EFFECT OF BLEND COMPOSITION ON THE STRUCTURE-PROPERTIES RELATIONSHIPS OF NANOSTRUCTURED POLYMER COMPOSITES FROM POLYCONDENSATE/POLYOLEFIN BLENDS

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Nanostructured polymer composites (NPC) are obtained by melt-blending of poly(ethylene terephtalate) (PET) and polypropylene (PP) as well as polyamide 66 (PA66) and PP in wt. ratio 70/30, 50/50 and 30/70, followed by cold drawing of the extruded bristle and compression molding of the drawn bristles in form of film. The blends are studied by X-ray diffraction, scanning electron microscopy (SEM), and static mechanical testing. SEM and X-ray reveal different blend morphologies created during the stages of NPC manufacturing: isotropic blend after extrusion, fibrillization of both components after drawing, izotropization of the PP matrix with preservation of the PET- or PA66 fibrils after hot pressing. Also observed was a strong epitaxial effect of the nanostructured microfibrils of PET or PA66 on the non-isothermal crystallization of PP during cooling after compression molding at 215°C. Thus, the cold drawn and thermally treated PET/PP and PA66/PP blends represent anisotropic transcrystalline structures. The PP crystallites in the transcrystalline layers are reoriented at aprox. 40° with respect to the drawn direction (fiber axis). This is valid for the whole amount of PP in the case of PET/PP blend and only partially for the blend PA66/PP. These morphological peculiarities affect the mechanical properties of the NPC: the Youngs modulus and the tensile strength

of the compression molded films are respectively about 4−6 and about 10−15 times higher (depending of the chemical composition and proportions of the components in the blends) than those of the compression molded neat PP.

Keywords: polymer blends, polymer-polymer composites, transcrystallization, morphology, mechanical properties

INTRODUCTION

Usually, both polymer composites and blends are defined as materials consisting of two or more distinct components with recognizable interfaces or interphases [1,2]. This definition is generally restricted in practice to composites containing fibrous or other reinforcements, e.g., platelets or flakes, with different length and cross−section dimensions described by the aspect ratio, that are embedded in a continuous rigid matrix. The incorporation of these reinforcements normally improves the mechanical performance of the matrix material [3].

During the last decades a new type of polymer-polymer composites, originally called "microfibrillar reinforced composites" (MFC) [4−12] and later renamed as nanostructured polymer composites (NPC), was developed. The reason for this modification of the name is the fact that, in many cases, the smallest size of fibrils, the diameters [9], renders the upper size limits of nanocomposites although the NPC can hardly be regarded as typical representatives of this class of materials. Contrasting the classical composites, those reinforced by short-or by continuous fibers, the new type of composites can not be manufactured using the common approach *via* melt-blending of the two starting components, the matrix and the reinforcing material. Since the reinforcing element in the nanostructured polymer composites, the microfibril, does not exist as a separate material, a special technique should be applied for their creation as well as for the matrix they are reinforcing [4−12].

A *fibril* may be defined as a structural entity with material properties that are biased predominantly along a linear dimension or symmetry axis [13]. Similarly to the natural materials, such as cellulosic structures and collageneous composites, man−made polymeric materials, such as ultrahighly drawn polymer solids, liquid−crystalline polymers and hard elastic materials, show outstanding mechanical properties since their basic organizational units are microfibrillar in nature.

With respect to the size of the reinforcing elements, NPC take an intermediate position between the two extreme groups of polymer composites: macrocomposites (e.g., short fiber−reinforced composites)

and the real molecular composites [14]. Bundles of highly oriented microfibrils play the role of reinforcing elements in NPC.

The manufacture of the nanostructured polymer composites starts with blending of immiscible polymer partners that should have different melting points, T_{m}. The essential stages of MFC preparation are as follows: (i) blending and extrusion, (ii) drawing (with good orientation of all components), and (iii) thermal treatment being above the T_m of the lower−melting component but below the T_m of the higher−melding one. During the drawing step, the blend components are oriented and nanostructured fibrils are created (*fibrillization step*). In the subsequent step, when melting of the lower−melting component occurs (*isotropization step*), it is necessary to ensure that the fibrillar structure of the higher−melting component is preserved. It is important to note here that NPC are based on polymer blends but they should not be considered as "drawn blends" reported, for example, by Aharoni [15,16], since the izotropization step results in the formation of an isotropic, relaxed matrix reinforced by fibrils of the higher−melting component, i.e, one finally deals with a typical composite material.

The outlined steps with the corresponding structural changes have been already observed by wide-angle X-ray scattering (WAXS) and scanning electron microscopy (SEM) in different blend systems based on condensation polymers: poly(ethylene terephtalate) (PET) polyamide 6 (PA6) (blend PET/PA6) [4,5,7−9,11], PET and poly(buthylene terephtalate) (PBT) (blend PET/PBT) [6], polyamide 66 (PA66) (blend PA66/PA6) [10], and the triple blends PET/PA6/PBT and PET/PA6/PA66 [10,12].

