Microfibrillar Reinforced Composites from Binary and Ternary Blends of Polyesters and Nylon 6

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ABSTRACT: Binary (1:1 by weight) and ternary (1:1:1 by weight) blends of poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and Nylon 6 (PA 6) as well as the homopolymers are extruded as strips and ultraquenched from the melt. After zone drawing and additional annealing at T_a = 220 or 240 °C for 5 or 25 h with fixed ends in vacuum, the samples are studied by DSC, WAXS, solubility, and mechanical testing. It is found that all components in the blends are oriented and perfection of the structure is observed at T_a = 220 °C. At T_a = 240 °C isotropization of PBT and PA 6 takes place in their blends with PET, the orientation of the latter being preserved; i.e., microfibrillar reinforced composites are obtained. Their mechanical properties are comparable to those of glass fiber reinforced PBT and PA 6. During prolonged thermal treatment, in addition to isotropization, chemical interactions (additional condensation and exchange reactions) take place at the interfaces, resulting in the formation of copolycondensates playing the role of compatibilizers. The initially multiblock copolymers randomize with the progress of annealing, losing their crystallization ability, as proved by DSC, WAXS, and solubility measurements. Finally, the entire amounts of PBT and PA 6 become involved in the copolymers, converting in this way the starting homopolymer matrix of the microfibrillar reinforced composite into a copolymer one. This change in the chemical composition affects the overall behavior of the composites.

I. Introduction

Three are the basic approaches to the obtaining of polymeric materials with "tailored" properties: (i) synthesis of new polymers, (ii) chemical or physical modification of the supermolecular structure of known and widely applied polymers, and (iii) preparation of di- or multicomponent blends. Most of the studies of polymer blends based on linear polycondensates (polyesters, polyamides, and polycarbonates) deal with the relationship between the morphology and compatibility of homopolymers and the blending conditions as well as with the final properties of the blends.[1-11] It is established that due to the chemical nature of this class of polymers, chemical interactions could occur between the components during blending (simultaneous injection molding or extrusion of two or more linear homopolycondensates). These interactions could also affect the homopolymer morphology as well as the properties of the blends.

Recently, considerable interest has been focused on blends based on polyesters and small amounts (5–15% by weight) of thermotropic liquid crystalline polymers (LPC).[12-17] By molding or extrusion of the blends a reinforcing effect is achieved in situ in the polymer matrix by the rodlike LCP molecules or domains; i.e., one deals with molecular composites. It is important to note that in the majority of cases dealing with blends isotropic systems are studied.

In a previous paper of ours[18] we demonstrated that a new type of composites, i.e., microfibrillar reinforced ones, can be created by annealing of oriented blends above the melting temperature of one of the components so as to cause its isotropization. The mechanical properties of these materials are comparable to those of the glass fiber reinforced composites having the same matrix.[18]

During such a thermal treatment of condensation polymer blends, in addition to the isotropization of one of the components, chemical interactions take place at the interface, resulting in the formation of copolycondensates which play the role of compatibilizers.[18,19] Prolonged annealing at high temperatures (however below the melting point of the fibrillized component) can transform in this way the starting homopolymer matrix into a copolymer one.

The present study aims to establish and to distinguish between the contribution of the physical and chemical changes to the formation of the final structure in drawn binary and ternary blends of poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and Nylon 6 (PA 6) as dependent on the annealing temperature and duration. The effect of the change in the supermolecular organization and chemical composition on some properties of the blends is also considered.

II. Experimental Section

The polymers used were PET (Merge 1934F, Goodyear, $\bar{M}_n$ = 23400), PA 6 (Capron 8200, Allied Co., $\bar{M}_n$ = 20600), and PBT (RE6131, DuPont, $\bar{M}_n$ = 21300). These polymers were finely ground (after cooling in liquid nitrogen) and then mixed in the solid state (1:1 or 1:1:1 by weight). Films of these blends and of the respective homopolymers were prepared according to the following procedure: a capillary rheometer, flushed with argon and heated to ca. 280 °C, was loaded with dried powdered material. The melt obtained was kept in the rheometer for 5–6 min and then extruded through the capillary (1-mm diameter) on metal rolls rotating at ca. 30 rpm. The rolls were immersed in a quenching bath of liquid nitrogen. In this way strips of homopolymers and binary or ternary blends were prepared, their thickness (0.10–0.15 mm) and width (4–5 mm) depending on the extrusion rate and distance between the rolls.

All samples were oriented according to the method of zone drawing[20,21] under the following conditions: as quenched films under tension (15 MPa) were subjected to the action of a heating zone using a narrow heating device (glass tube, diameter of 3 mm, containing a heating element) attached to the crosshead of an Instron machine. The heater was moved from the lower to the upper part of the samples under tension at a crosshead speed of 10 mm min^{-1}. The temperature of the heating zone was as high as 180 °C for PA 6 and the PBT/PA and PBT/PA/PET blends (probably due to the high crystallinity of PA 6) and 85 °C for PET, PBT, and the PET/PBT blend (since breaking of the polyester samples was observed at higher temperatures). The drawn samples were then subjected to isothermal annealing with

