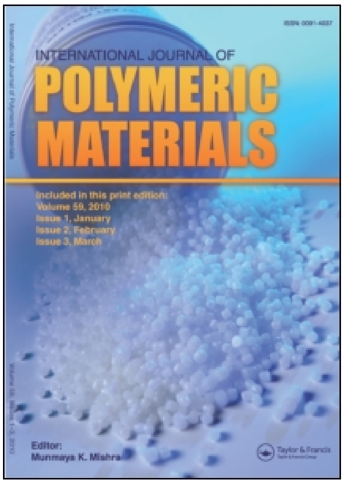

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TRANSCRYSTALLIZATION WITH REORIENTATION OF POLYETHYLENE IN A DRAWN PET/PE BLEND AS REVEALED BY WAXS OF SYNCHROTRON RADIATION

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A cold drawn blend of poly(ethylene terephthalate) (PET) and polyethylene (PE) (50/50 by wt.) was investigated during heating, melting, and subsequent crystallization upon cooling of PE by means of wide-angle X-ray scattering (WAXS) of synchrotron radiation. Strong epitaxial effects of the highly oriented PET on the very first stages of non-isothermal crystallization of PE during cooling of the cold drawn blend from 160°C to room temperature were found. WAXS shows that transcrystalline PE layers are formed around the PET fibrils. Within these layers, the PE crystallites are partly oriented at 90° with respect to their initial orientation (draw direction).

Keywords: transcrystallization, PET/PE blend, reorientation, synchrotron radiation

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INTRODUCTION

A special case of crystallization frequently observed in short-fiber reinforced thermoplastic composites is the transcrystallization [1]. It takes place when heterogeneous nucleation occurs with sufficiently high density along a fiber surface. The resulting crystal growth is then restricted to the lateral direction (perpendicular to the fiber axis (FA)) so that a columnar crystalline polymer layer develops around the embedded fiber. The transcrystallization is a function of nucleating activity of the fiber surface, the relative shearing between the fibers and the molten polymer, and the crystallization kinetics of the latter. The thickness of such a layer can be in the range of several microns. They can be observed in a polarized light microscope on microtomed thin sections, taken parallel to the fiber direction.

At a longer distance from the glass fibers, that is, outside the columnar structures, the polymer matrix crystallizes in form of spherulites, which do not have any preferred orientation with respect to the glass fibers axis.

The contribution of the transcrystalline layers to the improvement of the adhesion between the matrix and the reinforcing component as well as their effect on the entire mechanical behavior of glass-fiber reinforced composites was extensively studied by various authors, for example References [2–3]. Unfortunately, this is not the case for both the orientation of macromolecules in the transcrystalline layers with respect to the axis of the fibers as well as the effect of the substrate material on the molecular orientation. The reason might be that the most common technique for determining the molecular orientation is the X-ray scattering, which is not applicable for this purpose to bulk composites because the scattering of the relatively thin transcrystalline layers is masked by the scattering of the huge amount of isotropically crystallized bulk matrix. Obviously, a technique has to be looked for that is able to register chain orientation in real time. In this way, epitaxial chain orientation during the very first stages of the crystallization process, that is, when the major fraction of the crystallized matrix material is close to the oriented substrate, can be observed. Such an opportunity is offered by the X-ray radiation from synchrotron because of the extremely high intensity (by a factor of 1,000 in comparison to the common X-ray sources), so that the possibility to follow the structural changes in real time is possible. As a matter of fact, this possibility was used recently on the system poly(ethylene terephthalate) (PET) melt blended with polyamide 12 (PA12) and cold drawn via necking [4] as well as the blends PET/polypropylene (PET/PP) and polyamide 66/PP (PA66/PP) [5]. It was found that the extruded and cold drawn bristles of the blends show well expressed texture on the wide-angle X-ray scattering (WAXS) pattern taken with X-rays from synchrotron source. The two blend components are oriented in the same direction, namely the drawing one (FA) [4–5]. The next step is melting of the low-melting component (PA12 or PP, respectively) at 220°C, where the WAXS pattern indicates only a completely isotropic amorphous halo coexisting with the PET reflections remaining unchanged. The subsequent non-isothermal crystallization during the cooling to room temperature leads to texture that does not preserve its original orientation, that is, parallel to the FA but becomes perpendicular to it (for PA12 [4]) or tilted by approximately 40° (for PP [5]). Thus, there is a process of transcrystallization with drastic reorientation.