Another peculiarity of the nanostructured polymer composites is the well documented transcrystallization phenomenon [17−20]. It takes place when heterogeneous nucleation occurs with sufficiently high density along the fiber surface and the resulting crystal growth is restricted to the lateral direction, so that a columnar layer develops around the embedded fiber. The formation of transcrystallized layers is thought to be central to the improvement of some composite properties. The transcrystallization is a function of the nucleating activity of the fiber surface and the crystallization kinetics of the resin matrix. Different cases for mutual arrangement of the polymer chains in the reinforced fibers and the surrounding matrix are reported. For instance, in cellulose/PP composites, the chains of PP are parallel to the fiber axis [21]. The same case dominates in some advanced polymer composites based on polyetherketoneketone and polyetheretherketone reinforced by carbon fibers [22].

In a study on aramid and carbon fiber reinforced PA66 composites, atomic force microscopy reveals radial regularity in the transcrystalline layer, relative to the fiber, and X-ray diffraction investigations of the isolated layer suggest that the polymer chain is oriented predominantly perpendicular to the fiber axis [23].

Very recently we reported on an uncommon phenomenon—transcrystallization with change of the initial orientation of polyamide 12 and PP after melting of those components and subsequent crystallization in the drawn PET/PA [24] or PET/PP blends [25]. During the crystallization from the melt the PA12 component in the PET/PA12 blend experiences in the transcristalline layers a reorientation at $90°$ with respect to the initial drawing direction; the reorientation of the PP in the PET/PP blend is at about $45°$.

It looks challenging to extend the experience, gained so far, from blends of condensation polymers [4−12] to blends of polyolefins and polycondensates. It should be note that, if in such blends the polyolefin used is not functionalized for suppressing of the incompatibility, only physical tools, as for example the transcrystallization phenomenon, are available for doing so [1]. Because of the strong ability of PP to form transcrystalline layers in fiber reinforced composites [3,21], and the essential role of this phenomenon for the improvement of the adhesion between fibers and matrix, it was interesting to find out to what extent transcrystallization, if any, contributes in this direction in polycondensate/polyolefin systems. In addition, attempts have been undertaken for optimization of the processing conditions by varying the blend composition, components ratio and applying short thermal treatment for isotropization of the matrix. In fact, these are the objectives of the present study, along with the aim to prepare prepregs (films) suitable for manufacturing of laminate structures from NPCs.

EXPERIMENTAL

Materials and Sample Preparation

Commercial, engineering grade PET (Yambolen, Bulgaria), PA66 (Ultramid, BASF, Germany) and PP (Burgas, Bulgaria) were dried in an oven at $100°C$ for 24 h and blends PET/PP and PA66/PP were prepared in weight ratio of 70/30, 50/50 and 30/70 by extrusion in a Brabender single screw (30 mm diameter) extruder with L/D ratio 25 at 30−35 rpm. The temperature zones starting from the feed to the die were set at 210, 240, 260, 270 and finally $240°C$ at the die. The extrudate from a 2 mm capillary die was immediately quenched in a

water bath at $15-18°C$. The bristles were moved through the bath by means of two rotating rubber cylinders at a rate of about 90 rpm.

All blends, as well as extruded bristles of neat PET and PA66, were drawn in a tensile testing machine (Zwick 1464) at room temperature and a strain rate of 80 mm/min to a draw ratio $\lambda = 3.6-3.8$ which resulted in a final diameter of about 1 mm. A thermal fixation was performed after drawing by means of blowing warm (about $80°C$) air for 1 min at the stretched materials.

Strip-like prepregs (films), about 3 mm wide and 0.25 mm thick, were prepared from the oriented bristles, using a PW 10 Paul Weber hot press under the following conditions: temperature of the plates $-215°C$, load -4 kN, time under pressure -10 s. Hot pressing was performed at constant strain of the bristles.

X-Ray Diffraction

Wide-angle X-ray scattering patterns of PET/PP and PA66/PP blends (50/50 by wt) were obtained using synchrotron radiation generated at the beamline A2 of HASYLAB in Hamburg, Germany. Diffraction patterns were registered by means of a 2D image-plate detector. It was expected to get in this way information about both the states of orientation and crystallization phenomena during the various states of the blend treatment (after extrusion, drawing, and compression molding of the drawn bristles).

Scanning Electron Microscopy

A JEOL HSM 5400 scanning microscope with an acceleration voltage of 20 kV was used for studying the morphology of the PET/PP and PA66/PP (50/50 by wt) specimens. To this purpose, the samples from the various manufacturing and processing stages of MFC were broken in a brittle manner at liquid nitrogen temperature in order to study their fracture surface. All specimens were coated with a thin gold layer prior to SEM analysis.

