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Microfibrillar reinforced composites — the role of the chemical interactions at the fibril–matrix interface

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Abstract—The preparation, structure and some of the properties of microfibrillar reinforced composites (MFC) based on polyamide-6 (PA6) as a polymer matrix and poly(ethylene terephthalate) (PET) in the form of reinforcing microfibrils are briefly discussed. It is demonstrated that the PA6–PET MFC displays comparable or even better mechanical properties than a conventional composite consisting of short glass fibers in a PA6 matrix. This effect is attributed to the interface between the PA6 polymer matrix and the PET microfibrils resulting in the formation of a new phase — a PET–PA6 copolymer which plays the role of a selfcompatibilizer. The progress of the chemical interactions between PET and PA6 amorphous phases leads ultimately to the involvement of the entire amount of PA6 into a block copolymer, thus changing the orginal homopolymeric PA6 matrix into a copolymeric PET–PA6 one. In such a way it is possible to overcome the immiscibility of the MFC components and to obtain control over mechanical properties of the PA6–PET MCF.

Keywords: Microfibrillar reinforced composites; polyamide-6 (PA6); poly(ethyleneterephthalate) (PET); copolymer; miscibility; transreactions; mechanical properties.

1. INTRODUCTION

Both polymer blends and composites are of high commercial importance. During the last two decades, high performance polymer composites have been increasingly used in many engineering applications, such as aerospace, aircraft, automotive and sport industries, and there is quite a clear indication that this trend will continue [1]. This rapid growth has mainly been achieved by the replacement of traditional materials, primarily metals, suggesting that, in some respects, composite materials have superior properties.

Recently, a new type of polymer composites has been developed and characterized in which microfibrils are the reinforcing elements [2–6]. Obviously these composites can be classified neither to the classical macrocomposites (e.g. glass or carbon fiber reinforced ones), nor to the molecular composites (with single-rod macromolecules as reinforcing elements). Nevertheless, these materials satisfy to a great extent the three basic points that should be included in a definition of an acceptable composite material for use in structural applications [1]:

(i) they consist of at least two physically distinct and mechanically separable materials;

(ii) they can be prepared by admixing the separate materials, with application of special treatment, so as to achieve optimum properties; and

(iii) they possess a set of properties being superior to that of the individual components.

All this justifies the introduction of a third group of polymer composites, namely, the microfibrillar reinforced composites (MFC). In this case, the admixing of at least two different polymers is an inevitable part of the MFC manufacturing. However, because most polymers lack miscibility [7], a particular problem often appears at their interface. High interfacial energy translates into very coarse phase structures with the formation of large domains of separate polymers that do not stick together [8]. The result is that the blend or polymer alloy as a rule has very poor properties.

As one may expect, also in the case of MFC, the adhesion between the reinforced elements and the polymer matrix is one of the most important parameters defining the performance of these materials [9]. Therefore, improvements in composite properties will largely depend on the control of the interaction forces at the interface. To solve this problem in polymer blends, adhesion promoters or previously prepared compatibilizers are added, the latter often representing AB block copolymers of the homopolymers A and B to be blended [10]. In the case of polycondensation homopolymer systems, the addition of ready-made AB block copolymer compatibilizers may be avoided. This is due to the fact that in the process of blend preparation such block copolymers with various length may be formed due to transreactions between functional groups belonging to different homopolymer molecules. Obviously, in immiscible polymer blends these reactions will affect the interface and help to obtain control over the adhesion between the components in such systems.

The aim of the present work is to clarify the role and importance of transreactions in MFC comprising PA6 as a polymer matrix and PET in the role of reinforcing microfibrils.

2. PREPARATION OF MFC FROM A PA6/PET BLEND

The PA6–PET MFC were prepared in the Laboratory of Polymers of the University of Sofia employing a procedure described previously [4–6]. General features of these materials are: (i) that an introduction of a third component acting as adhesion promoter is not necessary; and (ii) that they may be obtained *in situ*.