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Table I. Sample Preparation Conditions

sample design	zone drawing[a] temp (°C)	λ	annealing in vacuum (with fixed ends) T_a (°C)	t_a (h)
PA-I	180	3.8		
PA-I-1	180	3.8	220	5
PA-I-2	180	3.8	220	25
PBT-I	85	3.8		
PBT-I-1	85	3.8	220	5
PBT-I-2	85	3.8	220	25
PET-I	85	4.0		
PET-I-1	85	4.0	220	5
PET-I-2	85	4.0	220	25
PET-I-4	85	4.0	240	25
PET/PBT blend				
A-I	85	4.3		
A-I-1	85	4.3	220	5
A-I-2	85	4.3	220	25
A-I-3	85	4.3	240	5
A-I-3-I	same as A-I-e but additionally drawn at room temperature to ε of ca. 120%			
PBT/PA blend				
C-I	180	4.0		
C-I-1	180	4.0	220	5
C-I-2	180	4.0	220	25
PET/PA/PBT blend				
T-I	180	4.5		
T-I-1	180	4.5	220	5
T-I-2	180	4.5	220	25
T-I-3	180	4.5	240	5
T-I-4	180	4.5	240	25
T-I-3-I	same as T-I-3 but additionally drawn at room temperature to ε of ca. 180%			

[a] All samples were zone drawn at a moving speed of the heater of 10 mm min^{-1}; tension applied: 15 MPa.

fixed ends at 220 or 240 °C for 5 or 25 h in vacuum. The sample preparation conditions are given in Table I.

DSC measurements of all samples were carried out on a Perkin-Elmer thermoanalyzer at a heating (and cooling) rate of 10 °C min^{-1}. After keeping the sample at a maximal temperature of 290 °C for 1 min, nonisothermal crystallization from the melt was performed. The samples thus crystallized, having different thermal prehistory during annealing with fixed ends, were subjected to a second melting. The DSC curves obtained served for the determination of the heats of fusion during the first ($\Delta H_f'$) and the second ($\Delta H_f''$) melting as well as those of nonisothermal crystallization from the melt (ΔH_c) of the homopolymers in the blends. The degree of crystallinity w_c(DSC) of homopolymers and of their fractions in the blends was determined according to the equation $w_c(\text{DSC}) = \Delta H_f/F\Delta H°$, where ΔH_f is the heat of fusion, F is the homopolymer weight fraction in the blend, and $\Delta H° = 140$ kJ/kg[22] and $\Delta H° = 144.5$ kJ/kg[23] are the ideal heats of fusion of PET and PBT, respectively.

By means of a Siemens diffractometer with Ni-filtered Cu Kα radiation, WAXS transmission patterns as well as equatorial diffractograms were obtained of all drawn and annealed blends.

Mechanical tests were carried out in a static mode using a Zwick 1464 machine equipped with an incremental extensiometer at room temperature and crosshead speed of 5 mm min^{-1}. Young's modulus (E, in the deformation range from 0.05% to 0.5%) and tensile strength (σ) were determined from the stress–strain curves, as well as the relative deformation at break (ϵ). All values are averaged from five measurements.

III. Results

1. **Thermal Properties.** Figures 1 and 2 show melting curves of zone-drawn films, additionally annealed at different temperatures and for different times, of PBT/PA and PET/PA/PBT blends, respectively. The melting behavior of the PET/PBT blend is similar to that of the ternary blend (Figure 2), and for this reason the respective melting curves are not shown.

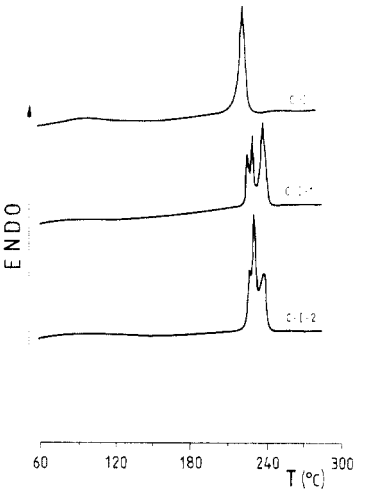

Figure 1. DSC curves taken during the first heating of PBT/PA blends zone drawn and additionally annealed at different temperatures and durations. For sample designations, see Table I.

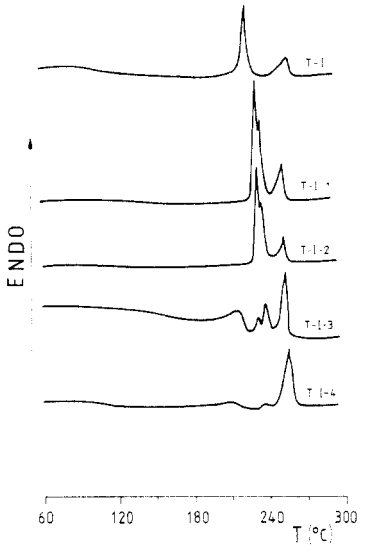

Figure 2. DSC curves taken during the first heating of PET/PA/PBT blends zone drawn and additionally annealed at different temperatures and durations. For sample designations, see Table I.

DSC data obtained from the curves of first melting of all blends studied are presented in Table II. It is seen that the heats of first melting $\Delta H_f'$ of the two components in the PET/PBT blend increase after annealing at 220 °C for 5 h (sample A-I-1), resulting in a higher total heat of fusion ($\sum\Delta H_f'$) of the system. At the same time, prolonged annealing (for 25 h) at 220 °C and particularly at 240 °C leads to a strong decrease of $\sum\Delta H_f'$ of the blend. The data in Table II suggest a stronger drop of the heat of melting of the PBT component than that of the PET component with the rise of the annealing temperature.