Mechanical Characterization

Static mechanical tests of the as extruded, drawn and hot pressed PET/PP and PA66/PP blends as well as the neat polymers were carried out at room temperature and a cross-head speed of 5 mm/min using an Zwick 1464 tensile tester. The Young' modulus (E) and the tensile strength (σ) (by the use of an incremental extensiometer) were determined from the load-extension curves. All experimental data presented below are average values of seven measurements.

The calculated according to equations (1) and (2) values of the E and σ based on the blend components are also obtained [2].

$$E_{av} = E^{PET}V^{PET} + E^{PP}(1 - V^{PET}) \qquad (1)$$

and

$$\sigma_{av} = \sigma^{PET}V^{PET} + \sigma^{PP}(1 - V^{PET}), \qquad (2)$$

where E^{PET}, E^{PP}, σ^{PET}, σ^{PP} are the Young' modulus and the tensile strength of the PET and PP homopolymers, respectively, after drawing and hot pressing, as obtained in the present study. The same eqs. (1) and (2) were applied for the blend PA66/PP. The volume fractions of neat PET and PA66 (V^{PE} and V^{PA66}), respectively in the blends were calculated using the following density values: 1,35 and 1,10 kg/m^3 for drawn samples as well as 1,41 and 1,14 kg/m^3 for the samples after hot pressing, respectively. For these calculations a density of 0,91 kg/m^3 was used for PP component in the blends.

RESULTS

X-Ray Observations

Qualitative trends in changing of morphology during processing can be seen in the X-ray diffraction and SEM results. In Figure 1 are shown the WAXS patterns obtained from PET/PP and PA66/PP (50/50 by wt) compositions, each for the as extruded state, after drawing, and after drawing plus hot pressing at 215°C. In the as extruded state all phases of both blends are isotropic, i.e., they exhibit complete isointensity Debye rings. The crystalline reflections arize mainly from PP fraction of the blends (Fig. 1a and 1d). This suggestion is supported by the well known fact that PP crystallizes faster than PA66 and much faster than PET. After drawing, the phases are highly oriented, with chains strongly aligned along the draw direction (FA). The formation of crystalline phases of PET and PA66 is observed too. This is due to the stress-induced crystallization as well as to the thermal fixation after drawing (Fig. 1b and 1e).

After hot pressing at 215°C, i.e. above the T$_m$ of PP, a completely different blend structure is created (Fig. 1c and 1f). The PET and PA66 fractions in the blends practically preserve their orientation, as evidenced from their *hk0* spots being situated on the equator. At the same time one can see a slight tendency to disorientation of these crystallites. This is due to the fact that pressing causes some disorientation
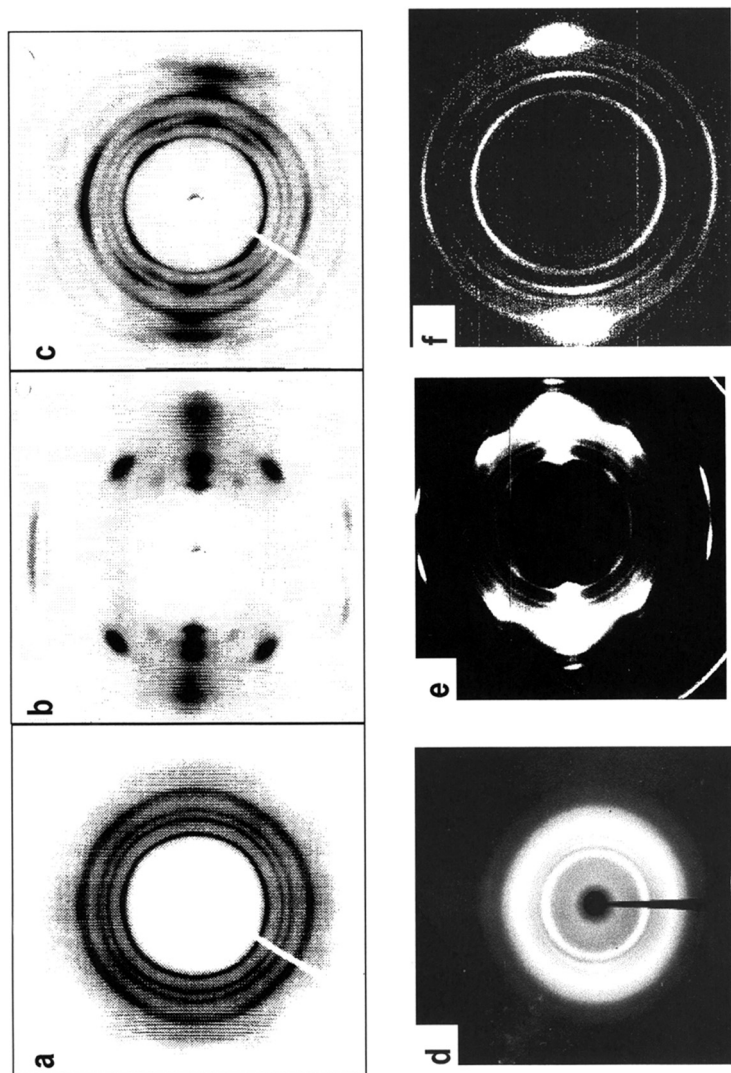
FIGURE 1 Wide-angle X-ray scattering patterns of PET/PP (a, b, c) and PA66/PP (d, e, f) (50/50 by wt) blends taken at room temperature: (a) and (d) after blending and extruding, (b) and (e) after cold drawing, and (c) and (f) after hot pressing at 215°C and cooling down to room temperature.