The basic stages of the preparation procedure of these MFC are: (a) blending of the immiscible homopolymer components differing in their melting temperatures; (b) fibrillization of the polymer blend by cold-drawing; (c) melting of the lower melting PA6 polymer matrix (isotropization) with preservation of the orientated microfibrillar structure of the higher PET component. All these stages are schematically shown in Fig. 1a.

In addition to the isotropization during the short (from several minutes up to hours) thermal treatment, chemical reactions such as ester–amide transreactions and additional polycondensations can take place at the interface, resulting in the formation of a copolymeric interphase (Fig. 1b). The latter plays the role of a selfcompatibilizer, and, as mentioned above, makes unnecessary the introduction of a separately prepared adhesion promoter or compatibilizing component, such as block copolymers. But if the latter is used, this can accelerate the chemical reactions remarkably.

3. EVIDENCE FOR TRANSREACTIONS DURING THE ANNEALING ABOVE T_m^{PA6}

It is important to note here that compabilitzation can be effective only at the initial stages of the ester–amide interaction. With the progress of the thermal treatment, the interphase grows and involves all of the isotropic (molten) PA6 (denoted as type A units) and the amorphous portion of the fibrillized PET (type B units) in a PA6–PET block copolymer, thus transforming the homopolymeric matrix into a block copolymeric one:

$$(\mathrm{A})_n + (\mathrm{B})_m \rightarrow \cdots (\mathrm{A})_k - (\mathrm{B})_l - (\mathrm{A})_p - (\mathrm{B})_q \cdots.$$

In recent DSC and NMR studies [11], it was demonstrated that with the progress of transreactions at 290°C in a model isotropic equimolar PET–PA6 blend, the length of both polyamide and polyester blocks decreases, reaching an equilibrium value of about four units. This is accompanied by a complete loss of copolymer crystallizability. Thus, contrary to our previous suggestions [4–6], this effect is not to be attributed to a complete randomization (i.e. $k = l = p = q = 2$) that is unlikely to take place within finite annealing times. But even sequences comprising four PET or PA6 units are not long enough to form crystalline lamellae. The DSC and NMR traces as a base for these suggestions are given in Figs 2 and 3, respectively.

The PET sequence length is calculated from the NMR peak intensity (carbonyl C-atom region) using the following formula [12]:

$$\mathrm{L}_{\mathrm{PET}} = \mathrm{I}_{\mathrm{PET}}/\mathrm{I}_{\mathrm{PET-PA6}} + 1,$$

where $\mathrm{L}_{\mathrm{PET}}$ is the PET sequence average length (number of PET repeating units), $\mathrm{I}_{\mathrm{PET}}$ and $\mathrm{I}_{\mathrm{PET-PA6}}$ are the intensities of the NMR peaks for PET carbonyl group and for the carbonyl group of a transition structure built up by PET and PA6 residues.

