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Morphology of microfibrillar reinforced composites PET/PA 6 blend

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Extruded isotropic films of a poly(ethylene terephthalate) (PET) and polyamide 6 (PA 6) blend are subjected to drawing and annealing at different temperatures and durations in order to produce microfibrillar reinforced composites (MFC). In conformity with previous X-ray studies of the same system, the present scanning electron microscopic (SEM) observations show that drawing results in the formation of a highly oriented fibrillar structure of PET which is preserved even after annealing above the melting point of PA 6. Further raising of both annealing temperature and duration up to 240°C and 25 h, respectively, results in a strong decrease of the solubility of the PA 6 fraction in formic acid (by 5×) as well as in a continuous increase of the intensity of the infra-red spectral band at 3300 cm^{-1} which is characteristic of the amide group. SEM observations of these samples reveal larger aggregates of fibrillized PET arising from the gradual incorporation of PET in a copolymer matrix, the latter being insoluble in formic acid. The observed changes are explained by the occurrence of chemical interactions between PET and PA 6 under these conditions, as concluded earlier from the complete loss of crystallinity of the PA 6 component. Starting from the present and previous results on MFC, a model is proposed, illustrating the morphological changes on the macro- and molecular levels, during their preparation. Copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: PET, PA 6; polymer blend; morphology)

INTRODUCTION

Composites and blends can both be considered as mechanical mixtures of two or more components. Blending results in new materials combining the properties of the separate components and revealing to some extent synergistic effects[1,2]. It should be noted, however, that the realization of synergism requires: (i) a strictly defined and reproducible distribution of the size and dispersity of the components; and (ii) good adhesion and compatibility of the separate phases in composites and blends[2].

The first requirement is most often satisfied by varying the processing parameters, e.g. simultaneous melting of the components, annealing of the melt with its subsequent moulding or extrusion. On the other hand, improvement of the adhesion between the reinforcing elements and the matrix in composites is achieved by preliminary treatment of the fibres with various coupling agents[1]. In the case of polymer blends the same effect is observed by the addition of small amounts of copolymers. They are situated at the homopolymer interphase boundaries, thus decreasing the surface energy difference between the components[2] and playing the role of compatibilizers.

With respect to the size of the reinforcing components, polymer composites can be divided into two extreme groups: (i) macrocomposites (e.g. glass fibre reinforced ones); and (ii) molecular composites (with single rod-like macromolecules or, more probably, bundles of them, e.g. liquid crystalline polymers, as reinforcing elements). The interest in molecular composites is driven by the fact that by increasing the aspect ratio, either by raising the length or by decreasing the diameter of the fibres, the mechanical behaviour of the respective material can be improved substantially[3]. Following this reasoning, theoretically the ultimate reinforcement would be achieved by single, extended rigid-rod polymer molecules.

Recently we observed a similar type of distribution of the reinforcing elements in the so-called microfibrillar reinforced composites (MFC)[4–7]. In these polymer–polymer composites, the reinforcing elements represent polymer microfibrils of one or more homopolymers, distributed anisotropically in an anisotropic or isotropic polymer matrix. With respect to the size of the reinforcing elements, MFC have an intermediate position between fibre reinforced composites and 'molecular' ones.

The preparation of MFC is quite different from that of conventional composites, in so far as microfibrils are not

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available as a separate material. They should be created during the manufacturing of MFC by drawing of the isotropic polymer blend and annealing at a temperature below the melting point of at least one of the components. Under these conditions fusion and isotropization of the lower-melting component as well as further crystallization of the fibrillized higher-melting one take place, with the simultaneous occurrence of chemical interactions (additional condensation and exchange reactions which are characteristic of polycondensates both in the molten and in the solid state[8,9]). The latter results in the formation of copolymer layers between the components which improve their compatibility and, with the progress of the reactions, change the chemical composition of the blend, strongly affecting its morphology.

In previous studies of ours[4–7], the above outlined stages of MFC preparation as well as the structural and chemical changes taking place were proved by differential scanning calorimetry (d.s.c.), wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS), selective colouring, density and mechanical (both static and dynamic[10]) measurements. Thus, the very first (fibrillization) stage, was proved unambiguously by WAXS patterns showing a rather perfect molecular orientation, particularly after annealing with fixed ends below the melting of the components[4–6]. The second essential stage, isotropization, is clearly demonstrated again by WAXS after annealing above T_m of the lower-melting component[5]. In the case of a poly(ethylene terephthalate) (PET)/polyamide 6 (PA 6) blend one observes homogeneous rings of isotropic crystallized PA 6 together with sharp arcs of PET[4–6]. Conclusions about the occurrence of chemical interactions between PET and PA 6 are drawn from the application of different techniques: (i) d.s.c. and WAXS show a drastic decrease in the PA 6 crystallinity after annealing at 240°C for 5 h due to formation of block copolymers and complete amorphization of PA 6 (melting peak and X-ray reflections disappear) after annealing at the same temperature for 25 h due to randomization of the copolymers[5,6,11]; (ii) dynamic mechanical thermal analysis (d.m.t.a.) applied in order to follow the behaviour of the non-crystalline phases reveals two glass transition temperatures (T_gs) up to T_a below 240°C, and for $T_a = 240°C$ only one T_g can be observed, which is close to that of PET since PA 6 disappears as a separate phase after its complete involvement in copolymers[10]; (iii) the chemical interactions are visualized by the changes in the distribution of a selective dyestuff (PA 6-oriented) in thin slices of the samples[7].