The zone-drawn sample of the PBT/PA blend (sample C-I, Figure 1) shows a single melting peak at ca. 220 °C, i.e., in the temperature range of melting of the two homopolymers. For this reason the determination of the heats of melting and the respective degrees of crystallinity w_c(DSC) of the two components of the blend proved impossible (Table II). The triplets appearing after annealing (samples C-I-1 and C-I-2) are an indication of phase separation and, due to the high crystallization ability of PBT and PA 6, the two components crystallize separately under these conditions. Unlike the PET/PBT blend, here the total heat of fusion increases at prolonged annealing (Table II, samples C-I-1 and C-I-2).

Table II. DSC and WAXS Data of Zone-Drawn and Annealed Blends PET/PBT, PA/PBT (1:1 by weight), and PET/PA/PBT (1:1:1 by weight) after First Heating ($\Delta H_f'$), Crystallization from the Melt (ΔH_c), and Second Heating ($\Delta H_f''$)[a]

	first heating								crystallization				second heating			
	T_m (°C)			$\Delta H_f'$ (kJ/kg)		$\sum\Delta H_f'$ (kj/kg)	w_c(DSC)		temp range (°C)	T_c (°C)		$\sum\Delta H_c$ (kJ/kg)	T_m (°C)			$\sum\Delta H_f''$ (kJ/kg)
	PBT		PET	PBT	PET	PBT + PET	PBT	PET				PBT + PET				PBT + PET
A-I	221		253	48	57	53	0.33	0.41	197–156	167		44	209		239	38
A-I-1	233		253	75	66	71	0.52	0.47	166–106	132		30		212		28
A-I-2	203	240	255	42	58	54	0.29	9.42	163–106	133		23		225		23
A-I-3	197		258	29	56	41	0.20	0.36	161–101	124		16		225		20
						PBT + PA						PBT + PA				PBT + PA
C-I		220				68			199–154	180	192	54	210		215	52
C-I-1	222	229	239			72			199–154	180		48	210		215	46
C-I-2	221	223	237			80			197–148	178		52	210		216	48
	PA + PBT		PET	PA + PBT	PET	PET + PA + PBT		PET				PEt + PA + PBT				PET + PA + PBT
T-I	220		253	56	55	55		0.39	202–168	186		47	210	217	238	34
T-I-1	229	234	251	81	52	72		0.37	188–145	177		38	208	215	233	27
T-I-2	229	234	250	78	50	68		0.35	190–147	178		35	206	213	235	24
T-I-3	210	236	251	44	60	48		0.43	185–148	177		31	210		231	20
T-I-4	210	236	255	8	71	29		0.51	200–146	178		26	208		240	15

[a] $\Delta H_f'$ is corrected per gram of homopolymer in the blends; T_c corresponds to the maximum.

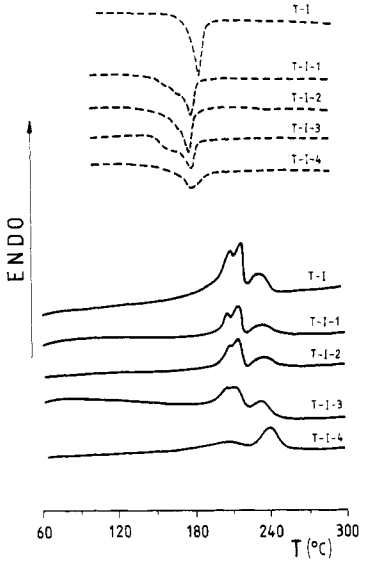

Figure 3. DSC curves of PET/PA/PBT blends taken at the cooling mode (broken lines) and during the second heating (solid lines). For sample designations, see Table I.

Table III. DSC Data of Zone-Drawn and Annealed PA 6, PBT, and PET after First Heating and Crystallization from the Melt

	first heating				crystallization from the melt		
sample	T_m (°C)		$\Delta H_f'$ (kJ/kg)	w_c(DSC)	T_c (°C)	ΔH_c (kJ/kg)	temp range (°C)
PA-I	218		75	0.32	186	56	192–157
PA-I-1	229		81	0.35	185	49	190–154
PA-I-2	212	231	73	0.31	185	50	190–156
PBT-I	220		66	0.45	188	51	204–164
PBT-I-1	240		72	0.50	182	44	200–160
PBT-I-2	228	240	72	0.50	182	46	203–156
PET-I	255		58	0.41	208	44	221–190
PET-I-1	258		74	0.51	205	36	214–185
PET-I-2	260		71	0.49	203	34	216–185
PET-I-4	270		69	0.48	201	30	211–184

As seen in Figure 2, the PBT and PA 6 components of the ternary PET/PA/PBT blend behave as in the case of the binary blend (Figure 1) after zone drawing (sample T-I) and annealing at 220 °C (samples T-I-1 and T-I-2). Annealing at 220 °C does not affect the melting peak of the PBT component, suggesting that $\Delta H_f'$ and crystallinity of PET remain unchanged, too (Table II). The observed increase of the total heat of fusion of these samples is due mainly to the contributions of the PBT and PA 6 components since their $\Delta H_f'$ values are higher by ca. 45% than those of the zone-drawn sample T-I.