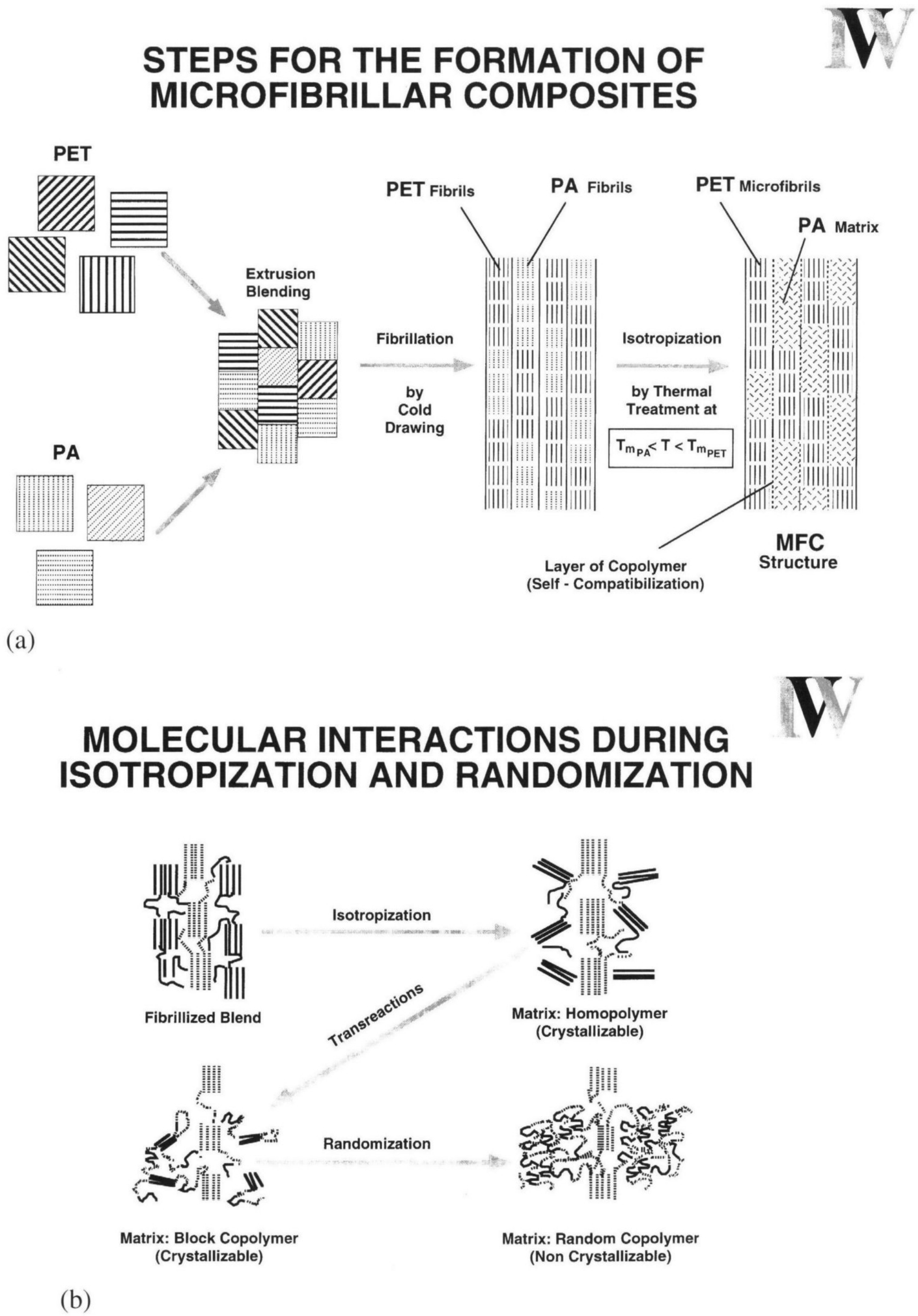

Figure 1. Schematic presentation of a MFC preparation: (a) at macroscopic level; (b) at molecular level.

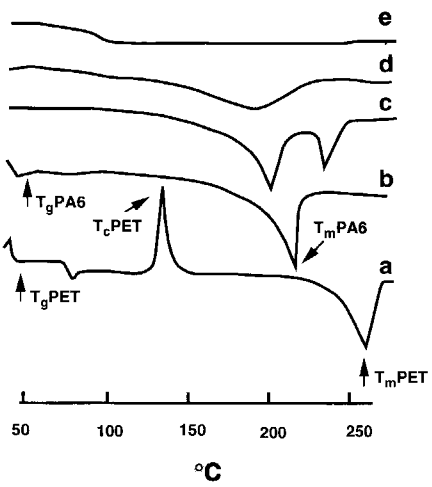

Figure 2. DSC traces at 10 °C/min heating rate of an equimolar PA6–PET model blend after different time of annealing at 290 °C: (a) homo PET and (b) homo PA6; no annealing, blend annealed at 290 °C for $t_a = 10$ min (c), 120 (d) and 190 (e) min.