Despite the numerous reports of chemical interactions in molten and dissolved blends of condensation polymers, summarized by Fakirov[9], and our proofs of their occurrence in MFC[4–7,10,11], we are still looking for additional arguments in favour of the above statements. Some supporting results in this direction, gained from an infra-red (i.r.) study and weight control of selectively extracted (removal of the PA 6 component) films of a PET/PA 6 blend (1 : 1 by wt) are described in the present paper. However, the main purpose of these studies is to visualize the different stages of MFC preparation in a morphological aspect using SEM as a more illustrative tool.

EXPERIMENTAL

The polymers used were PET (Goodyear Merge 1934F, $M_n = 23\,400$) and PA 6 (Allied Signal Capron 8200, $M_n = 20\,600$). After cooling in liquid nitrogen, these polymers were ground to a particle size of less than 0.4 mm and then mixed in the solid state (1 : 1 w/w). Films of this blend were prepared by extrusion in a capillary rheometer after heating the melt to about 280°C for 5 min. The hot extrudate from the capillary (diameter of 1 mm) was quenched on metal rolls immersed in liquid nitrogen and rotating at 30 rpm. The films obtained from both homopolymers and from their blend were about 0.12 mm thick and 4 mm wide, depending on the extrusion rate and the force applied between the rolls.

All as-quenched films were oriented according to the method of zone drawing[12] by moving of a heater, representing a narrow cylindrical element, diameter of 2 mm, temperature of 180°C, attached to the crosshead of a Zwick tensile testing machine, from the lower to the upper part of the sample. The moving speed was 10 mm min^{-1} and the tension applied to the film—15 MPa. The zone drawn films were then annealed in vacuum with fixed ends at 220 or 240°C for 5 or 25 h. The sample designations and preparation conditions are given in *Table 1*.

Slices (0.04–0.05 mm thick) of the differently treated blend were cut transverse to the film length by means of a steel microtome at room temperature after embedding the film in a resin (Kanakulit, Bulgaria). For the selective extraction of the polyamide component, all samples were treated with formic acid (98%, Merck) for 72 h at room temperature with subsequent washing with water and drying in a vacuum oven at 110°C for 6 h. Additional samples were prepared by etching of the films for 5 min in diluted trifluoroacetic acid (TFA, Fisher Scientific Co.), acid : water = 1 : 3 (v/v) and subsequent selective dissolution of the polyamide in formic acid for 20 h at room temperature. In both cases of treatment with formic acid it was shown independently by extraction to constant weight that the times of 72 and 20 h, respectively, are sufficient for the complete removal of the soluble fraction of the PA 6 component.

I.r. spectra of all extracted films were recorded in the solid state on a Perkin-Elmer 936 spectrometer in the range of 2800–3800 cm^{-1} comprising the band characteristic of the amide group at 3300 cm^{-1} [13]. The morphological studies were carried out by means of a Philips 525-M SEM at 250 kV on gold coated samples.

Table 1 Designation and sample preparation conditions of PET/PA 6 blend (1 : 1 w/w)

Sample	Zone drawing[a] temperature (°C)	Draw ratio λ	Annealing in vacuum with fixed ends	
			T_a (°C)	t_a (h)
B—as quenched	–	–		
B-I	180	4.2		–
B-I-1	180	4.2	220	5
B-I-2	180	4.2	220	25
B-I-3	180	4.2	240	5
B-I-4	180	4.2	240	25

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

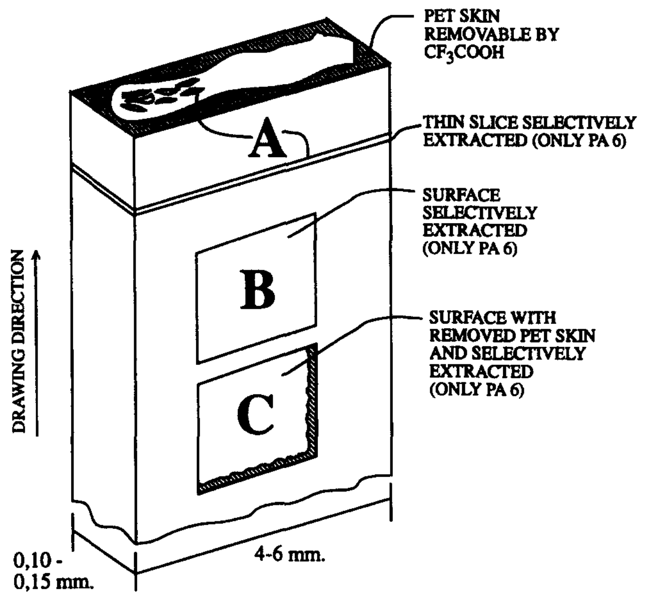

Figure 1 Schematic sample preparation for SEM observations of a film of PET/PA 6 blend (1 : 1 by wt) performed at different stages of MFC production

Table 2 Weight losses as a result of selective extraction of PA 6 (referred to the PA 6 content) of PET/PA 6 blend (1 : 1 w/w) at different stages of MFC preparation

Stages of MFC preparation	B	B-I	B-I-1	B-I-2	B-I-3	B-I-4
Weight loss (%)	98	96	91	80	62	22

The areas of the films used for SEM observations after the respective treatment are shown schematically in *Figure 1*.

