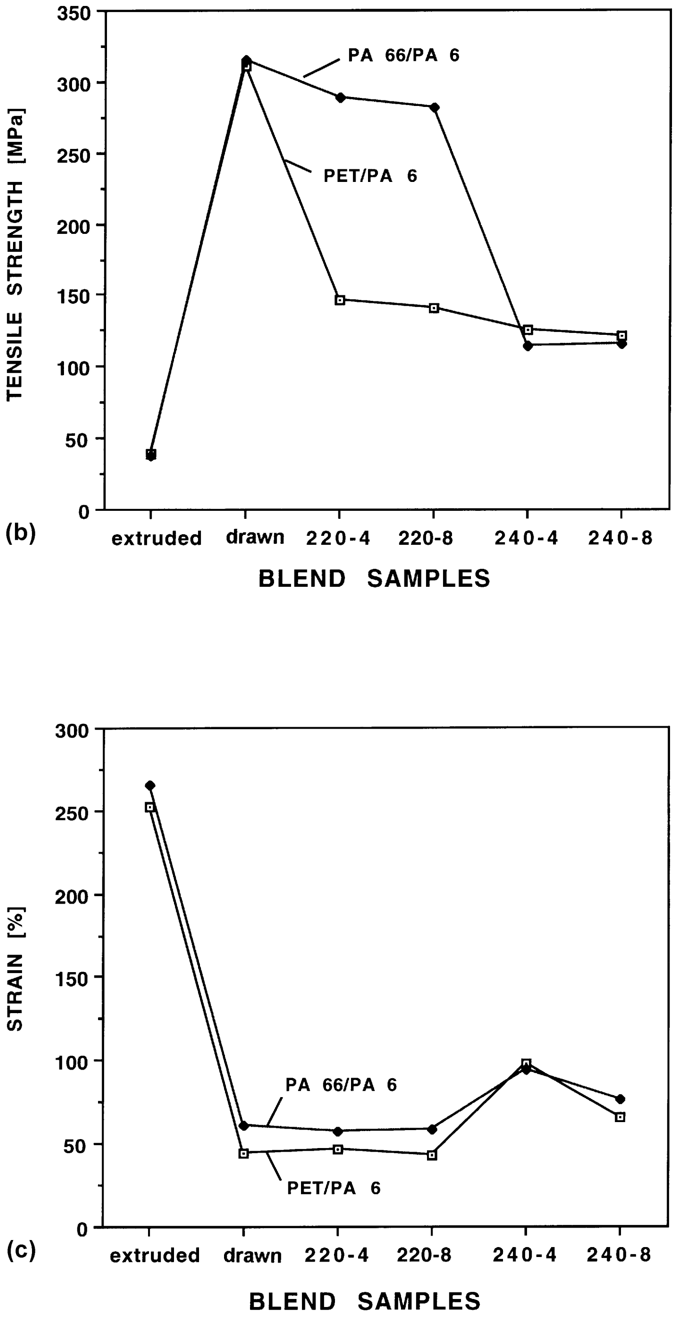

FIGURE 4 (Continued).

TABLE 2 Static mechanical properties of as-extruded, as-drawn and annealed PET/PA6 and PA66/PA6 (both 40/60 by wt) blends

Sample	*Young's modulus* (E, *GPa*)	*Tensile strength* (σ_t, *MPa*)	*Ultimate strain* (ε_u, %)
PET/PA6 blend			
A	1.41	39*	252
A-0	6.66	311	44
A-220-4	6.11	145	47
A-220-8	5.98	141	43
A-240-4	4.97	126	97
A-240-8	4.42	121	66
PA66/PA6 blend			
B	0.98	36*	266
B-0	3.83	315	61
B-220-4	3.76	288	57
B-220-8	3.84	282	59
B-240-4	3.06	114	94
B-240-8	2.72	116	72

* Yield strength.

1 : 1 weight ratio of the components [24], the E value is lower by about 35%. This is probably due to the different proportions of the components, as well as to the fact that in the present case E is calculated from the straight portion of the load-extension curve (deformation from 0 to 5%) while in [24] E is defined in the deformation range from 0.05 to 0.5 using an incremental extensiometer. The same samples show an ultimate strain ε_u that is 3.6 to 6 times lower than that of the as-extruded blends (Fig. 4c, Tab. 2).