4. STRUCTURE OF MFC FROM A PA6/PET BLEND

The occurence of chemical interactions on diffent stages of MFC manufacturing can be visualized by studying the corresponding WAXS patterns and SEM micrographs (Fig. 4). To obtain useful SEM images of the composite samples, the PA6 matrix has to be removed previously by selective dissolution in formic acid (HCOOH).

It becomes evident that melt-mixing of PET and PA6 results in an isotropic, predominantly amorphous product (Fig. 4a). During cold drawing of the blend (Fig. 4b), a well-expressed fibrillization of the system takes place that leads to an appearance of elliptic reflections in the WAXS pattern, both for PET and for PA6 components. The WAXS pattern after isotropization (annealing of the drawn system at 240°C, i.e. below T_m^{PET}, Table 1) (Fig. 4c), demonstrates that this is the stage where the MFC is produced. The latter is composed of an isotropic, semi-crystalline PA6 matrix as characterized in the WAXS pattern by continuous rings. It is reinforced by highly oriented PET microfibrils (the arc reflections). The SEM micrograph in the same figure visualizes the PET microfibrils even better due to the complete removal of the PA6 component.

As discussed above, prolonged heat-treatment of the MFC at 240°C leads to intensive interchange reactions between the matrix and the reinforcing material, resulting in the formation of a short block PA6–PET copolymer. In Fig. 4d (the WAXS pattern) this trend is demonstrated by the disappearance of the PA6 reflections. It seems the matrix homopolymer has disappeared from the system. In fact this is really the case because all of the PA6 polymer is now included in a PA6–PET amorphous copolymer. The latter is unable to crystallize because neither the polyamide, nor the polyester sequences are long enough to form lamellae (for example, for PET one needs 'blocks' of at least 5–7 sequences in order for the

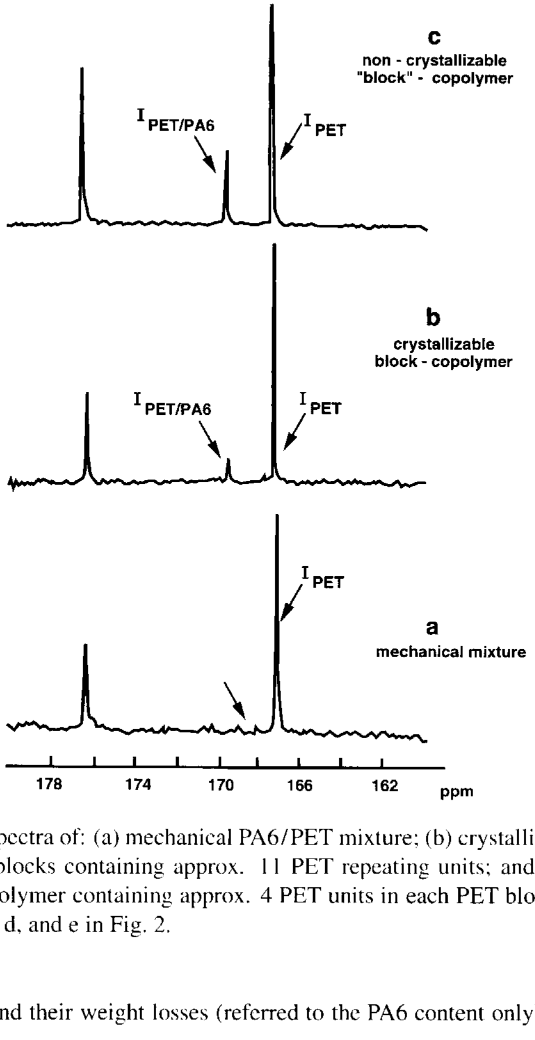

Figure 3. ^{13}C NMR spectra of: (a) mechanical PA6/PET mixture; (b) crystallizable block PA6–PET copolymer with PET blocks containing approx. 11 PET repeating units; and (c) non-crystallizable PA6–PET 'block' copolymer containing approx. 4 PET units in each PET block. These samples are the same as samples c, d, and e in Fig. 2.