Another peculiarity of the system PET/PA12 is that further increase of the degree of crystallinity of PA12 (through additional isothermal crystallization for certain time during the cooling) results in reducing of the observed effect due to the masking from the increasing isotropic crystalline mass in the bulk [4], as proven also for PET/PP with various compositions [6]. It seems important to recall here that the reported transcrystallization with reorientation takes place on substrate being highly crystalline microfibrils of PET, which has been documented by means of scanning electron microscopy [7].

Speaking about the chain orrientation in trancrystalline layers it seems noteworthy that studying the interfacial interaction between Kevlar filaments and polyamide 6 (PA6) matrix crystallized from the melt, two kinds of transcrystalline zones were observed around the filament surface [8]. It was confirmed by polarizing light microscopy, microbeam X-ray diffraction, and transmission electron microscopy that the PA6 chains crystallize epitaxially. The a^* and a axes of PA6 are directed along the radius of the Kevlar filament in the interfacial and intermediate zones, respectively. The b^* axis (molecular axis) and the c axis rotate around the a^* or a axis [8].

In a more recent study [9] on aramid and carbon fiber–reinforced PA66 composites, atomic force microscopy reveals radial regularity in the transcrystalline layers, 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.

Summarizing this brief review it should be stressed that there is no report (except the authors' own data on PET/PA12 [4], PET/PP [5–6] as well as PA66/PP [5]) dealing with the chain orientation in the transcrystalline layers for the case when starting from uniaxially oriented blends and composites and particularly when the chains in these layers are placed perpendicularly or tilted in respect to the initial FA direction after melting and second crystallization of the lower melting component. As a matter of fact, these blends represent nanostructured polymer composites (NPC) [7,10–13] where the polymer matrix is reinforced by polymer nanostructures of microfibrillar type. In contrast to the common glass-fiber reinforced composites when the polymer is melt-blended with fibers, the NPC are prepared by melt-blending of two components (distinguished by different melting temperatures), followed by cold drawing of the blend, aiming at a good orientation. The most essential step of the NPC manufacturing (after the orientational drawing) is the thermal treatment of the oriented blend at temperature between the melting temperatures of the two blend components. This treatment results in melting of the lower-melting component and subsequently in its isotropization. During the subsequent cooling, this component crystallizes, but not in the oriented state any more as proved by WAXS tests [10,13]. In this way, after isotropization of one of the blend components and preserving the microfibrillar nanostructure of the higher melting component, NPC is produced.

Very recently [14] the authors reported that polyethylene (PE) in contrast to PP does not show tendency for reorientation during transcrystallization of drawn and annealed PET/PE blend. The samples studied were again cold drawn bristles (diameter of 1 mm), but in contrast to the blends described earlier they were subjected additionally to compression molding at 215°C in order to prepare strip like prepregs (ca. 3 mm wide and 0.25 mm thick films). Because such a treatment far more than the melting temperature of PE can result in substantial disorientation (as observed by WAXS), it looked attractive to perform WAXS studies by means of synchrotron radiation in the same way as for the rest of the blends [4–6], that is, using drawn bristles and taking scattering patterns from the very first stages of crystallization after melting of PE or at least as soon as possible after cooling the partially molten PET/PE blend. In this way the question can be answered if the isointensity reflections observed after compression molding [14] are not a result of masking effect as indicated for the system PET/PA12 [4] and proven for PET/PP blend [6]. In fact, this is the goal of the present study.

EXPERIMENTAL

Commercial, engineering grade PET (Yambolen, Bulgaria) and PE (Burgas, Bulgaria) were dried at 100°C for 24 h. The blend (50/50 by wt.) was prepared by extrusion in a Brabender single screw (30 mm diameter) extruder with a length-to-diameter ratio of 25 at 30–35 rpm.