Heat treatment at 220°C results in a slight decrease of σ_t of the drawn PA66/PA6 blend while the respective E value remains unchanged. However, in the case of the PET/PA6 blend a strong decrease of tensile strength (by about 50%) is observed (Figs. 4b and a, respectively, Tab. 2). For both drawn blends, heat treatment at 220°C causes no significant change in elongation at break, relative to the as-drawn material (Fig. 4c, Tab. 2).

One observes an additional decrease in strength and modulus of the PA66/PA6 blends after annealing at 240°C while the PET/PA6 samples treated under the same conditions show some reduction in E and preservation of the same σ_t values (Figs. 4a and b). Concerning the ultimate strain, it is seen in Figure 4a and Table 2 that thermal treatment at 240°C for 4 h results in an increase of ε_u by about 50% while prolonged annealing (8 h) at the same temperature leads to a decrease of this magnitude. It should be noted that the E values of the PET/PA6 blends are higher by 40 – 50% than those of the PA66/PA6 samples regardless of their respective thermal prehistories (Tab. 2).

DISCUSSION

Effect of Physical Processes on the Mechanical Properties of the Blends and Composites

The above experimental results clearly indicate some differences in the supermolecular organization and the physical properties of the PET/PA6 and PA66/PA6 blends and composites having the same mechanical and thermal prehistory. It seems reasonable to assume that these differences result from the different degrees of miscibility of the blends' components. Thus for instance, Ellis [12] has shown theoretically and experimentally that PA66/PA6 blends are miscible in amorphous state, attributing this behavior to the similar chemical constitution of the two polyamides. Furthermore, both PA6 and PA66 contain the same volume fraction of methylene and amide units which, from the current theoretical perspective, provides a special situation whereby an athermal blend with an effective interaction parameter $\chi_{\text{blend}} = 0$ will result [12]. Another necessary requirement for miscibility is the occurrence of specific intermolecular interactions, and in the case of PA66/PA6 blends they are of the type of hydrogen (CO$\cdots$NH) bonding capable of overcoming the dispersion forces, thus contributing to mixing [33].

Another interesting property of the PA66/PA6 blends is random copolymerization as concluded from the DSC and WAXS data obtained from the same blend treated as described here [34]. Good miscibility of the blend components is a prerequisite for the occurrence of random copolymerization and for this reason this process is not possible in the PET/PA6 blends. Furthermore, at $T_a = 220°\text{C}$ the oriented (Fig. 1) and fibrillized (Figs. 2 and 3) structure of the two components is preserved and this is the basic reason for the preservation of the E values, compared to that of the as-drawn blend (Fig. 4a, Tab. 2). The strong decrease in σ_t (almost double, compared to the as-drawn blend) could be related to thermally induced phase separation of the homopolymers [14].

At $T_a = 240°\text{C}$, *i.e.*, at a temperature higher by 15°C than T_m of PA6, almost complete phase separation of the components takes place in both blend types, as evidenced by the appearance of two well expressed melting peaks [35]. At this higher annealing temperature perfecting of the crystalline structure of PET and PA66 takes place, the two homopolymers still preserving their oriented state, while the PA6 portions in the blends undergo disorientation (Fig. 1, samples 240°C, 4 and 8 h). PA6 disorientation is much greater in the PET/PA6 blend (Fig. 1, samples PET/PA6, 240°C, 4 and 8 h) but, nevertheless, complete disorientation of this component is not observed. This preservation of some orientation of PA6 could be related to the "preferred" crystallization of this polymer around and along the fibrillar crystallites of PET or PA66 components during cooling after annealing at

240°C. Such an epitaxial crystallization is favored by the nucleating effect of the fibrils which remain solid at 240°C; it has been observed with PA6 (from the melt) on the surface of poly(*p*-phenylene terephthalamide) filaments by Kumamaru *et al.* [36] and Kyu [37]. The columnar structures formed during cooling follow to some extent the fibrillar orientation and contribute to the better compatibility of the blends' components. It should be noted that this effect is better expressed at the PA66/PA6 interface, where the occurrence of partial cocrystallization [34] is also possible (Fig. 1, samples PA66/PA6, 240°C, 4 and 8 h).