Annealing at 240 °C, i.e., above the melting temperatures of PA 6 and PBT, strongly reduces the intensity of the melting peaks of these components in the blend while that of PET increases (sample T-I-3). This trend is even better expressed in the melting curve of samples T-I-4 annealed at the same temperature but for 25 h (Figure 2). As seen in Table II, as a result the heat of fusion of the PBT + PA fraction has a much lower value than that of the samples annealed at 220 °C, thus leading to a decrease of $\sum\Delta H_f'$ of the ternary blend regardless of the rise of the heat of fusion of the PET component (Table II, sample T-I-4).

Curves of nonisothermal crystallization (dashed lines) and second melting (solid lines) of zone-drawn and additionally annealed samples of the ternary blend are shown in Figure 3. It clearly demonstrates the broadening of the crystallization temperature range as well as the decrease of the intensity and the initial crystallization temperatures in the exotherms of the thermally treated samples. The values of these magnitudes for all three blends are given in Table II: the total heats of crystallization in the PET/PBT and PET/PA/PBT blends decrease with the rise of T_a while that of the PBT/PA blend remains unaffected by the annealing temperature. The same holds also for the temperature ranges and intensities of the crystallization peaks of the samples (Table II). One can assume that changes occur during annealing of the PET/PBT and PET/PA/PBT blends, strongly affecting their crystallization ability. This is supported also by the values of the total heats of fusion $\sum\Delta H_f''$ (Table II). While in the case of PBT/PA blend (samples C-I, C-I-1, and C-I-2) $\sum\Delta H_f''$ remains practically unchanged, the total heat of fusion gradually decreases in the PET/PBT and PET/PA/PBT blends with the rise of the annealing temperature and duration from samples A-I and T-I to samples A-I-4 and T-I-4, respectively. It should be noted that the $\sum\Delta H_f''$ value of sample T-I-4 is formed exclusively by the PET component in the blend while in samples T-I-1 to T-I-3 the PET contribution to the total heat of fusion is smaller (Figures 2 and 3).

Comparison of the values of the total heat of fusion $\sum\Delta H_f$ and those of crystallization of the blends studied (Table II) suggests that they are almost identical for the PET/PBT and PBT/PA blends while in the case of PET/PA/PBT the $\sum\Delta H_c$ values are higher than those of $\sum\Delta H_f''$. This fact is quite surprising, taking into account the

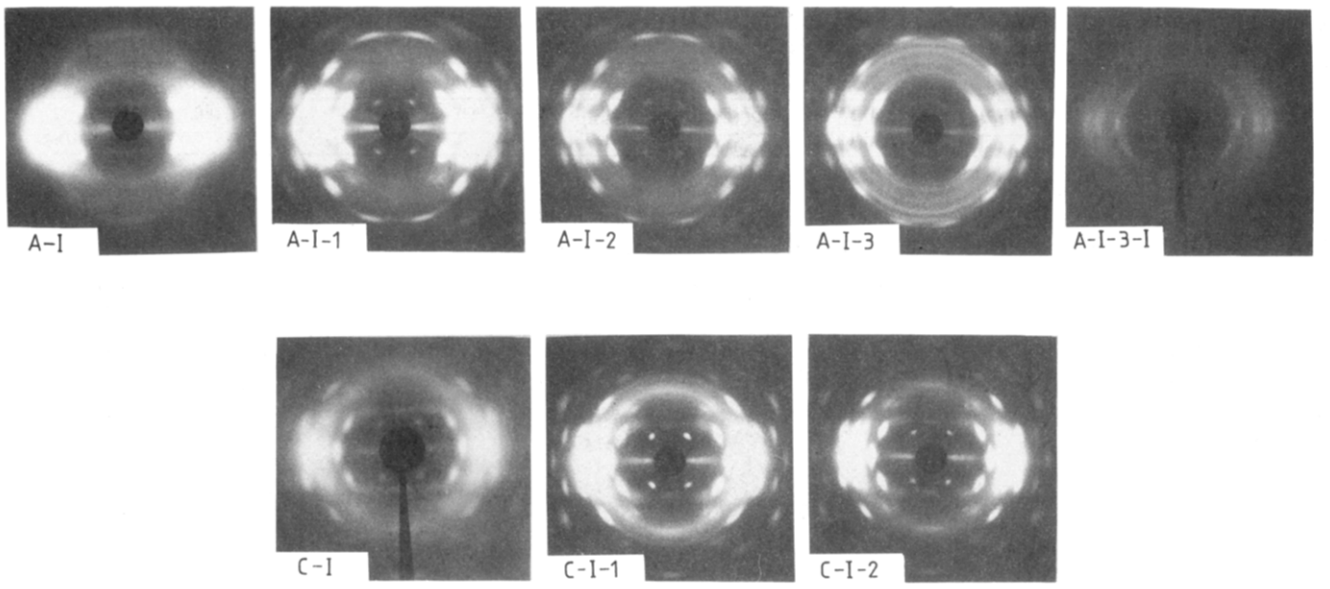

Figure 4. WAXS transmission patterns of PET/PBT and PBT/PA blends zone drawn and annealed at different temperatures and durations. For sample designations, see Table I.