RESULTS

Figure 2 shows i.r. spectra of PET/PA 6 films extracted with formic acid after being subjected to different thermal treatments indicated to the curves. It is seen that the peak intensities at 3300 cm^{-1} are quite different. Since this is the wavelength of the band characteristic of the amide group, the respective peak intensity can be considered as a measure of the amount of the PA 6 fraction in the blends. The results of the weight losses after extraction, are given in *Table 2*. *Figure 2* and *Table 2* clearly demonstrate that the intensities of interest of the as-quenched and drawn samples (B and B-I) are negligibly small; some rise is observed after annealing at 220°C (samples B-I-1 and B-I-2) while a maximal intensity is achieved after annealing at 240°C (samples B-I-3 and B-I-4). It should be stressed that these results are supported by the weight losses of the samples after extraction in formic acid which decrease with the rise of the intensities (*Table 2*).

Taking into account that the weight ratio of the components in the blend is 1 : 1 and that PET is insoluble in formic acid, the weight losses referred solely to PA 6 strongly depend on the annealing temperature—for the thermally untreated sample B-I they are about 100% while after annealing at 240°C for 25 h (sample B-I-4) they drop to 20% (*Table 2*). It can be concluded that the amount of the soluble fraction of PA 6 decreases with the rise of the annealing temperature and duration and this could be related solely to the chemical interaction between the two components resulting in the formation of a copolymer in increasing amount.

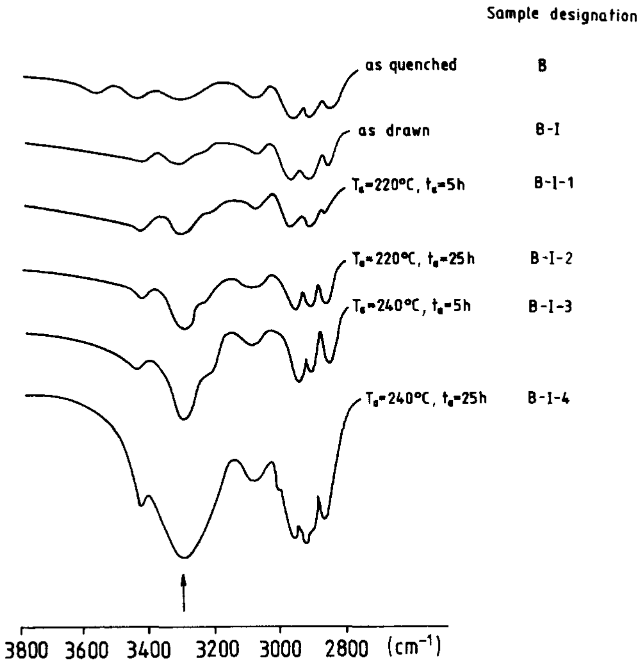

Figure 2 I.r. spectra recorded after extraction in formic acid of films of PET/PA 6 blend (1 : 1 by wt) with different thermal prehistory

Figure 3 shows SEM micrographs of transverse thin slices of PET/PA 6 films after extraction in formic acid (spot A in *Figure 1*). Two series of photographs at lower (500×) and higher (5000×) magnification are taken from each stage of MFC preparation. The first one (*Figure 3*, left column) gives an idea of the thickness of the films used as well as of the thickness variation from sample to sample. The dark regions appearing as holes correspond to the spaces occupied originally by the extracted soluble PA 6 fraction. It is clearly seen that the components in the film at each stage of MFC preparation form a sandwich-like lamellar structure which results from the processing conditions. The extrudate of the hot melt with originally circular cross-section is pressed between the quenching rolls and thus solidifies as a film. The observed layer structure is preserved after drawing and annealing of the samples, but the lamellae are getting closer to each other and interconnected with the rise of the annealing temperature (*Figure 3*, samples B, B-I-2, and B-I-4). These morphological changes could be related to chemical changes—progressive involvement of the PA 6 component into non-extractable copolymers with the rise of the annealing temperature and duration.

SEM micrographs of the films treated in the same manner, i.e. extraction with formic acid, but taken from their surface (spot B in *Figure 1*) are presented in *Figure 4*. The first striking observation is that the number of holes (the extracted PA 6 soluble component) is surprisingly small and differs strongly from the ratio of the two components in the blend. Further, in the case of the isotropic sample B, the holes have a circular shape and transform into elliptical ones after drawing (*Figure 4*, sample B-I). Although no systematic analysis