Table 1.
Samples preparation and their weight losses (referred to the PA6 content only) at different stages of MFC preparation

Samples designation of PA6/PET blend	Zone drawing[a] temperature (°C)	Draw ratio λ	Annealing in vacuum with fixed ends		Weight loss (%)
			T_a (°C)	t_a (h)	
As quenched	—	—	—	—	98
As drawn	180	4.2	—	—	96
Annealed	180	4.2	220	5	91
Annealed	180	4.2	220	25	80
Isotropized	180	4.2	240	5	62
Randomized	180	4.2	240	25	22

[a] All the samples were zone drawn at a 10 mm/min moving speed of the heater; tension applied = 15 MPa.

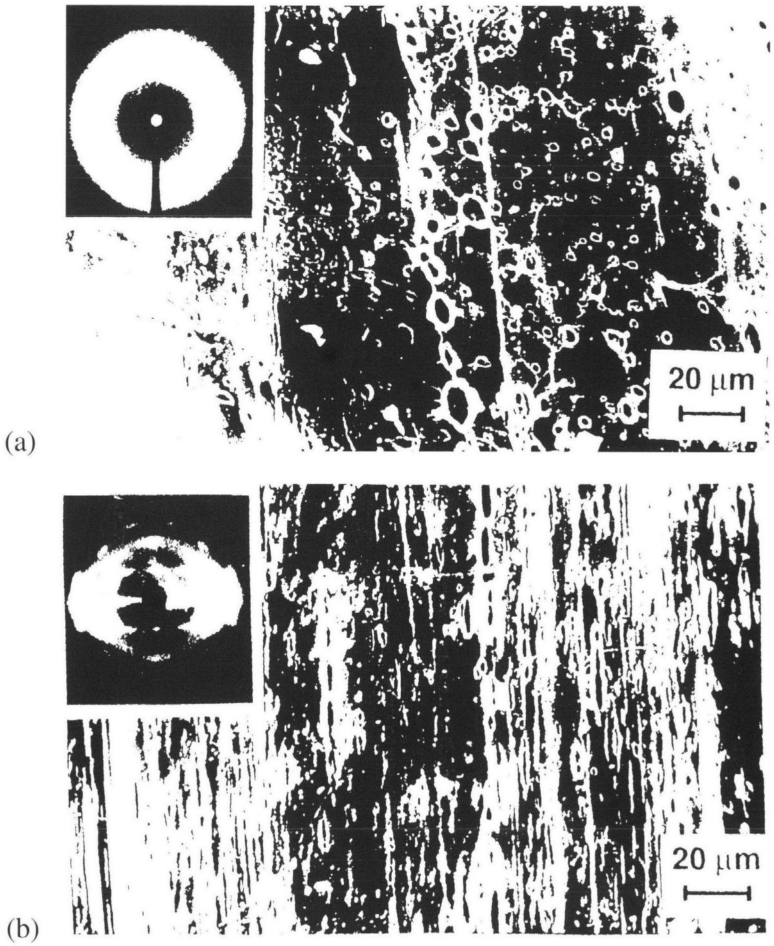

Figure 4. SEM and WAXS pictures taken at different stages of MFC manufacturing after selective removal of the PA6 matrix component (for SEM examinations only): (a) immediatly after blending of PA6 and PET; (b) after cold-drawing step; (c) after isotropization step by annealing the drawn blend at 240 °C; (d) after prolonged thermal treatment (randomization) at 240 °C.

thinnest lamellae of 50 Å to be formed). In the same figure (the SEM mircograph where the matrix material was removed), we can see that some additional material is attached to the PET microfibrils which is obviously the PET–PA6 copolymer, as it is insoluble in formic acid. Both WAXS and SEM patterns indicate that the PET fibrils remain in a highly orientated state. This effect can be explained by the fact that only the amorphous portion of the polyester takes part in the chemical transreaction with the polymer matrix.