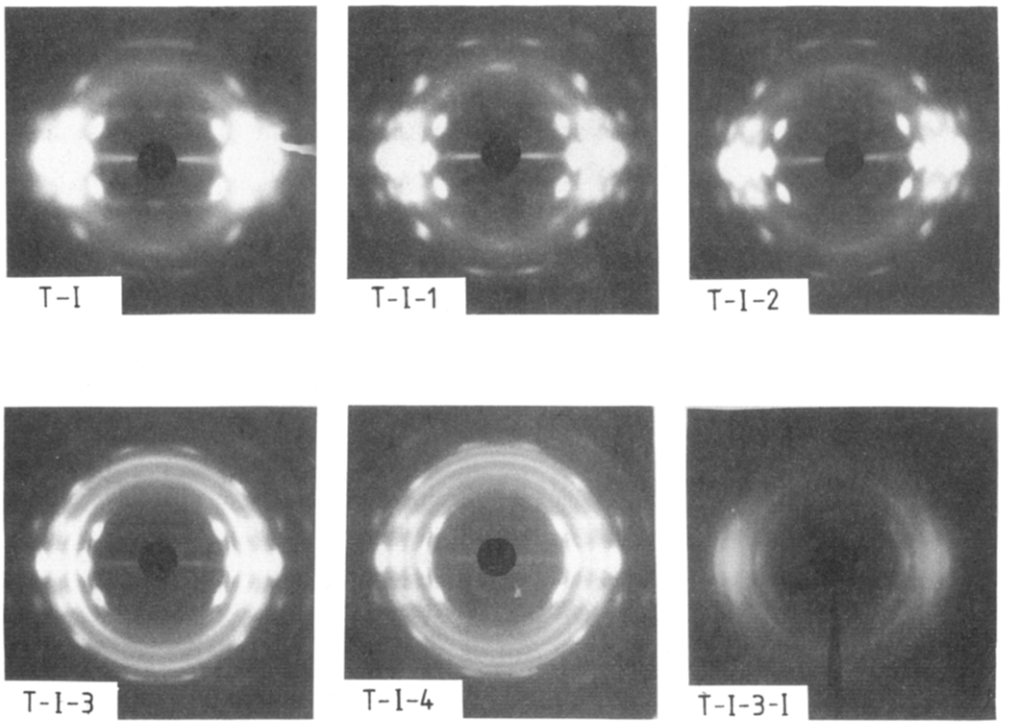

Figure 5. WAXS transmission patterns of PET/PA/PBT blends zone drawn and annealed at different temperatures and durations. For sample designations, see Table I.

possibility of additional crystallization of all samples during the second heating in the calorimeter.

DSC data obtained from the curves of melting and nonisothermal crystallization of films of PET, PA 6, and PBT homopolymers having the same thermal prehistory as the respective blends are summarized in Table III. Here also, the well-known fact that the temperature and heat of fusion as well as the degree of crystallinity of polymers grow with the annealing temperature is observed. It should be noted, however, that the values of these magnitudes for the PET component in all blends studied are lower than those for the pure homopolymer (Tables II and III) except for sample T-I-4, where such a difference in the $\Delta H_f'$ values is not observed. It should be noted here that annealing for 5 h leads to $\Delta H_f'$(PBT+PA) values that are quite close to the mean arithmetical heats of fusion of pure PBT and PA 6 homopolymers while at 240 °C $\Delta H_f'$(PBT+PA) decreases substantially (Tables II and III). Such a dependence of $\Delta H_f'$(PBT+PA) on the annealing temperature shows that the processes suppressing the crystallization ability of the blend components depend mostly on the temperature rather than on the composition. It is also seen that the heats of crystallization of the pure homopolymers also decrease after the thermal treatment but the differences are smaller than in the blends.

2. X-ray Measurements. Figures 4 and 5 show photographs of WAXS patterns of films of PET/PBT, PBT/PA, and PET/PA/PBT blends zone drawn and annealed at various temperatures and durations. It is seen that zone drawing leads to a much better orientation of the macrochains in the draw direction as well as to the formation of crystallites of different size and perfection

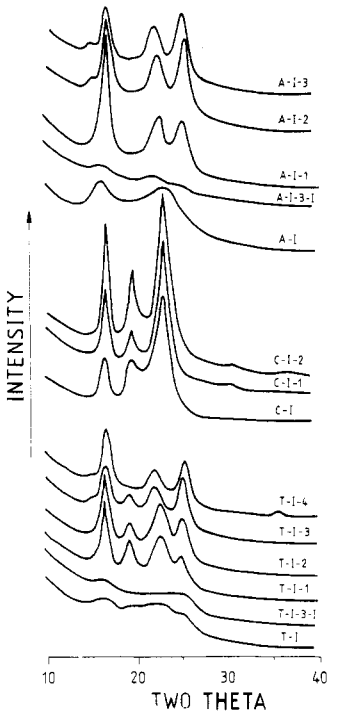

Figure 6. WAXS equatorial transmission diffractograms of PET/PBT, PBT/PA, and PET/PA/PBT blends zone drawn and annealed at different temperatures and durations. For sample designations, see Table I.

of the components of the blends. These differences are due to the different temperature of zone drawing, i.e., 180 °C for samples C-I and T-I and 85 °C for sample A-I; in the latter case the crystalline structure is less perfect.

The sharpening of the reflections and the disappearance of the halo in the equatorial direction as a result of additional annealing at 220 °C (samples A-I-1, A-I-2, C-I-1, C-I-2, T-I-1, and T-I-2) are indications of crystallite growth and perfection as well as of improved orientation of the polymer components of the blends. The perfection of the crystallite structure in these samples is clearly seen in their WAXS diffractograms presented in Figure 6.