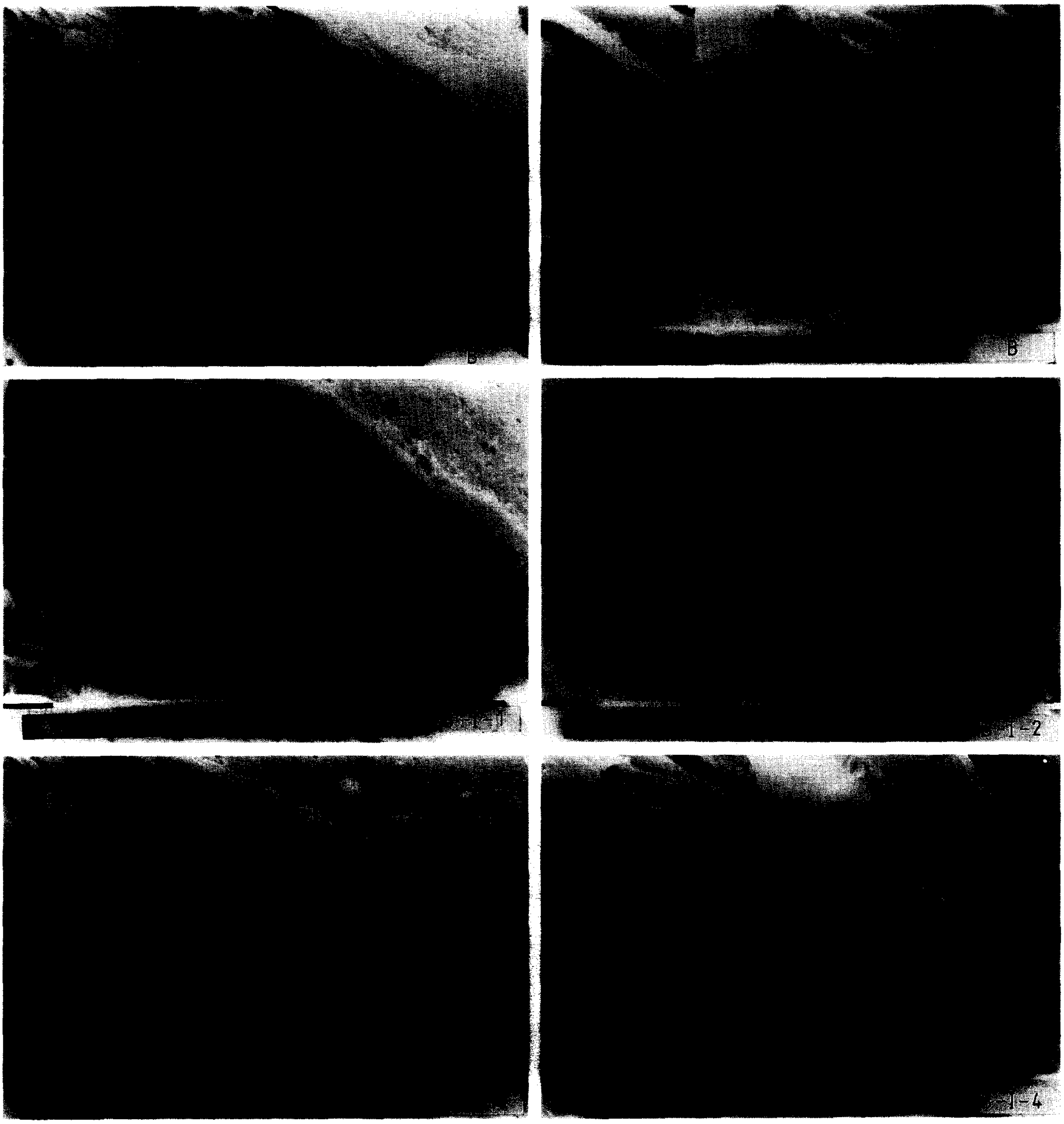

Figure 3 SEM micrographs (magnification 500×, left column; 5000×, right column) of transverse (spot A in *Figure 1*) thin slices of films of PET/PA 6 blend (1 : 1 by wt) after extraction of the polyamide fraction wtih formic acid. The boundary between the sample edges and the resin used for embedding is shown by a black solid line. For sample designation see *Table 1*

of the holes size and distribution is carried out, a rough qualitative estimation suggests an aspect ratio of the elliptical holes of about 1:4 which corresponds to the draw ratio used (*Table 1*). In the same time annealing results in an increase in the aspect ratio of the extracted and non-extracted regions (*Figure 4*, samples B-I-1 and B-I-2), indicating a finer fibrillization.

A completely different morphology is observed with the samples annealed at 240°C (*Figure 4*, samples B-I-3 and B-I-4). Instead of fine fibrils, a small number of holes is seen in sample B-I-3 together with globular particles, the number of which rises significantly at the expense of their dimensions in sample B-I-4 (*Figure 4*). One can assume that the spherical particles arise as a result of coagulation of the PA 6 portion in the copolymer formed at 240°C, hampering its dissolution. This assumption is supported by the weight losses of the samples, as shown in *Table 2*.

At first glance, the conclusion about the content of PA 6 in the thermally untreated samples (*Figure 4*, samples B and B-I) drawn exclusively from the photographs of the sample surface (*Figure 1*, spot B) contradicts the results presented in *Figure 2*, i.e. they disagree the conclusion about the amount of soluble PA 6. The reason for this apparent disagreement should be sought in the morphological peculiarities of the blends. It was assumed that the