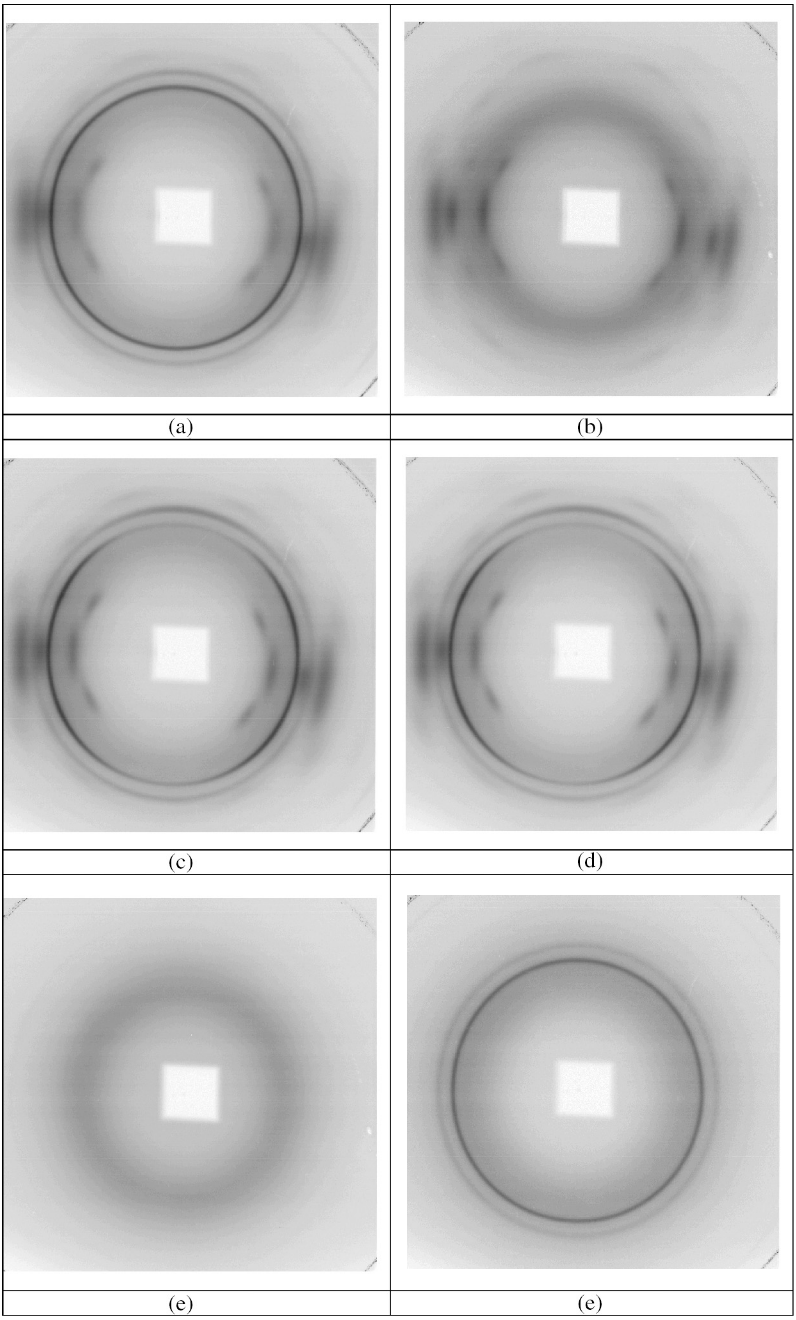
The temperature zones starting from the feed to the die were set at 210, 240, 270, 280, and finally 240°C at the die. The extrudate from a 2 mm capillary die was immediately quenched in a water bath at 15 to 18°C. The bristles were moved trough the bath by means of two rotating rubber cylinders (60 mm diameter) at a rate of about 90 rpm. Thereafter the blend was drawn in a tensile testing machine Zwick 1464 at room temperature and a strain rate of 80 mm/min to a draw ratio $\lambda = 3.6-4.0$, which resulted in a final diameter of about 1 mm, followed by annealing with fixed ends at 120°C for 6 h in a vacuum oven.

WAXS patterns were obtained from the described samples using synchrotron radiation generated at the beamline A2 of HASYLAB in Hamburg, Germany. The sample-to-detector distance was set to 150 mm. Diffraction patterns were registered by means of a 2D image-plate detector. The exposure time was between 10 and 30 s. WAXS images were taken at room temperature, at 160°C when PE is in a completely molten state and again at room temperature after subsequent cooling with a cooling rate of 50°C/min. At these conditions, similarly to the other blends [4–6], transcrystallization with reorientation of PE was observed.

RESULTS AND DISCUSSION

Figure 1 presents selected WAXS patterns taken from synchrotron source after different sample treatment. Figure 1a corresponds to the starting material, that is, melt blended, cold drawn, and annealed at 120°C for 6 h with fixed ends PET/PE (50/50 by wt.) blend. Two completely different types of scattering patterns can be observed. In accordance with expectation, PET shows a pattern typical for highly drawn crystalline polymer with arc-like reflexes. This is not surprising because after the cold drawing the blend experienced only annealing far below the melting temperature of PET ($T_m = 255°C$ according to the differential scanning calorimetry (DSC) measurement) where only crystallization of the drawn material can take place.