Annealing at 240 °C of the blends of Figure 4 (samples A-I-3) and Figure 5 (sample T-I-3) results in the isotropization of the PBT component in PET/PBT and of the PA 6 component in PET/PA/PBT while the PET component in both blends remains almost unchanged. Isotropization of the PBT component in the ternary blend takes place only after annealing at 240 °C for 25 h (sample T-I-4, Figure 5). Under these conditions an improvement in orientation and perfection of the PET crystallites is observed together with the disappearance of the crystallite reflection of PA 6. This is better expressed in Figure 6: the maximal and integral intensities of samples A-I-3, T-I-3, and T-I-4 annealed at 240 °C are lower than those of the samples subjected to annealing at 220 °C. Taking into account that the scattering power of the blends represents a sum of the scattering of the crystalline phases of the homopolymers, the observed drop in the intensities of the blends annealed at 240 °C could be attributed to the decrease in the perfection and to the drop in the volume fraction of the lower-melting crystallites of PBT and PA 6. The diffractograms of samples T-I-3 and T-I-4 (Figure 6) show that one of the reasons for the decrease in the crystallinity in these cases is the abrupt drop (sample T-I-3) and even disappearance (sample T-I-4) of the crystalline phase of the polyamide component of the blend. The PBT component also contributes to the crystallinity decrease in these samples, particularly after isotropization of this component, as observed with samples T-I-4 and A-I-3 (Figures 4–6). Thus, X-ray data also support the above assumption concerning the processes suppressing the crystallization ability of the components which take place during prolonged annealing at 240 °C; for instance, PA 6 is losing completely its crystallization ability (Figure 6, sample T-I-4).

Concerning the PBT/PA blend, it is seen in Table II and Figure 6 that, similarly to pure homopolymers (Table III), the intensities of the WAXS curves as well as the total degree of crystallinity increase at prolonged annealing at 220 °C.

Figures 4 and 5 show also WAXS patterns of samples A-I-3-I and T-I-3-I obtained by additional drawing at room temperature of samples A-I-3 (ϵ = 120%) and T-I-3 (ϵ = 180%), respectively. As a result of this additional mechanical treatment a strong disorientation of the PET component and some orientation of the isotropic PBT and PA 6 take place. Furthermore, a surprisingly strong decrease of the crystallinity in samples A-I-3-I and T-I-3-I is observed. This fact could be explained solely by the assumption that the crystallites in these blends are destroyed under the action of the external mechanical field. The almost complete disappearance of crystallite reflections in the diffractograms of these samples (Figure 6) confirms this assumption.

3. Mechanical Properties. Some mechanical properties of zone-drawn and additionally annealed PET, PA 6, PBT, and their blends, determined in a static mode, are shown in Table IV. All zone-drawn samples reveal relatively high values of the Young's modulus (E) and tensile strength (σ) accompanied by a relatively low deformation ability (ϵ). This behavior of the drawn blends is directly related to the supermolecular organization of homopolymers—a very good orientation of the chains in the axial direction.

Annealing at 220 °C for 5 h results in the increase of E and σ while after thermal treatment for 25 h at the same temperature these magnitudes slightly decrease in the cases of PET/PBT and PET/PA/PBT blends. A further decrease in the Young's modulus and tensile strength is observed after annealing at 240 °C for 5 h while the deformation ability of the same blends strongly increases (137% for sample A-I-3 and 200% for sample T-I-3). A slight increase in E and σ and a drastic drop (by nearly an order of magnitude) of ϵ are achieved after annealing at the same temperature for 25 h (sample T-I-4, Table IV).

Table IV shows that while the modulus, strength, and deformation of the PBT/PA blend represent to some extent the mean arithmetical values of the respective magnitudes of the homopolymers treated at the same temperatures, in the cases of PET/PBT and PET/PA/PBT blends the E and σ values are higher than those of the homopolymers treated under the same thermal conditions. Particularly for the tensile strength, this synergetic effect reaches 50% in samples T-I, T-I-1, and T-I-4 as compared to the respective mean values of the homopolymers (Table IV). The same mechanical parameters determined for short glass fiber reinforced composites are given in Table IV for the sake of comparison.

IV. Discussion

1. Solid-State Reactions. The experimental results of the present study clearly suggest that the structure and properties of zone-drawn and annealed PBT/PA blends represent a mechanical sum of those of the pure homopolymers subjected to the same treatment. However,

Table IV. Mechanical Data of Zone-Drawn and Annealed Pure PA 6, PBT, and PET, Their Blends, and Short Glass Fiber Reinforced Composites