Figure 5 shows IR spectra of PA6/PET films extracted with formic acid after being subjected to various thermal treatments (indicated in the curves and in Table 1). It can be seen that the peak intensities at 3300 cm^{-1} are quite different. Since this the characteristic wavelength for the amide group, the respective peak

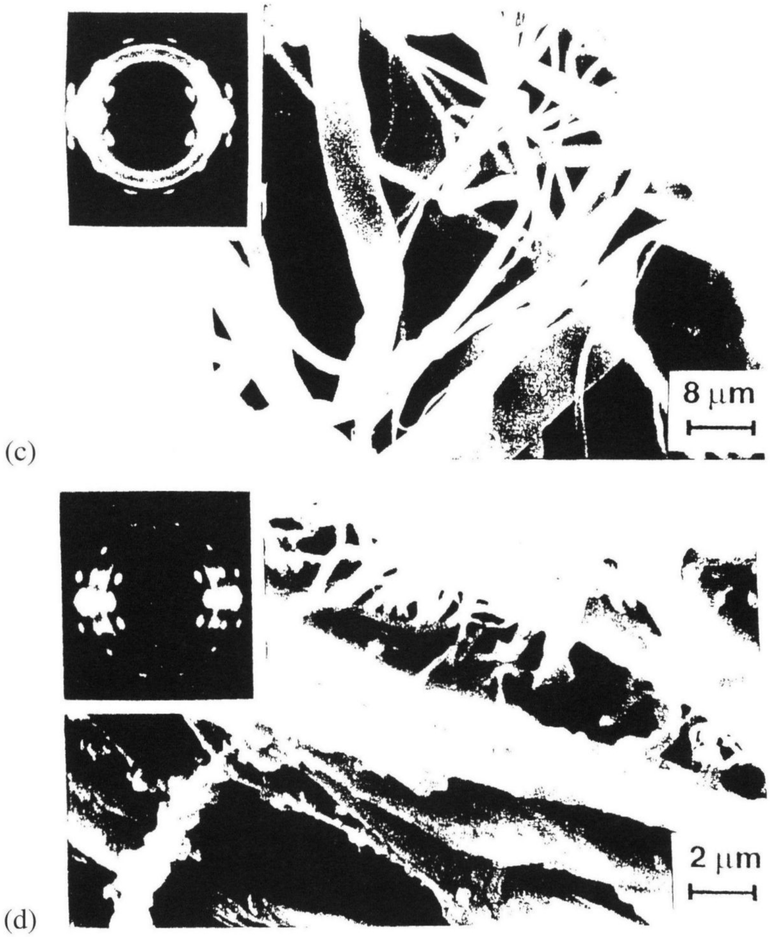

Figure 4. (Continued).

intensity can be used as a measure for the amount of PA6 in the blend. The weight losses after extraction of the samples (Table 1) and the IR spectra in Fig. 5 clearly indicate that the intensities of interest for both the as-quenched and as-drawn samples are negligibly small. This means that practically the entire PA6 fraction is extracted from not-annealed samples where no chemical reactions took place. Some rise in the non-extractable amide-containing fraction is observed after annealing at 240°C. It becomes well-pronounced after increasing the annealing duration up to 25 h. In the latter sample where most intensive chemical reactions are expected, the amide peak is most intensive which is accompanied by a copolymer weight loss after extraction of only 11% or, if referred to the PA6 content, 22% (Table 1, Fig. 5). Those effects should be attributed to chemical changes, i.e. progressive involvement of the PA6 component into non-extractable copolymers, the latter strongly affecting the morphology of MFC as previously indicated.