Contrary to the pattern arising from PET, PE shows almost a complete isotropic crystalline structure although before annealing at 120°C it has also been in a drawn state. Because this temperature is around the melting intervals of various PE types, it can be assumed that during annealing the sample melts and thus transforms in a completely isotropic state during the relatively long annealing time (6 h). In order to check this assumption the T_m of the PE used was determined by means of DSC. T_m was found to be 104°C for the sample presenting non-drawn, non-annealed melt-blended PET/PE (50/50 by


(a)
(b)
(c)
(d)
(e)
(e)

wt.). This result as well as a previous observation [15] that at least 4 h are required for complete isotropization of PE in PET/PE (50/50 by wt.) blend during annealing at 180°C, allows one to conclude that in the present case (Figure 1a) isotropization of the molten at 120°C PE takes place, too. For this reason during the subsequent cooling to room temperature the sample crystallizes in isotropic state, as demonstrated in Figure 1a.

If the isotropically crystallized sample (Figure 1a) is heated up to 160°C and after 1 min a WAXS pattern is taken at this temperature, the result is that shown in Figure 1b. Again PET preserves its highly oriented state, but PE shows only isotropic amorphous halo because the annealing temperature $T_a = 160°C$ is much above $T_m = 104°C$ of PE.

The most surprising result is when the PE molten at 160°C is cooled down to room temperature at a rate of 50°C/min and a scattering pattern is taken immediately at room temperature (Figure 1c). The two PE reflexes are not in the shape of isointensity circles any more (Figure 1a) but present relatively long arcs. This fact indicates that PE crystallites that have been created during the cooling are not randomly distributed.

The same scattering patterns as those in Figure 1b and 1c are observed if the melt annealing is expanded up to 60 or 200 min and thereafter the sample is cooled down to room temperature where WAXS pattern is taken. At high temperature PE is in an isotropic molten state (Figure 1b) and thereafter at room temperature PE shows a tendency to crystallize in an oriented state.

In a previous work [14] the authors showed that in the WAXS pattern of the present blend after extrusion and drawing, the PE reflexes (110) (inner) and (200) (outer) are situated on the equator thus indicating fiber [001] texture. This type of orientation is well known and fully described by crystallites, oriented with the *c*-axis along FA and randomly oriented in all other directions lying in the plane perpendicular to FA. A thorough inspection of Figure 1d shows that the PE reflexes can be considered as a sum of two sets of reflexes: (1) The usual set of reflexes, described earlier, where the PE reflexes (110)

◀

FIGURE 1 Wide-angle X-ray scattering patterns of melt blended cold drawn and annealed for 6 h at 120°C PET/PE sample (50/50 by wt.): (a) initial sample, image taken at room temperature; (b) after 1 min at 160°C, image taken at 160°C; (c) after 1 min at 160°C, image taken at 30°C; (d) after 200 min at 160°C, image taken at 30°C; (e) after 5 min at 280°C, image taken at 280°C; and (f) after 5 min at 280°C, image taken at 30°C. FA is vertical and lies in the plane of the sheet.

(inner) and (200) (outer) are of equatorial type and 2) another set of reflexes, where the reflexes (110) are situated on the equator and (200)—on the meridian.

The authors tried to find the indexes of the new PE texture and assumed that it is [100]. Following Cullity [16] and accepting the following orthorhombic unit cell parameters of PE: $a = 7.417$, $b = 4.945$, $c = 2.547$ Å [17], the authors calculated the angles between several low-indexes planes. Subsequently, they compared these angles with the measured ones, having in mind that some PE reflexes can be close to each other and may mutually superimpose or be superimposed by strong PET reflexes and thus their position can vary in some limits. Thus, the assumed PE texture [100] led to angles $\alpha = 0°$ for (200) and $\alpha = 55°$ for (110), where the angle α is measured from the meridian toward the equator. The theoretical value of 55° can also be accepted as the observed one (Figure 1d), namely as a superposition of the closest two (110) PE reflexes (two on left and two on the right), in addition superimposed by the strong equatorial $(\bar{1}10)$ PET reflex. Thus, after 200 min at 160°C and subsequent cooling of the blend to 30°C, PE reveals double [001] + [100] texture.

An alternative explanation is also possible: an assumed additional [710] to the basic [001] PE texture leads to $\alpha = 12°$ for (200) and $\alpha = 43°$ for (110). The observed (110) reflex (Figure 1d) can be obtained as already mentioned as a superposition of the (110) PE and the equatorial $(\bar{1}10)$ PET reflexes. On the other hand, every one of the observed meridional (200) reflexes presents superposition of two (200) PE reflexes, lying at 12° left and right off the meridian. If this explanation is accepted, then the double PE texture (Figure 1d) is [001] + [710]. In fact, the two possible cases of double textures do not differ much because the angle between the planes (100) and (710) (and between their normals, respectively) is only 12°, which is within the limits of the orientation distribution as can be concluded from the length (in degrees) of the azimuthal PE arcs (Figure 1d).