Effect of Chemical Processes on the Mechanical Properties of the Blends and Composites

Parallel to the physical changes (crystallization, relaxation) discussed above, solid state exchange reactions also take place at the interphase boundaries in the blend at high annealing temperatures and strongly depend on T_a, annealing duration and presence of catalyst [28–30]. Exchange reactions (transesterification in polyester/polyester, ester-amide in PET/PA6 and amidolysis in PA66/PA6 blends) are reported [3–14, 28–30] to be a possible method for improving the miscibility or compatibility of immiscible thermoplastic polycondensates. These reactions proceed relatively rapidly in the melt. In the present case, the blends studied are obtained by melt extrusion at 280–310°C for about 5 min, with 0.35% (by wt) of *p*-toluenesulfonic acid as a catalyst, these parameters being very similar to those reported in [6]. For this reason, one can assume the formation to some extent of segmented block copolymers. The decreased crystallizability of the higher-melting homopolymers in the as-extruded blends is observed in the decrease of the area of the crystallization peaks from the melt, compared to the neat PET or PA66 [35], as well as in the shift of T_m and heat of fusion of PA6 to lower values in both blends [35]. These observations are consistent with some degree of copolymerization during melt blending. Such a decrease in the crystallizability of homopolymers as a result of exchange reactions in the melt has been reported previously [3–11].

In the present case at $T_a = 240$°C, *i.e.*, at the temperature at which the greatest changes in the thermophysical properties of the blends are established [35], PA6 and the copolymers are molten while PET and PA66 preserve their highly oriented structure (Fig. 1, samples for 240°C and 8 h). For this reason, the only reactive chains in the PET and PA66 components are situated in the amorphous regions or at the surfaces of crystallites, while the entire mass of the molten PA6 and the block copolymers can participate in the chemical interactions, and additional amounts of copolymers are formed. It was demonstrated [35] that the blends annealed at 240°C reveal substantially lower T_m and heat of fusion values during the second heating in the DSC than the neat homopolymers, the as-extruded, as-drawn blends, as well as the blends annealed at 220°C. Furthermore, samples A-240 – 4, A-240 – 8, B-240 – 4 and B-240 – 8 reveal the lowest crystalization temperature [35]. A similar loss of crystallizability of homopolymers in blends subjected to prolonged annealing has been observed by other authors [3 – 11, 22]. It is attributed to the formation of copolymers with relatively short blocks. The similar behavior in the present blends is likewise related to the formation of block copolymers.

Solid state reactions also occur when the material is annealed at 220°C, although at a lower rate [30] because all blend components are in solid state (Fig. 1, samples annealed at 220°C).

The formation of new block copolymeric interphase layers play the role of *in situ* compatibilizers of the homopolymers in the blends. This holds to the greatest extent for the immiscible PET/PA6 blend. Due to the good adhesion between the fibrillized PET and the partially isotropic PA6 matrix, in this case, the σ_t values of the samples annealed at 240°C are comparable to those of the material annealed at 220°C (Tab. 2, Fig. 4b), *i.e.*, at the temperature at which both blend components are in the fibrillized state (Fig. 1, samples annealed at 220°C).

The differences in the E values of the as-drawn and annealed blends of PET/PA6 and PA66/PA6 result from the chemical nature and physical properties of the homopolymers, as well as from the amount of the fibrillized material [23 – 27]. The less stiff PA66 fibrils, reinforcing the PA66/PA6 composite, impart a higher compliance, while the stiffer PET fibrils contribute to the higher E value of the PET/PA6 composite (Tab. 2, Fig. 4a). However, due to additional chemical conversions at $T_a = 240$°C, the weight, volume and molar ratios of the components in the blends do not correspond to their initial values. This decrease in the volume fraction of reinforcing elements, as well as the changed chemical structure and partial disorientation (Fig. 1, samples annealed at 240°C) of the matrix are the reasons for the strong decrease of E in both blends after annealing at 240°C (Tab. 2, Fig. 4a). Nevertheless, the Young's modulus and tensile strength of these samples are about three times higher than the respective values for the as-extruded blends (Tab. 2, Figs. 4a, b) and for semicrystalline isotropic PA6 ($E \sim 1$ GPa and $\sigma \sim 45$ MPa [38]). This is also an indication of the reinforcing role of the fibrillized components, as well as of their good adhesion with the matrix in the microfibrillar reinforced blends.

Note Added in Proof

A referee brought to our attention an earlier work by Aharoni [39] describing a melt-processing method of preparing on an industrial scale nylon-6 fibers reinforced by microfibrillar PET with interfacial bonding between the two polymers. In addition to the method of preparation, the mechanical properties and morphologies of unbonded and interfacially bonded fibers are described in said article.

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