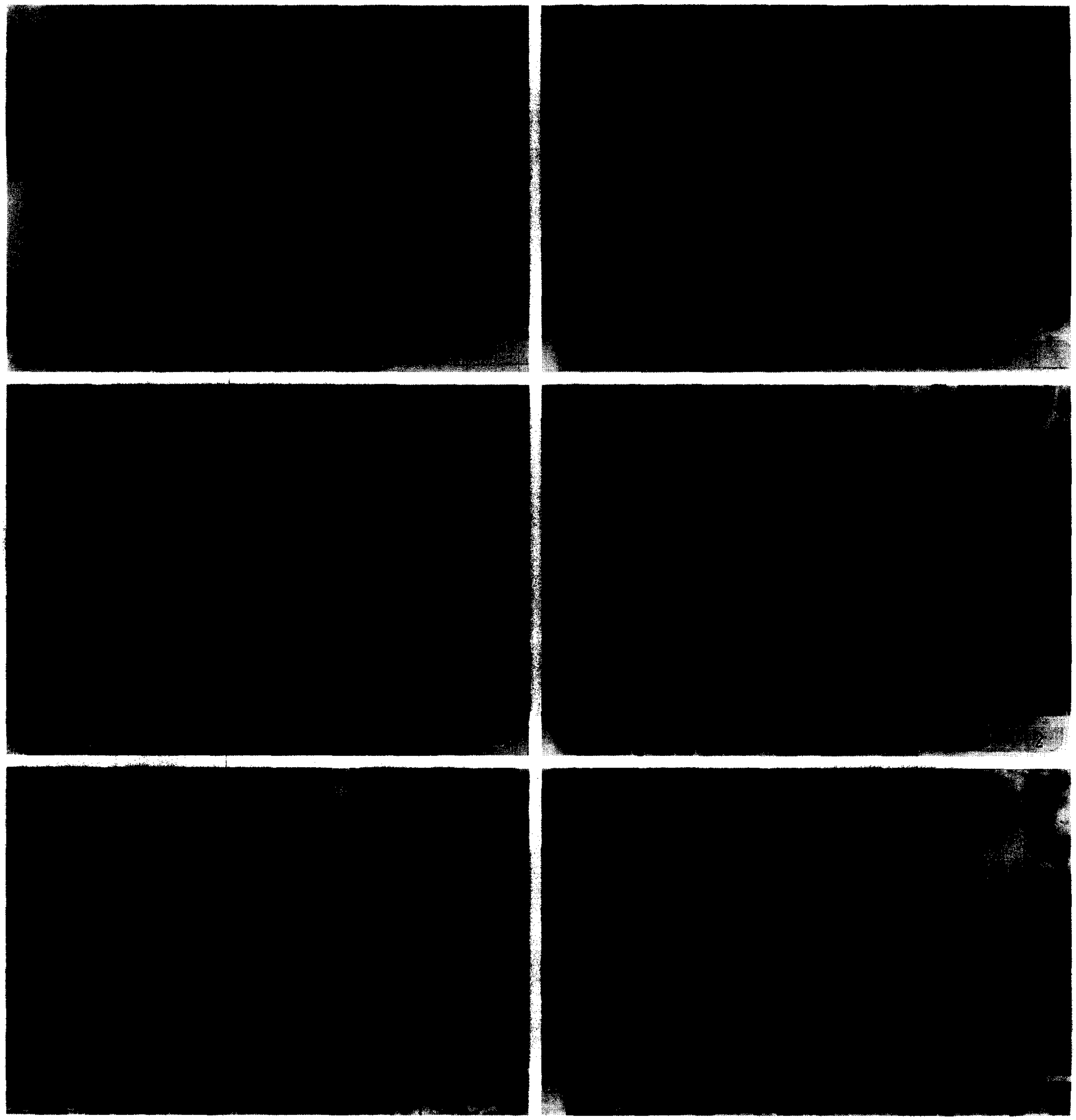

Figure 4 SEM micrographs (magnification 5000× except for sample B-I-1 where the magnification is 500×) taken from the surface (spot B in *Figure 1*) of films of PET/PA 6 blend (1 : 1 by wt) after extraction in formic acid. For sample designation see *Table 1*

films are coated by a thin PET skin which contains a small amount of PA 6 and does not reflect the average blend composition. Furthermore, this skin hinders the penetration of the selective solvent into the bulk of the samples. The presence of such PET skin was proved by using a selective PET solvent (diluted trifluoroacetic acid) as etching agent and then checking qualitatively the different dyeing ability of the PA 6 fraction (with an acid PA 6–oriented dye) in the unetched and etched samples. It turned out that the original samples are quite insensitive to the dyestuff while the etched ones remain intensively coloured even after boiling for 20 min in an alkaline (pH = 9) solution when discolouration is supposed to occur. It should be noted here that the appearance of a skin when dealing with polymer blends is a rather general phenomenon[2]. Since the factors affecting the skin formation are not controlled during the preparation and processing of the films, the detailed analysis of the skin formation is beyond the scope of this paper. Our interest in this respect was limited to the proving of the existence of skin and to its removal.

After the removal of the PET skin, another series of SEM observations was carried out, this time dealing with the film surface free of PET skin and soluble PA 6 fraction (*Figure 1*, spot C). Thus it was possible to get a direct morphological information about the internal structure of MFC at the different stages of their