sample	E (GPa)	E^{av} (GPa)	E/ρ (GPa)	σ (MPa)	σ^{av} (MPa)	σ/ρ (MPa)	ϵ (%)	ϵ^{av} (%)
PA-I	4.5		4.0	342		304	31	
PA-I-1	4.8		4.1	312		268	36	
PA-I-2	2.7		2.2	99		84	55	
PBT-I	3.2		2.4	141		109	24	
PBT-I-1	4.4		3.2	156		105	46	
PBT-I-2	2.3		1.6	106		79	61	
PET-I	9.5		7.0	221		163	9	
PET-I-1	10.6		7.4	288		200	17	
PET-I-2	11.4		8.0	316		221	14	
PET-I-4	9.6		7.1	208		146	28	
PET/PBT blend								
A-I	8.4	6.3	6.3	237	181	176	26	17
A-I-1	8.9	7.4	6.4	244	220	177	30	31
A-I-2	6.6	6.8	4.8	146	204	106	116	38
A-I-3	6.1		4.6	126		92	137	
PBT/PA blend								
C-I	3.7	3.8	3.0	320	241	264	30	27
C-I-1	4.2	4.6	3.4	215	234	174	36	40
C-I-2	4.8	2.5	3.9	200	101	160	28	56
PET/PA/PBT blend								
T-I	8.4	5.7	6.7	326	234	259	20	21
ThI-1	8.9	6.2	6.9	337	232	260	38	33
T-I-2	6.8	4.8	5.3	219	173	171	46	43
T-I-3	5.0		4.0	124		97	200	
T-I-4	6.1	4.0	4.3	138	95	98	22	310
Short Glass Fiber Reinforced Composites (30% by weight)[a]								
PA 66[b]	7.8		5.6	157		115	2	
PBT[c]	8.5		5.5	134		87	3	
PET[d]	9.0		5.7	158		101	3	

[a] Manufacturer data catalogues. [b] ZYTEL 706-30HSL (DuPont); [c] KRASTIN SK 605 (Ciba Geigy); [d] RYNITE 530 (DuPont).

this is not the case for PET/PBT and PET/PA/PBT blends, showing specific supermolecular organization and properties. A confirmation of this observation can be found in the different solubility of the blends studied in boiling trifluoroacetic acid. It was established that pure polymers and zone-drawn (unannealed) blends are practically completely soluble, while after annealing of the PET/PBT and PET/PA/PBT blends their solubility decreases from A-I-1 to A-I-2 and from T-I-1 to T-I-2 and disappears completely in samples A-I-3, T-I-3, and T-I-4. As expected, the PBT/PA blend (samples C-I-1 and C-I-2) dissolves almost completely in this solvent.

Furthermore, as shown in Table II, the total heat of fusion at the first melting ($\sum\Delta H_f$) and the total crystallinity in the cases of the PET/PBT and PET/PA/PBT blends strongly decrease with the rise of the annealing temperature and duration; i.e., they change in the same direction as the solubility of the samples (from A-I-1 to A-I-3 and from T-I-1 to T-I-4). The total heat of crystallization ($\sum\Delta H_c$) follows the same trend (Table II) and the crystallization range broadens, which in turn indicates a decrease in the crystallization ability of the components with the rise of the temperature and duration of the previous annealing. A similar behavior was established by us for PET/PA blends drawn and additionally annealed at the same temperatures.

These changes in the thermophysical characteristics of the annealed PET/PBT and PET/PA/PBT blends could be related not only to typically physical properties (crystallization, relaxation, and melting) but also to chemical changes (solid-state condensation and exchange reactions). Chemical interactions are characteristic of linear polycondensates, and in the oriented state they are favored by the large interface and the great number of entanglements of taut macrochains.[24-26] At T_a = 240 °C, i.e., at the temperature at which the strongest changes in the thermophysical properties of the blends are established, PBT in PBT/PA as well as in the PA + PBT fraction of the ternary blend and particularly in sample T-I-4 is in the molten state while the PET component preserves its highly oriented structure (Figures 4 and 5). For this reason, the only reactive macrochains of the PET component are situated in the amorphous regions of the homopolymer while PBT and PA 6 participate with their almost entire amounts in the chemical interactions. It is for this reason that the copolymers formed under these conditions are probably built up of relatively long PBT and PA 6 blocks (samples A-I-3 and T-I-3) and relatively short ones of the PET component. The presence of longer blocks favors the crystallization but the perfection, amount, and size of crystallites would be lower than those of pure homopolymers. Actually, Figures 4 and 5 show that the PBT component in sample A-I-3 and the PA 6 component in sample T-I-3 have relatively slight and isotropic crystallite reflections. Furthermore, the PBT reflections in sample T-I-4 strongly increase and become commensurable with those of the same component in sample A-I-3 while the crystalline phase of PA 6 disappears completely (Figures 5 and 6). The absence of PA 6 crystallites in sample T-I-4 could be explained by the complete involvement of this component in the copolymer chains and formation of shorter blocks as a result of randomization processes occurring during prolonged annealing.

A similar loss of the crystallization ability of PET is observed by other authors with PET/polycarbonate blends subjected to prolonged annealing in the molten state at 300 °C.[10] It is attributed to the formation of copolymers with relatively short PET blocks in the melt of crystallizing PET and noncrystallizing polycarbonate. It should be noted, however, that in our case chemical interactions take place between melts of PBT (sample A-I-3), PA 6 (sample T-I-3), and PA + PBT (sample T-I-4) and the amorphous fraction of the solid and fibrillized PET component. This is the reason for the preservation of the crystallization

ability of the PET component in the blends as well as for the lower rate and degree of transformation than in the case cited above.[10]

At prolonged annealing at 220 °C, typical solid-state reactions also occur, although with lower rate due to the fact that all components of the blends are in the solid state. An indication of this lower rate could be found in the lower total heats of crystallization from the melt ($\sum\Delta H_c$) and of second melting ($\sum\Delta H_f''$) of samples A-I-2 and T-I-2 annealed at 220 °C for 25 h as compared to those of samples A-I-1 and T-I-1 annealed at the same temperature but for a shorter time (5 h) and particularly to those of the zone-drawn samples A-I and T-I (Table II).