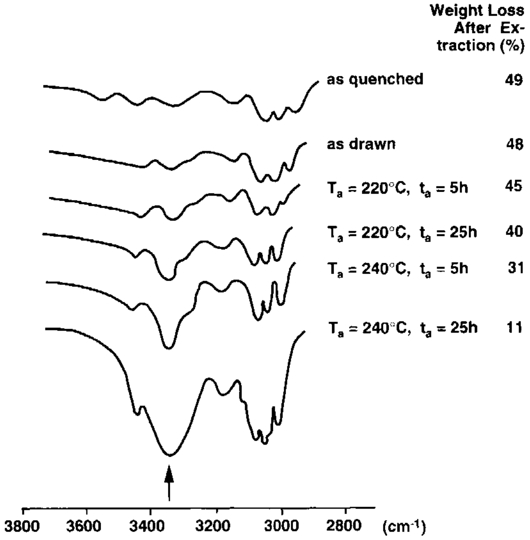

Figure 5. IR spectra of films of PA6/PET blend (1 : 1 by weight) with different thermal prehistory recorded after extraction in formic acid. Note: the weight losses refer to the entire PA6–PET copolymer.

5. MECHANICAL PROPERTIES OF PA6-PET MFC — THE OPTIMAL BLEND COMPOSITION

It is interesting to follow the mechanical properties of the PA6–PET MFC as a function of blend composition. In Fig. 6a and 6b the tensile shear strength and the *E*-modulus values are drawn against the PET/PA6 ratio at every stage of the MFC preparation–blending, cold-drawing and matrix isotropization. As one may expect, the lowest values for σ and E are determined with all composites immediately after melt mixing. However, if the extruded cable produced in this step is cold-drawn, a drastic increase of the σ and E values is established (in average up to six times), depending on the starting component ratio. A similar improvement of the mechanical properties is also valid for the next step of matrix isotropization, achieved by hot pressing. The experimental data are a little lower than those in the stage of cold-drawing, but are still higher than those for the as-extruded cable.

As seen from the curve behavior, a rather good improvement of the PA6-matrix properties is already achieved at a PA6/PET ratio of 70/30, i.e. at a PET content of 30 wt%. This amounts to 27 vol%. Although a further increase of the PET content leads to a further improvement in the mechanical properties of the MFC, it should be mentioned here that the 70/30 MFC composition can be considered to be the most advantageous system that can be used, e.g. as a prepreg for the preparation of laminates. In addition, a further increase of the PET content seems to result in a deterioration of the interlayer adhesion. Further, it can be seen from Fig. 6a, that the 70/30 composition in the hot pressed state (isotropized condition, i.e. closer to application) displays an E modulus which is lower by about 25% than