217

with respect to the FA direction. The PP component in the two blends under consideration shows a tendency to isotropization after hot pressing because its scattering pattern is close to those shown in Fig. 1a and 1d. In the same time, some orientation of PP crystallites can be observed since the Debye rings of PP are not completely of isointensity type as the case is after extusion (Fig. 1a and 1d).

What should be stressed here is the fact that orientation of PP crystallites in the drawn bristles and in those after hot pressing is different. In the first case the *hk0* spots are laying on the equator while in the second case they are tilted in azimuthal direction (compare Fig. 1b with 1c and 1e with 1f).

SEM Observations

Scanning electron micrographs of the cryogenic fracture surfaces of the as extruded, as drawn and hot pressed PET/PP and PA66/PP (50/50 by wt) blends are shown in Figures 2. These specimens were prepared by fracturing perpendicularly to the bristle axis in liquid nitrogen. It should be noted that samples behaved differently during the fracturing, suggesting different morphology of the studied blends.
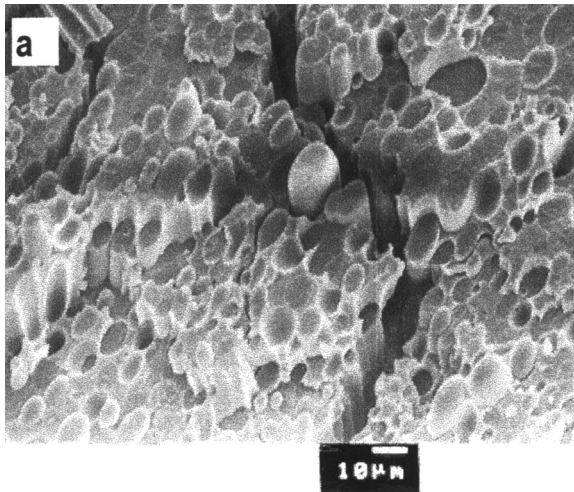

FIGURE 2 Scanning electron micrographs of the cryogenic fracture surfaces of PET/PP (a, b, c) and PA66/PP (d, e, f) (50/50 by wt) blend taken at room temperature: (a) and (d) after blending and extruding, (b) and (e) after cold drawing, and (c) and (f) after hot pressing at 215°C and cooling down to room temperature. (*Continued*).
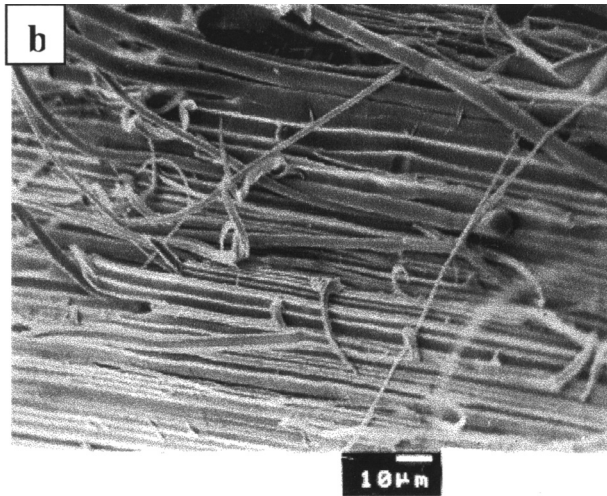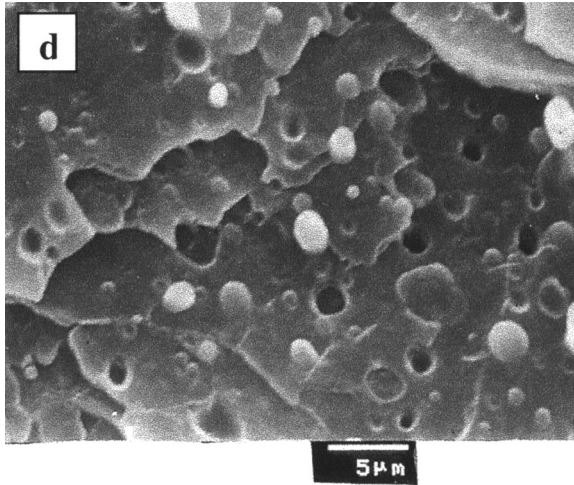
FIGURE 2 (*Continued*).