On the basis of the results discussed above it can be concluded that the high-temperature treatment of the PET/PBT and PET/PA/PBT blends leads to the formation of binary and ternary copoymer layers at the homopolymer interfaces. The copolymer amounts strongly depend on the annealing temperature and duration. These copolymer layers cause changes in both the chemical composition and properties of the blends and, on the other hand, they play the role of compatibilizers of the homopolymers. The great deformation ability of samples A-I-2, A-I-3, and T-I-3 (Table IV) is due not only to orientation of the isotropic matrices but also to changes in the chemical compositions of the respective blends. The strong chemical bonds between the homopolymers created by the copolymer layers are the main reason for the high disorientation of the PET component and the incomplete orientation of the isotropic PBT (sample A-I-3-I) and PA 6 (sample T-I-3-I) under the action of an external mechanical field (Figures 4 and 5). Furthermore, the compatibilizing effect of the copolymer layers prevents the separation of the components in the blends. Thus for instance, cleavage or pull-out effects of the highly oriented PET component from the isotropic matrix are not observed even at extremely high deformations (ϵ = 137%, sample A-I-3, and ϵ = 200%, sample T-I-3, Table IV). However, such a macroscopic separation is observed with the PBT/PA blend.[27] This experimental result and the above-discussed one lead to the assumption that chemical interactions do not occur in this blend at 220 °C, i.e., at a temperature at which both homopolymers are not in the molten state; the probable reason is the high crystallization ability of these polymers and the relatively small dimensions of their amorphous regions—the sole regions where chemical reactions could take place. However, the reactivity of PBT and PA 6 is relatively high in the molten state (at T_a = 240 °C), as can be concluded from DSC and WAXS data (Table II and Figures 4–6) of these components in the PET/PBT and PET/PA/PBT blends as well as in PET/PA ones.[18]

2. Microfibrillar Reinforcement. As already mentioned, after thermal treatment at 220 °C of zone-drawn PET/PBT, PBT/PA, and PET/PA/PBT blends, considerable changes in the morphology of the components are observed. These changes are expressed by the increased volume fraction and perfection of crystallites, by the improved orientation, and by the alternating (microfibrillar) structure arising in the components of the blends (Table II, Figures 4–6). Isotropization of the lower-melting PBT and PA 6 components accompanied by preservation or even improvement of the perfection of the PET component is established after annealing at 240 °C (Figures 4–6, samples A-I-3 and T-I-4). The structure arising under these conditions is similar to that of composite materials, i.e., an isotropic, partially crystalline matrix reinforced by partially crystalline microfibrillized PET. The isotropization of the PBT and PA 6 components at 240 °C and the change in the chemical composition as a result of chemical interactions are the main reasons for the decrease of the Young's modulus and tensile strength with the rise of the annealing temperature (from sample A-I-1 to sample A-I-3 and from sample T-I-1 to sample T-I-3, Table IV), i.e., with the decrease of the amount of highly oriented components in the blends. However, the modulus and strength of the samples with composite-like structure (samples A-I-3, T-I-3, and T-I-4) are commensurable with those of glass fiber reinforced polyamides and polyestes ($E \sim$ 7–9 GPa and $\sigma \sim$ 140–160 MPa, Table IV) and several times higher than those of isotropic semicrystalline homopolymers ($E \sim$ 1–2 GPa and $\sigma \sim$ 40–60 MPa). It follows that microfibrillized PET is the structural element determining to the greatest extent the properties of the blends. The presence of this reinforcing element prevents elongation of the samples as a result of softening even when PBT and PA 6 are completely in the molten state (at T_a = 240 °C); microfibrillized PET predetermines to some extent the thermophysical properties of the annealed blends as well.

Another peculiarity of the microfibrillar reinforced composites is the fact that their specific Young's modulus (E/ρ) and specific tensile strength (σ/ρ) values are close to those of the short glass fiber reinforced composites having the same polymer matrix (Table IV) while the values of E/ρ and σ/ρ of isotropic PBT and PA 6 are ca. 2 GPa and 60 MPa, respectively.

V. Conclusions

In addition to our previous studies of the same PET, PA 6, and PBT blends, new evidences of the existence of microfibrillar reinforcement are found. This new class of composites can be placed between the two extreme cases of molecular composites and fiber-reinforced ones, taking into account the dimensions of the reinforcing elements. The approach is rather universal—the only requirement for its realization consists in the difference in the melting temperatures of the blending components, allowing the isotropization of the lower-melting polymer with simultaneous preservation of the good orientation and the microfibrillar morphology of the higher-melting component.

When condensation polymers are blended, in addition to microfibrillar reinforcement, effects are expected originating from the ability of solid-state reactions. With short annealing times (several hours) at temperatures close to but below the melting point of the fibrillized component, copolycondensates are formed at the interface involving solely the amorphous regions of the components. These copolymers play the role of compatibilizers. At prolonged thermal treatment the entire amount of the isotropic (molten) components is involved in block copolymers which gradually randomize. Randomization has two important consequences: (i) loss of crystallization ability and (ii) transformation of the starting homopolymer matrix of the microfibrillar reinforced composite into a copolymer one, affecting the overall behavior of the composite.

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