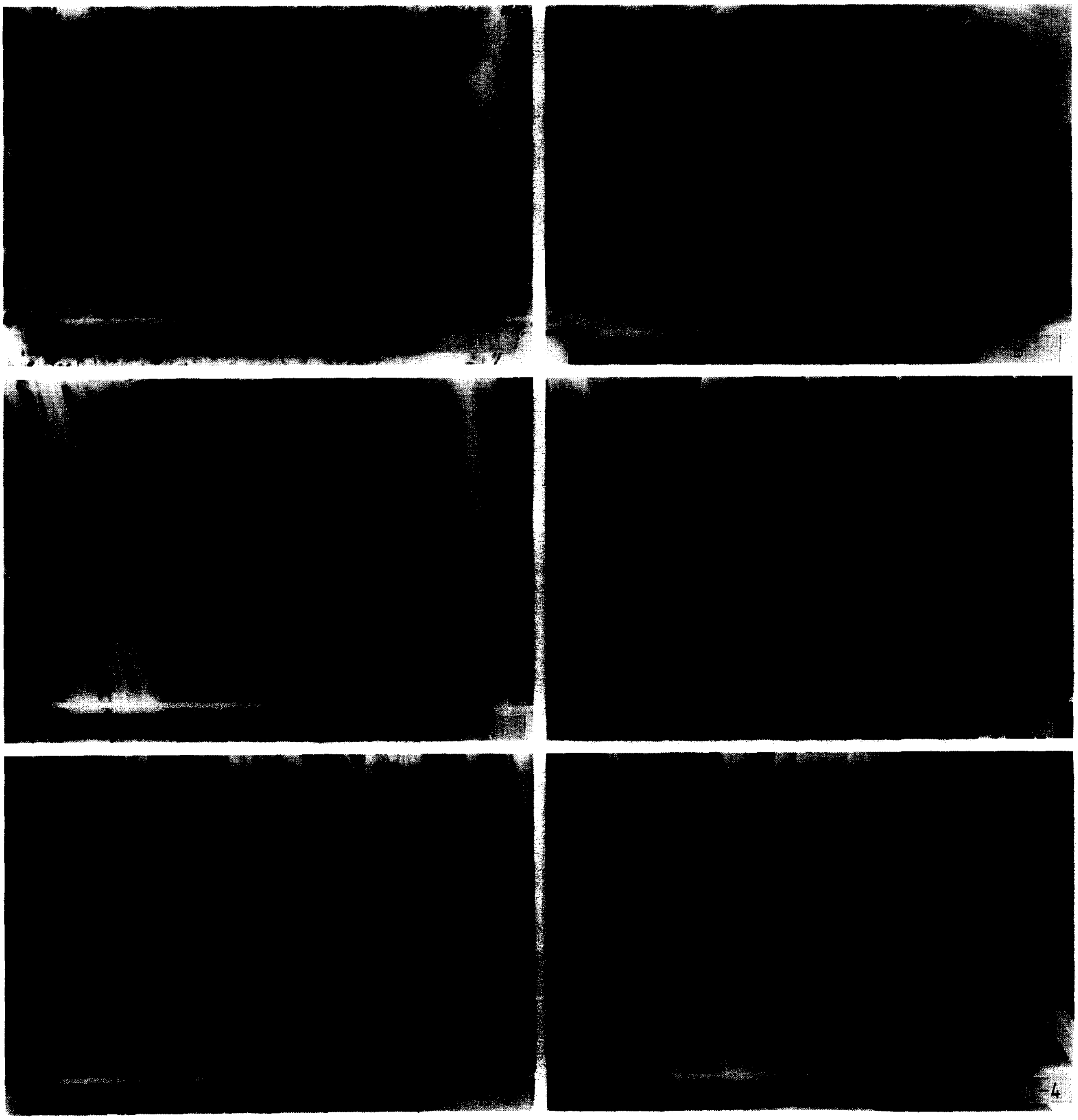

Figure 5 SEM micrographs (magnification 500×, left column; 5000×, right column) taken from the surface (spot C in *Figure 1*) of films of PET/PA 6 blend (1 : 1 by wt) after etching with TFA followed by extraction with formic acid. For sample designation see *Table 1*

preparation. The SEM micrographs of the films subjected to etching with TFA and to subsequent extraction with formic acid (*Figure 1*, spot C) are displayed in *Figure 5*. As expected, due to the facilitated access of formic acid after the removal of the PET skin, the morphological differences in the separate samples are clearly seen (compare *Figures 4* and *5*). Again two types of magnification are used, 500× (*Figure 5*, left column) and 5000× (right column). In contrast to the surface observations (*Figure 4*), the isotropic sample B reveals a high dispersity and uniform distribution of the two homopolymers, indicating also a qualitatively equal presence of the two components (*Figure 5*, sample B). The higher magnification of the same sample B (*Figure 5*, right column) reveals that the blend morphology represents, even in the isotropic state, interpenetrating globular structures arising from the two components. After drawing (sample B-I) a highly fibrillized PET structure is formed and this structure is preserved after annealing (*Figure 5*, sample B-I-2). Fibrils with diameters of about 1 μm are predominant. It should be noted that at $T_a = 240°C$ these perfect individual fibrils form highly oriented aggregates which are presumably chemically bonded with the matrix which, at this stage of MFC preparation, should represent a PET–PA 6 copolymer, i.e. a product insoluble in formic acid (*Figure 5*, sample B-I-4).

DISCUSSION

The results presented in *Figures 2–5* offer two kinds of complementary information. While the microscopic observations clearly illustrate the morphological changes during the transition of the blend from an isotropic into an anisotropic state and the formation of reinforcing microfibrillar elements, the i.r. and weight loss measurements shed more light on the chemical processes taking place during the MFC preparation. The initial undrawn blend is characterized by a rather homogeneous distribution of the two components in the form of spherical interpenetrating structures (*Figure 5*, sample B). The subsequent combined thermal and mechanical treatment (zone annealing) leads to the formation of bundles of chains highly oriented in the axial direction, as proved previously by WAXS[4–6] (*Figure 5*, sample B-I). This holds for both PET and PA 6 components of the blend[4,5] but the SEM micrographs reveal only the morphological entities originating from PET since the soluble PA 6 fraction is already extracted.