As extruded blend broke exactly perpendicularly to the bristles axis, while the as drawn and compression molded samples split along the draw direction. The SEM of these samples are taken from precisely these surfaces.
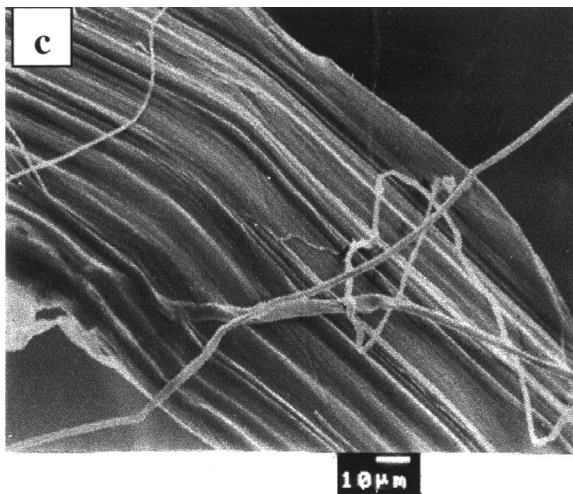
FIGURE 2 (*Continued*).
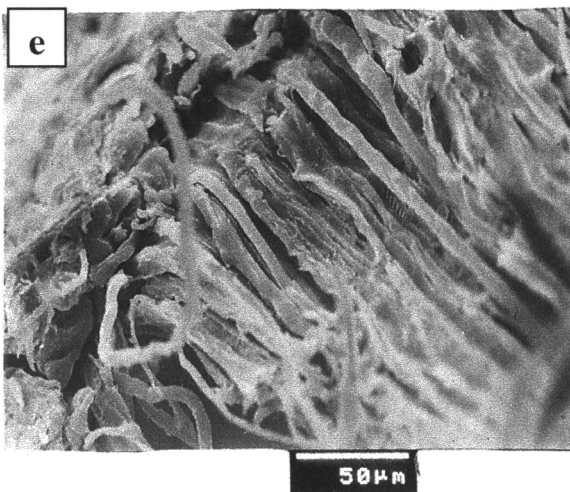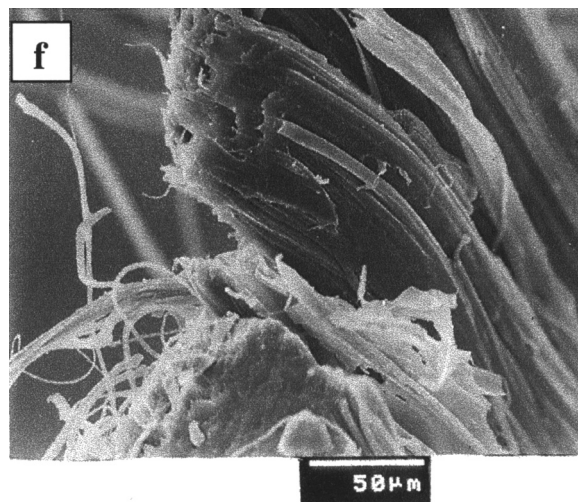
FIGURE 2 (*Continued*).

It is seen in Fig. 2a and 2d that PET and PA66 components in the as extruded PET/PP and PA66/PP blends are uniformly dispersed in PP medium in the form of large number of elliptic particles with diameters of 5−10 μm. Holes of the same shape and size are also observed; so it can be concluded that the latter result from the pullout

FIGURE 2 (*Continued*).
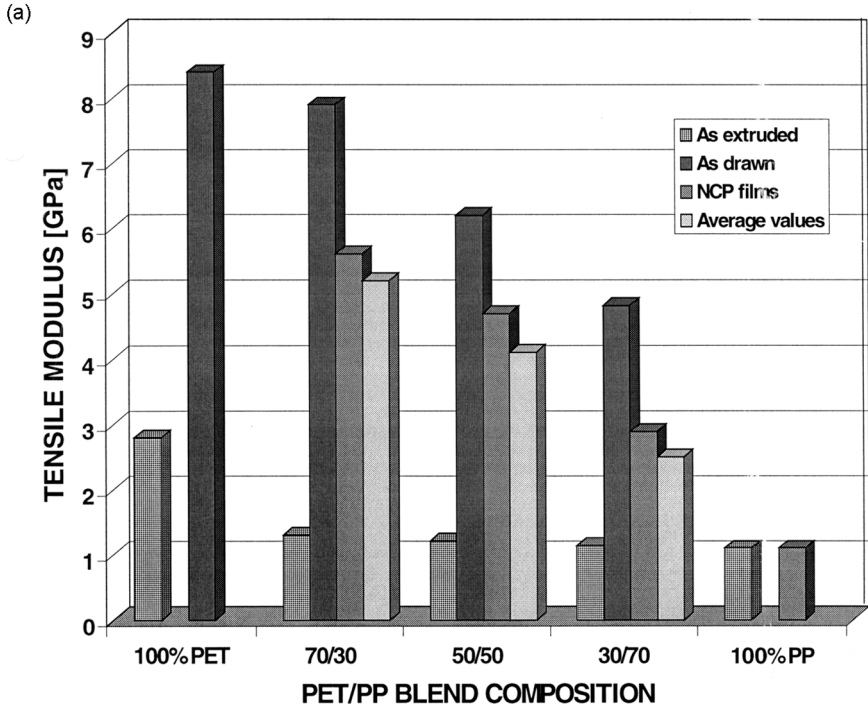
FIGURE 2 (*Continued*).