Because after the recrystallization (Figure 1d) the (100) plane is normal to FA and contains the *c*-axis, similarly to the systems PET/PA12 [4], PET/PP [5–6] as well as PA66/PP [5] one deals in the present case with transcrystallization with reorientation with respect to the draw direction (FA). As in other cases, the well-documented PET microfibrils [7,10] play the role of a nucleating agent, similar to various reinforcing fibers [2,8,18] in the 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 parallel any more to the chain direction of PET, as well as to their own orientation direction before annealing (160°C in the present case). To the best of our knowledge such a transcrystallization with reorientation of PE is reported for the first time.

This assumption about the crucial role of PET nanostructures for the crystallization and orientation of the low-melting blend component can be easily checked by heating the blend up to the temperature well above the T_m of PET, followed by cooling down to room temperature in order to allow again a non-isothermal crystallization. Figure 1e shows the WAXS pattern of the PET/PE sample taken at 280°C. Only one isointensity amorphous halo can be seen in Figure 1e, proving that at this temperature the two polymers are in a molten isotropic state.

The situation does not change after cooling down as far as the isotropy is concerned. As can be concluded from the two isointensity circles, belonging to PE, during the relatively rapid cooling PE crystallizes in a completely isotropic state, whereas PET is quenched in an amorphous isotropic state, as demonstrated by the residues of the amorphous halo well expressed in Figure 1f. Such behavior of PET is not surprising because whereas PE is distinguished by the highest crystallization rate among the common polymers, PET belongs to those that crystallize very slowly.

From the last two scattering patterns (Figure 1e and 1f) it is easy to conclude that PET nanostructures of microfibrillar type [7] have a strong epitaxial effect on the orientation during transcrystallization.

An interesting question arises at this point—Why after annealing the PET/PE blend for 6 h at 120°C and cooling down is oriented crystallization not observed (Figure 1a) as in the case when annealing is performed at 160°C? possible reason for this discrepancy in the behaviour of the same system can be the difference in the treatment conditions. At 120°C melting and recrystallization of PE can be expected because T_m of 105°C is measured for not optimally crystallized material (undrawn and unannealed one). If such recrystallization takes place, the new, more perfect crystals will melt above 120°C, that is, a fraction of PE is in the crystalline, possibly isotropic state even at 120°C, which could not be the case with annealing temperature of 160°C. In addition, for the cooling down from 120°C no extra attempts have been undertaken to speed this process as in the second case; the oven was let to cool down for a couple of hours.

The assumption about recrystallization at 120°C was checked by measuring the T_m of PE in the PET/PE blend after this treatment. T_m of 108°C was found for the sample, crystallized for 6 h at 120°C (the initial sample) that excludes this suggestion. Obviously, the difference in the scattering patterns (Figure 1a and Figure 1c, 1d) is related to the drastic difference in the cooling conditions—hours against 3 min. It is quite clear that during the much slower cooling down from 120°C the PE crystallizes to a larger degree, involving the bulk in contrast to the rapid cooling from 160°C where the crystalization is limited mostly to transcrystalline layers.

This additional experiment as well as the basic results (Figure 1a and 1c) prove that PE also shows a tendency to crystallization with reorientation similarly to the other systems [4–6]. This effect can be observed only if it is possible to get information about the orientation by means of WAXS during the very first stages of crystallization, that is, during the transcrystallization and before the crystallization in the bulk progresses. Otherwise the latter masks the scattering pattern arising only from the transcrystalline layers as shown for the PET/PA12 [4] and PET/PP [5–6] systems and observed in the present case (compare Figure 1a with 1c).

In conclusion, by analogy with the previous systems [4–6] the reflections of PE show detectable anisotropy (Figure 1c and 1d), which can be interpreted as an indication that the chains in a part of the crystalline phase are tilted to 90° with respect to the original draw direction and part of them preserve their original orientation (FA) after recrystallization (Figure 1c and 1d). Very early stages of crystallization were followed and a strong epitaxial effect was observed of the nanostructures of microfibrillar type (PET) on the non-isothermal crystallization behavior of PE during its cooling from 160°C to room temperature. Thus, the transcrystalline layers of cold drawn and annealed blends of PET/PE present anisotropic crystalline structures. The PE crystallites of these layers in the PET/PE blend are partially reoriented at 90° with respect to the draw direction.

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