Some substantial changes in the two fibrillized components occur in their internal structure during annealing below their melting ($T_a = 220°C$). As demonstrated earlier by X-ray measurements on the same[4–6] and similar[14–16] systems, crystallite growth and perfection take place at this temperature, together with the formation of an alternating structure in the microfibrils, giving rise to SAXS[5,14,15]. The latter is characteristic of both components up to $T_a = 220°C$. However, at $T_a = 240°C$ the PA 6 component undergoes isotropization after melting and subsequent crystallization during cooling, while the PET one preserves its microfibrillar, highly oriented crystalline state, both cases being proved by WAXS[4–6]. In this way a composite-like structure arises in the drawn blends comprising an isotropic crystalline matrix reinforced with microfibrillized PET. This structure resembles that of the polymer–polymer composites reinforced by liquid crystalline polymers[17,18].

The described changes in the internal arrangement of the macromolecules (isotropic or oriented crystallization, alternating structures) deduced mostly from scattering techniques cannot be visualized by SEM. The microscopic observations demonstrate in the best way the creation of the reinforcing elements in the new polymer–polymer composites, i.e. the microfibrils, starting from an isotropic polymer blend. Photographs from film surfaces show the transformation of the spherical particles into elliptical ones during drawing (*Figure 4*, samples B and B-I). The formation and perfection of the reinforcing PET microfibrils is particularly clear when both the PET skin and the soluble PA 6 fraction are removed (*Figure 5*, samples B-I and B-I-2). The microfibrils are perfectly oriented in the draw direction, in accordance with the chain orientation derived from WAXS for the same samples[4–6]. In addition to the illustrated possibility of obtaining MFC from polymer blends (*Figure 5*, samples B, B-I, B-I-2), the approach applied (blending, drawing, annealing, extraction of one of the components) allows the production of an almost 'neat' microfibrillar disintegrated homopolymer, i.e. fibrils free of interfibrillar material (*Figure 5*, sample B-I-2).

The highly oriented PET aggregates observable in samples B-I and B-I-2 disappear in sample B-I-4 (*Figure 5*). At first glance this fact is surprising. However one should consider the chemical processes taking place at this high temperature (240°C) and extended annealing time (25 h). Our previous studies by WAXS, d.s.c. and d.m.t.a.[4–6,10,11] suggest the assumption that due to transreactions between PET and PA 6[8,9] a new copolymeric matrix comprising the entire amount of PA 6 and the amorphous part of PET is formed. This new matrix is resistant to the selective solvent and the microphotographs reveal tightly interconnected lamellae (*Figure 3*, sample B-I-4) or microfibrils (*Figure 5*, sample B-I-4) forming larger morphological entities.

The changes in the chemical composition of the matrix with the rise of the annealing temperature and duration assumed earlier[4–6,10,11] are supported also by the i.r. and weight loss measurements in the present study. The results are shown in *Figure 2* and *Table 2*. It is seen that practically the entire PA 6 fraction is extracted in thermally untreated samples B and B-I, while the PA 6 extraction decreases from sample B-I-1 to B-I-3, attaining only about 20% in sample B-I-4 (*Table 2*) where the most intensive chemical interactions are taking place as a result of the rise of the annealing temperature and duration. The rise in the intensity of the i.r. absorption bands at $3300\,cm^{-1}$ as well as in the range of 2200–$2800\,cm^{-1}$, which is characteristic of the vibrations of the $-CH_2-$ groups, follows the same trend since the copolymer is enriched in $-CH_2-$ groups as compared to homo-PET (*Figure 2*, *Table 2*). Thus it can be concluded that the PA 6 amount incorporated in a copolymer increases with the annealing temperature and duration and strongly affects the morphology of MFC. Only by these chemical changes it is possible to explain the absence of holes on the film surfaces (when the PET skin is still there, *Figure 3*, sample B-I-4). As already mentioned, the observed spherical particles on the same surfaces (*Figure 3*, samples B-I-3 and B-I-4) should represent coagulated PA 6 material, chemically bonded with PET.

The present results as well as those obtained previously[4–6,10,11], support the model proposed[7] which is depicted in *Figure 6*. This model illustrates the changes on a macro—and on a molecular level occuring in the blends at different stages of MFC preparation.

Microfibrillar reinforced composites can be obtained from incompatible polymer blends by extrusion and drawing (with good orientation—the fibrillization step, *Figure 6a*). This step is proved by WAXS[4–6] and by the present microscopic observations. The next step consists of annealing above the melting temperature T_m of the lower-melting component and below that of the higher-melting one at constant strain when isotropization of the molten component takes place together with preservation of the orientation and the morphological characteristics of the higher-melting component (isotropization step, *Figure 6a*). These changes in the crystalline order are supported by WAXS[4–6] measurements where the PET reflections show crystallization in the oriented state and those of PA 6—a completely isotropic one, although these last crystallites can be embedded into larger fibril-like morphological entities, as shown schematically in *Figure 6a*, component A. In contrast to PA 6, PET is highly oriented both as microfibrils and as macromolecules (*Figure 6a*, component B). During isotropization, as a result of the starting chemical interactions