of PET or PA66 (Fig. 2a and 2d, respectively) particles during cryogenic fracture.

Subsequent drawing results in drastic changes in the blends morphologies (Fig. 2b and 2e). As seen from the fracture surface of as drawn PET/PP and PA66/PP blends. Fibrils and bundles of them with diameters of 1−5 μm are generated during the drawing.

After hot pressing at 215°C where PP is completely molten the morphologic structure of PET and PA66 components remains almost unchanged—the uniaxially oriented fibrils which are now embedded in a significantly isotropized PP matrix from larger bundles. As a final result, a composite-like structure is observed (Fig. 2c and 2f).

Mechanical Properties

The results of the static mechanical tests of PET/PP and PA66 blends after various treatment stages together with the data for the neat components are shown in Figures 3 and 4, respectively. First of all, it should be noted that the lowest values of the Young's modulus E and the tensile strength σ are obtained with samples taken immediately after extrusion (Figs. 3 and 4). Cold drawing results in an abrupt increase in the E-and σ-values for all the samples under investigation. The tensile modulus of the drawn blends are 4 to 6 times, depending on the chemical composition and proportions of the components in the blends, than those of the as extruded samples (Figs. 3 and 4). This

(a)

FIGURE 3 Static tensile properties of as extruded, as drawn and compression molded PET/PP blends and homopolymers, calculated according to Eqs. (1) and (2) average values are also presented. (*Continued*).

bolds also for the values of the tensile strength, where the respective differences are even greater (up to 10−15 times).

Hot pressing at 215°C (isotropization step) results in a drop of the modulus and strength in accordance with expectation. The reduction of σ is by 23−35% and for the E it is higher especially in 30/70 composition (Figs. 3 and 4). It should be noted here that the same tendencies during NPC formation had already been observed in drawn PET/PA6 blends with the same composition (70/30, 50/50 and 30/70) and short time (10 s) hot pressing at 200°C (after isotropization of the PA6 component) [11].

Concerning the effect of the blend composition on the mechanical properties, one can conclude that the blends which are richer in PET or PA66 reveal almost always the highest E and σ values at each stage of NPC manufacturing. Another interesting observation is that the calculated according to eqs (1) and (2) values of E and σ of the NPC's, i.e after isotropization, prepared from 70/30, 50/50 and 30/70 blends

(b)
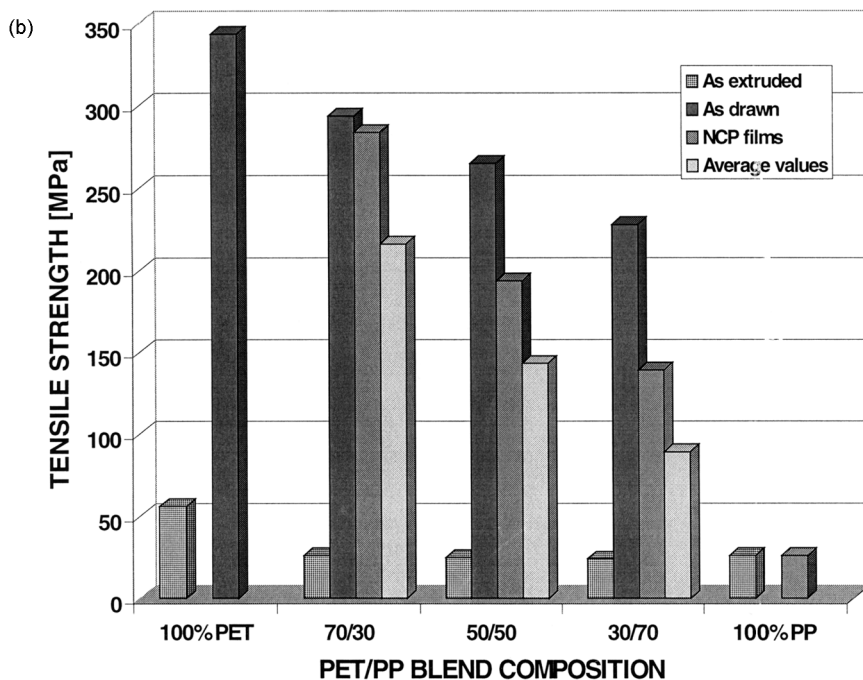
FIGURE 3 (*Continued*).

are almost the same (for PA66/PP samples) and smaller (for PET/PP samples) than the experimentally obtained (Figs. 3 and 4). This could mean that some synergetic effect must be involved (especially for PET/PP samples), exceeding the properties expected from the rule of mixtures approach.