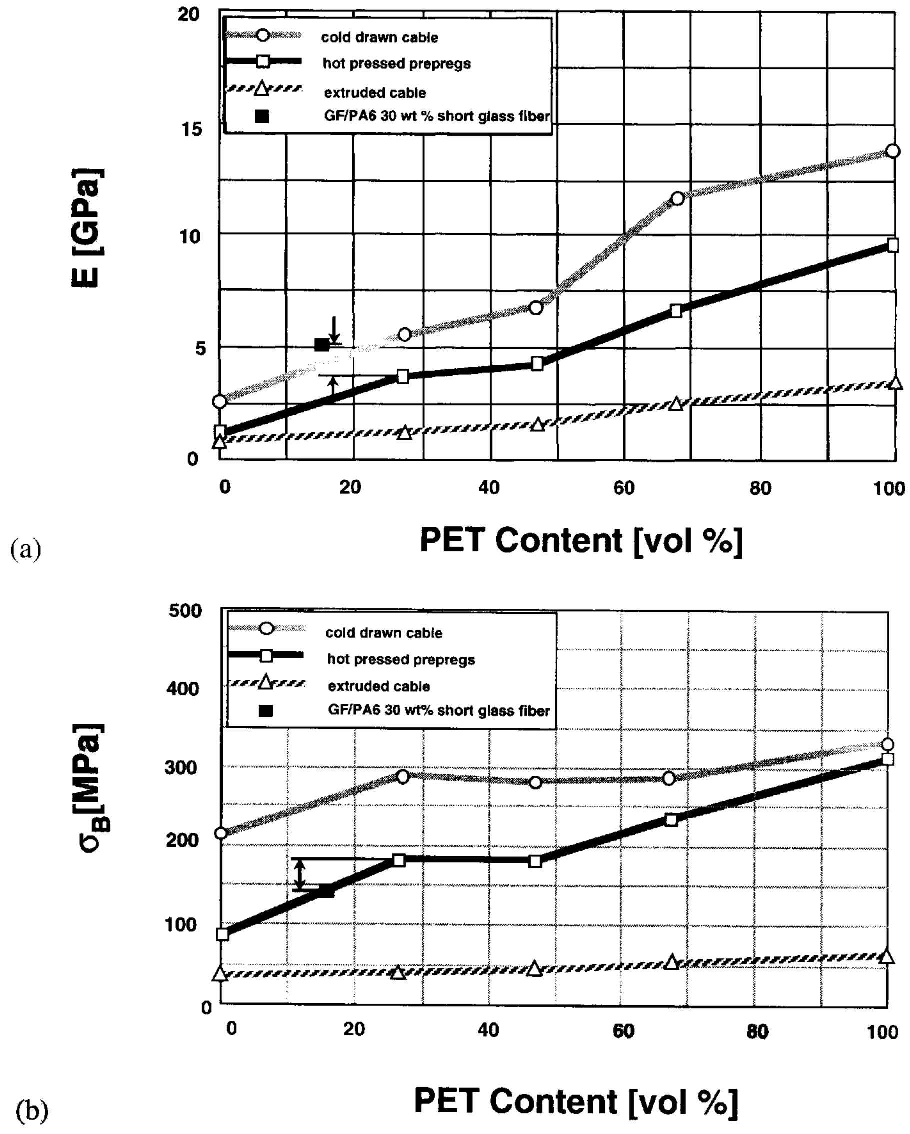

Figure 6. Mechanical properties of PA6–PET MFC as a function of the component ratio: (a) E-modulus; (b) strength σ.

that of a short glass fiber reinforced PA6 (30 wt% = 16 vol% glass fibers) [13]. This must be obvious because of the much higher modulus of the glass fibers (by about one order of magnitude compared to drawn PET). At the same time, however, the σ_B-value of the corresponding MFC is by a factor of 1.26 higher than that measured for the glass-fiber reinforced PA6 system. This fact can be attributed to the strong interfacial interaction between the PET-microfibrils and the surrounding PA6 matrix, which finally leads to reorientation of the matrix associated with strain hardening of the whole system prior to failure, at strains much higher than that known for the short glass fiber composites.

An additional comment should be made regarding the anisotropy of the different material states. It is obvious that the cold drawn cables possess the highest degree of anisotropy due to the drawn state of the two phases in the blend. Isotropization reduces the degree of anisotropy clearly but there remains still some preferred orientation of the PET-microfibrils in the original drawing direction. If isotropization is carried out during injection moulding of chopped cold drawn cables a similar orientation state, as expected for a short glass fiber reinforced system, is most probable which justifies the above mentioned comparison to this system. On the other hand, a comparison to continuous glass fiber composites does not seem to be realistic since the microfibrils are not continuous in length but also discontinuous as is the case in short glass fiber composites. Nevertheless, the as-drawn cables can also be used to perform a lamination process in a similar way as is common for continuous fiber reinforced composite prepregs. Isotropization takes place in this case after lamination of the cold drawn cables in the subsequent hot processing step. Attempts like this have also been carried out by the authors, and they are described in another paper [14].

6. CONCLUSIONS

The chemical changes, namely ester–amide transreactions that accompany the process of obtaining a PA6–PET MFC are proven by several independent methods. At the initial stages of MFC isotropization, the effect of self-compatibilization between the components of MFC is due to the formation of copolymers with long blocks. With a larger degree of interaction obtained through higher annealing temperatures and/or annealing duration, the amout of PA6–PET copolymer increases. At the same time, the homopolymer blocks become shorter until an equilibrium value of four PET units is reached that renders the resulting copolymer unable to crystallize. This trend results in a total change of the chemical composition of the PA6–PET MFC, the initial homo PA6 matrix being replaced by a new, copolymeric one. These chemical reactions considerably affect the structure and properties of MFC under investigation at each stage of its preparation.

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