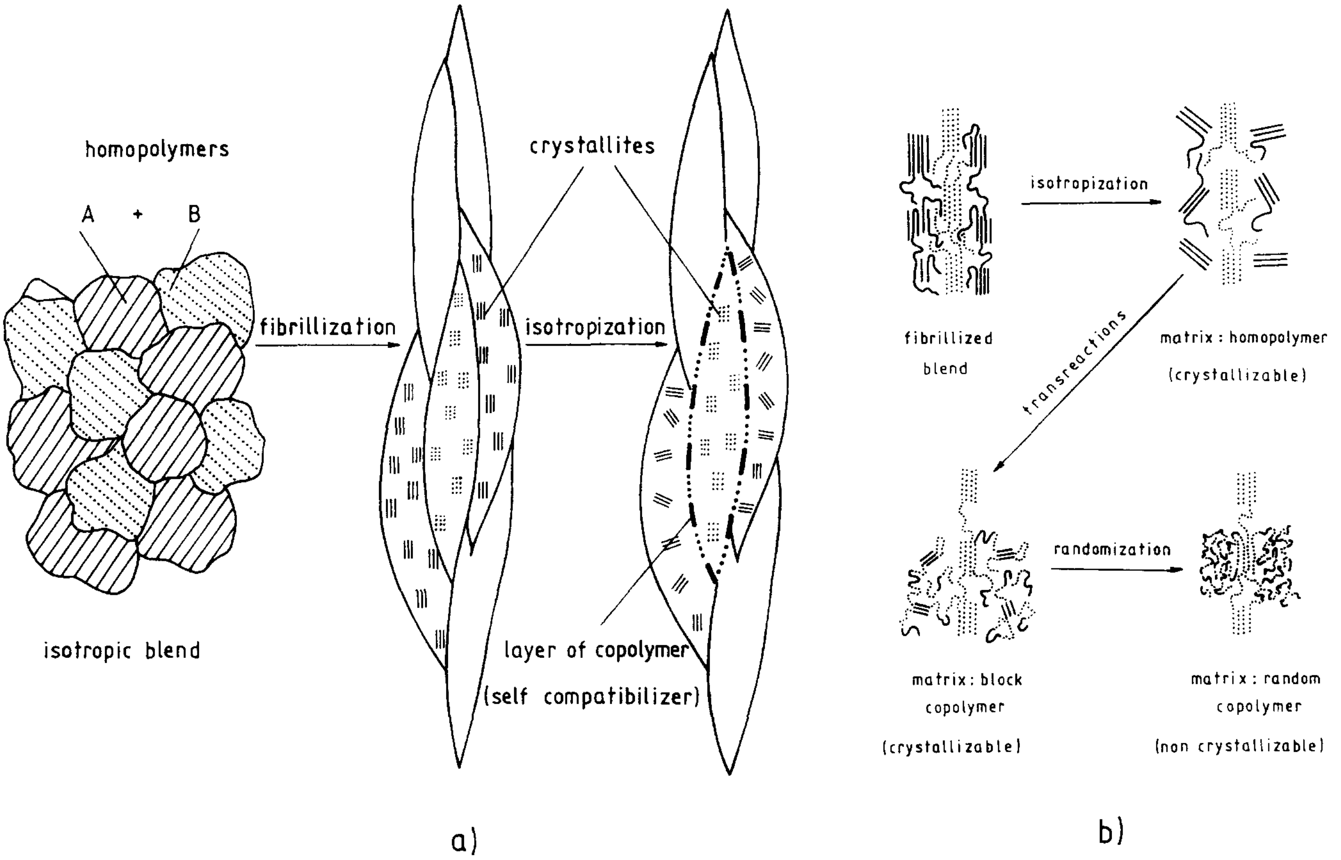

Figure 6 Schematic representation of the morphological and chemical changes taking place on a macrolevel (a) and on molecular level (b) at different stages of MFC manufacturing

between the components, a thin layer of a block copolymer is formed (in the case of condensation polymers) which plays the role of a compatibilizer (*Figure 6a*) and contributes to the improvement of mechanical properties of MFC[4,5].

Prolonged annealing at the highest temperature (240°C, 25 h) leads to the involvement of the entire amount of the molten component into a block copolymer and then into a random one due to the intensive chemical reactions occurring under these conditions (*Figure 6b*). Clear evidence in favour of these processes is offered by the WAXS and d.s.c. measurements since a significant decrease in PA 6 crystallinity at the stage of block copolymer formation and a complete lack of crystallinity after randomization (*Figure 6b*) are registered[5,6,11]. This behaviour of the crystalline phases is complemented by that of the amorphous ones—the originally observed two T_gs assigned to the separate PET and PA 6 amorphous phases merge into one at the completion of randomization[10]. More support in this respect is offered by the i.r. and weight loss measurements as well as by the morphological observations in the present study. Thus the matrix of MFC is transformed from a homopolymeric crystallizable matrix into a copolymeric non-crystallizable one (*Figure 6b*). It should be noted, however, that due to the preservation of the solid state of PET at $T_a = 240°C$, this component participates in the formation of the copolymer only with its segments originating from the non-crystallizing regions of the microfibrils. The rest of PET constitutes the semicrystalline, highly oriented (on a molecular level), parallel aligned in the draw direction ensembles of microfibrils, as demonstrated mostly by SEM in this work. These microfibrils play the role of reinforcing elements in microfibrillar reinforced composites (*Figure 6b*). A similar microfibrillar structure was observed in the PEE/PBT system as well[19]. Experiments with other systems are in progress.

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