DISCUSSIONS

The WAXS patterns as well as the SEM micrograph of the PET/PP and PA66/PP blends (Figs. 1 and 2, respectively) clearly show the morphological differences of the blends created during the various stages of NPC manufacturing, namely the isotropic blend after extrusion, the fibrillization of the both components after the drawing and, finally, the izotropization of the PP with preservation of the PET or PA66 fibrils as a result of the hot pressing. At the same time, due to the fact that these microfibrils are not affected by the thermal treatment at 215°C, they do not change their starting orientation (the draw direction, FA), as can be concluded from their X-ray patterns being of the type shown in Figs. 1c and 1f for the two blends. In contrast to the

(a)
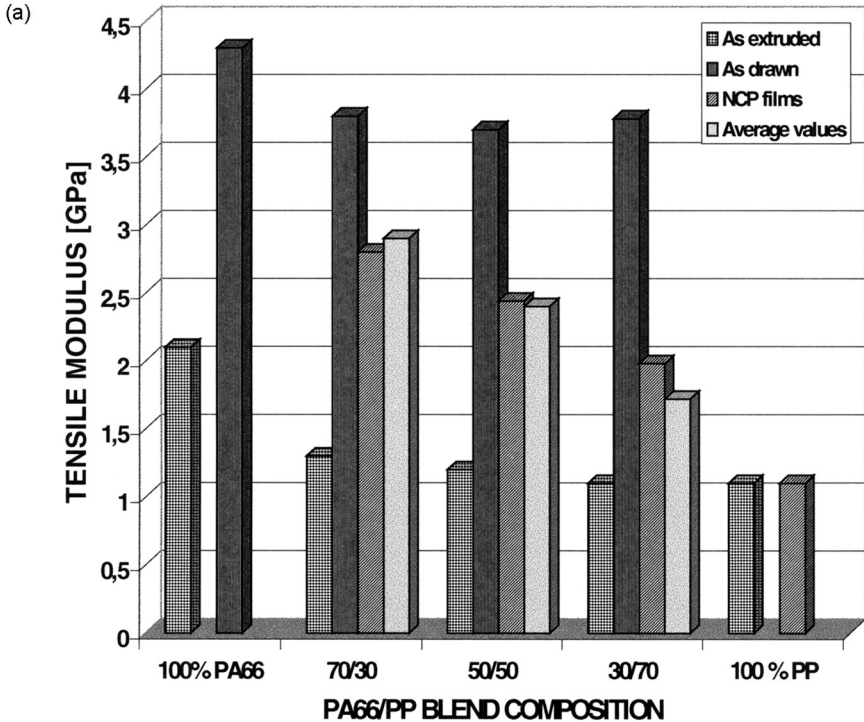
FIGURE 4 Static tensile properties of as extruded, as drawn and compression molded PA66/PP blends and homopolymers, calculated according to Eqs. (1) and (2) average values are also presented. (*Continued*).

behavior of the PET and PA66 components, the PP matrix crystallizes in a more or less isotropic manner, reaching a state closer to the starting isotropic material (as extruded) (Figs. 1a and 1d) rather than to the drawn state (Figs. 1b and 1e). As was mentioned above, quite similar changes in the morphology have already been observed during NPC preparation from blends of two condensation partners [4−12]. In those cases a completely isotropic matrix was obtained only after long melt annealing times (hours). Preservation of the orientation (to some extent) of the matrix material was observed in the cases when a short annealing time has been applied (minutes) or a catalyst was added during melt blending.

After a more detailed analysis of Fig. 1 one can see that WAXS pattern taken at room temperature after hot pressing at $215°C$ (Fig. 1c) is quite different from the foregoing ones (Fig. 1a and b) regarding the PP reflections. As a result of the non-isothermal crystallization during
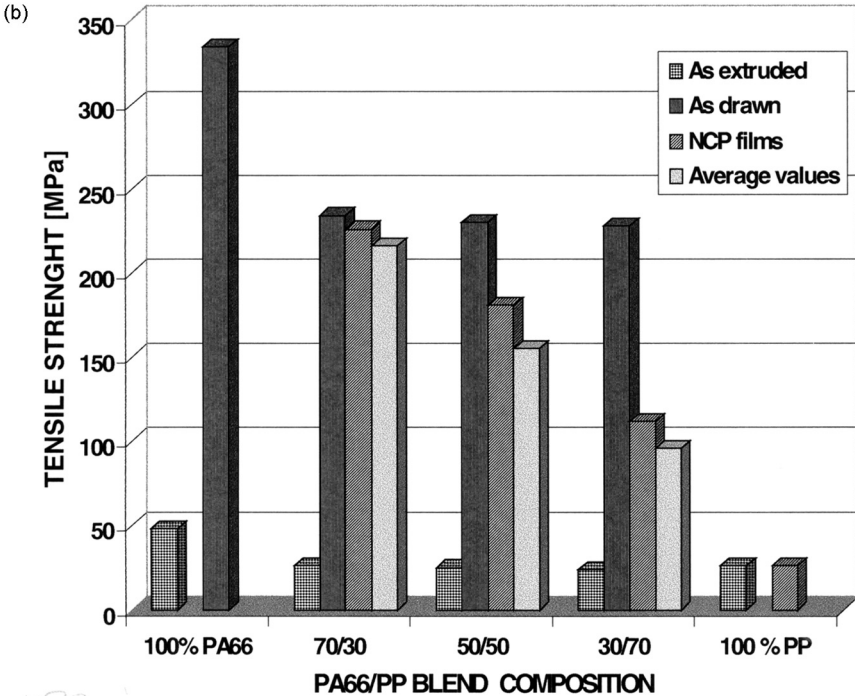
FIGURE 4 (*Continued*).

the cooling, one has to expect formation of a more or less isotropic crystalline PP phase, taking into account the fact that the melt of PP before cooling is supposed to have no orientation. Surprisingly enough, the distribution of PP reflections is rearranged, as can be concluded from the comparison of Figs. 1a and b. The displacement of reflections after crystallization shows that the chain axis of PP in the crystallites are tilted by approx. 40° with respect to FA, i.e., they are no longer parallel to the original draw direction as in the initial sample (Fig. 1b). In other words, similar to the system PET/PA12 [24] one deals in the present case with transcrystallization with changes of the orientation relative to the original orientation. The only difference between the case of PA12 and the present one is that in the first case the reorientation takes place at 90° [24], and in the second only at 40°.

Obviously, in both cases one deals with transcrystallization when the PET microfibrils play the role of a nucleating agent, similarly to various reinforcing fibers in common composites. The significant difference between the two cases—the classical composites and the NPC—is that in the second case the PET microfibrils not only promote

the crystallization, but they also affect the orientation of the matrix chains during the transcrystallization in such a way that they are not placed any more parallel to the chain direction of PET, as well as to their own orientation direction before melting (FA).

Concerning the PA66/PP blend the results look somewhat different. As can be seen from Fig. 1f, there are reflections which are almost isointensity circles while the reflection (100) of PA66 shows significant anisotropy, indicating that the orientation of the respective crystallites remain unchanged, i.e., parallel to the initial draw direction. By analogy with the PET/PP system (Fig. 1c), the reflections of PP in PA66/PP blend show detectable anisotropy (Fig. 1f), which can be interpreted as indication of the existence of a crystalline phase with chains inclined to some extent with respect to the original draw direction. But it looks that the majority of chains preserve their original orientation (FA) after recrystallization from the melt. The fact that in the case of PA66/PP blend the anisotropy of PP crystallites is lower, regardless of the actual position of the chain axes, allows one to conclude that the effect of PA66 nanostructured fibrils on the crystallization of PP from the melt is much weaker in comparison with that of PET. An explanation of this observation could be related to the differences in the chemical nature of the PET and PA66 as well as to the supermolecular structure and organization in both type of fibrils.

After this morphological and orientational characterization of the polycondensate/polyolefin blends, let us now look at the relationship between the gained structural characteristics and the mechanical properties of the samples. Concerning the samples of neat homo-polymers it was found that the drawn PET and PA66 bristles show a slight decrease in E and σ after compression molding at $215°C$ (Figs. 3 and 4). This observation could be explained by relaxation and partial disorientation of PET and PA66 fibrils during the thermal treatment needed for the compression molding. The strong reinforcing effect of PET microfibrils can be illustrated in the best way if one compares the E and σ values of the compression molded homo-PP samples with those of the NPC samples. The E-modulus of NPC is about $4-8$ times higher and the tensile strength is about $10-12$ times depending of the chemical composition and proportions of the components in the blends, i.e. amount of fibrillized material, than those of the neat PP (Figs. 3 and 4).

The differences in the tensile properties (especially in the E values) of the as drawn and compression molded PET/PP and PA66/PP blends (Fig. 3 and 4) result from the different chemical composition as well as from the physical properties of PET and PA66. The less stiff PA66 fibrils, reinforcing the PA66/PP composites, impart a higher

compliance, while the stiffer PET fibrils contribute to the approximately two times higher E values of the PET/PP samples.

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