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Transcrystallization with reorientation in drawn PET/PA12 blend as revealed by WAXS from synchrotron radiation

D. SAPOUNDJIEVA, Z. DENCHEV, M. EVSTATIEV, S. FAKIROV
Sofia University, Laboratory on Structure and Properties of Polymers, 1126, Sofia, Bulgaria

N. STRIBECK*
Institut für Technische und Makromolekulare Chemie, Universität Hamburg, 20146 Hamburg, Germany
E-mail: stribeck@vxdesy.desy.de

M. STAMM
Max-Plank-Institut für Polymerforschung, Postfach 3148, 55021 Mainz, Germany

Studying the isotropisation kinetics during melting of a drawn poly(ethylene terephthalate) (PET)/polyamide 12 (PA12) blend (60/40 wt %) at $T_m^{PA12} < T_a < T_m^{PET}$ by means of wide-angle X-ray scattering (WAXS) from synchrotron radiation a transcrystallization behaviour of PA12 was observed. It was also found that the nonisothermal transcrystallization behaviour of PA12 taking place during cooling down of the molten PA12 is characterized by reorientation of PA12 chain axis by 90° with respect of PET chains axis and of the starting chains axis direction as concluded from the WAXS patterns. A conclusion is drawn that PET microfibrils are not only effective nuclei for transcrystallization of the matrix but they cause a drastic reorientation of the matrix chains placing them perpendicular to the initial common for both PET and PA12 orientation direction. © *1999 Kluwer Academic Publishers*

1. Introduction

Blending two or more crystallizable polymers presumes good knowledge of the crystallization behaviour of the blend components. This behaviour determines to a great extent the processing and performing properties of the blend. Different cases of mutual influence between complete inhibition to strong promotion are known [1].

A special case of crystallization in such blends as short-fibre reinforced polymer composites is the transcrystallization [2]. It takes place when heterogeneous nucleation occurs with sufficiently high density along a fibre surface and the resulting crystal growth is restricted to the lateral direction, so that a columnar layer develops around the fibre. This nucleation of a transcrystallized region around the reinforcing fibre is thought to be central to the improvement of some composite properties [3]. The transcrystallization is a function of nucleating activity of the fibre surface and crystallization kinetics of the resin matrix.

A literature survey [4] shows that the fibre surface tends to induce nucleation of matrix under the following conditions: (i) a topographical match between the fibre and the matrix; (ii) a thermal conductivity mismatch between the fibre and the matrix; (iii) an extensional flow field developed by processing conditions, or (iv) a high surface free energy on the fibre.

Depending on the mechanism involved, different cases for the mutual arrangement of the polymer chains in the reinforced fibres and the surrounding matrix are reported. For instance, in cellulose/polypropylene (PP) composites the chains of PP are parallel to the fibre axis (F.A.) [5]. The same case dominates in some advanced polymer composites based on PEKK and PEEK reinforced by carbon, Kevlar or glass fibres [4].

In a detailed study on interfacial interaction between Kevlar filament and a polyamide 6 (PA6) matrix crystallized from the melt two kinds of transcrystalline zones were observed around the filament surface [6]. It was confirmed from polarizing light microscopy, microbeam X-ray diffraction, and transmission electron microscopy that PA6 molecular 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 c-axis rotate around the a^*- or a-axis [6].

In a more recent study [7] on aramid and carbon fibre reinforced PA66 composites, atomic force microscopy reveals radial regularity in the transcrystalline layer relative to the fibre, and X-ray diffraction investigations of the isolated layer suggest that the polymer chain is orientated predominantly perpendicular to the fibre axis.

Summarizing this brief review it should be stressed that there is no report dealing with the chains orientation

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* Author to whom all correspondence should be addressed.

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in the transcrystallizable materials for the case when one starts from uniaxially orientated blends and composites and particularly when the chains are placed perpendicular to the initial fibre axis direction.

Considering the transcrystallization phenomenon in polymer composites it should be recalled that a new type of polymer-polymer composite was developed recently [8–10], where the polymer matrix is reinforced by polymer microfibrils. In contrast to the common glass-fibre reinforced composites when the polymer is melt-blended with the fibres, microfibrillar reinforced composites (MFC) are prepared by melt blending of two components (distinguished by different melting temperatures T_m) followed by cold drawing of the blend aiming at a good orientation. The most essential step of the MFC manufacturing (after orientational drawing) is the thermal treatment of the oriented blend at temperatures being between the T_m of the two blend components. This treatment results in melting of the lower melting component and subsequently in its isotropisation. During the following cooling period this component crystallizes, but not any more in oriented state. In this way, after isotropisation of one of the blend components and preserving the microfibrillar structure of the higher melting component one is able to produce a MFC.

Because of the importance of this essential stage in the MFC manufacturing, it was of interest to follow the isotropisation kinetics by means of wide-angle X-ray scattering (WAXS) provided the low-melting component is a crystallizable one, and also to check to what extent the transcrystallization phenomenon is valid for this type of polymer-polymer composite. This was done using a synchrotron radiation source and a quite unusual process was observed when the transcrystallization takes place, namely a reorientation of the chain axis perpendicular to the initial direction. These results are briefly reported in the present short paper.

2. Experimental

Commercial poly(ethylene terephtalate) (PET) and polyamide 12 (PA12) were melt blended in a mini extruder at 280 °C and thereafter extruded as bristle with a diameter of 2 mm. The cold drawing of the bristles was performed using a Zwick 1614 machine at 25 mm/min up to a draw ratio $\lambda = 3.8$ to 4 (via necking). The stretched bristles were subsequently annealed with fixed ends in vacuum at $T_a = 220$ °C for 12 and for 24 h, respectively. The sample designation and the treatment conditions of the neat homopolymers and of the PET/PA12 blend (60/40 wt %) are given in Table I.

2.1. WAXS measurements

Wide-angle X-ray scattering patterns were obtained from the described samples using synchrotron radiation generated at the beamline A2 of the synchrotron in Hamburg, Germany. The sample-to-detector distance was set to 90 mm. Diffraction patterns were registered by means of a 2D image-plate detector. The exposure time was between 10 and 30 s. An area of 900 × 900 pixels, each with a size of 176 × 165 μm, was read out and used for the evaluation. Using *pv-wave* [11, 12] data were reduced by averaging over four adjacent pixels and masking of irrelevant regions. Images were resampled in order to obtain square pixels of 176 μm edge length, aligned, averaged over four quadrants and a 5 × 5 median filter was applied. It was checked that no step induced blurring of observable details.

TABLE I Sample designation and treatment conditions of neat homopolymers PET and PA12 as well as their blend (60/40 wt %)

Sample designation	As extruded	Cold drawing	Annealing temperature T_a (°C)	Annealing time t_a(h)
PET	+	+	220	12
PA12	+	+	130	1
AE	+	−	−	−
CD	+	+	−	−
220-12	+	+	220	12
220-24	+	+	220	24

3. Results

In Fig. 1 are presented the WAXS patterns taken at room temperature, using synchrotron radiation from drawn and annealed neat homopolymers PET and PA12 (Fig. 1a and b, respectively), as well as from their 60/40 wt % blend after extrusion (Fig. 1c), after cold drawing (Fig. 1d), and finally after drawing and annealing at 220 °C for 12 h (Fig. 1e) as well as for 24 h (Fig. 1f).

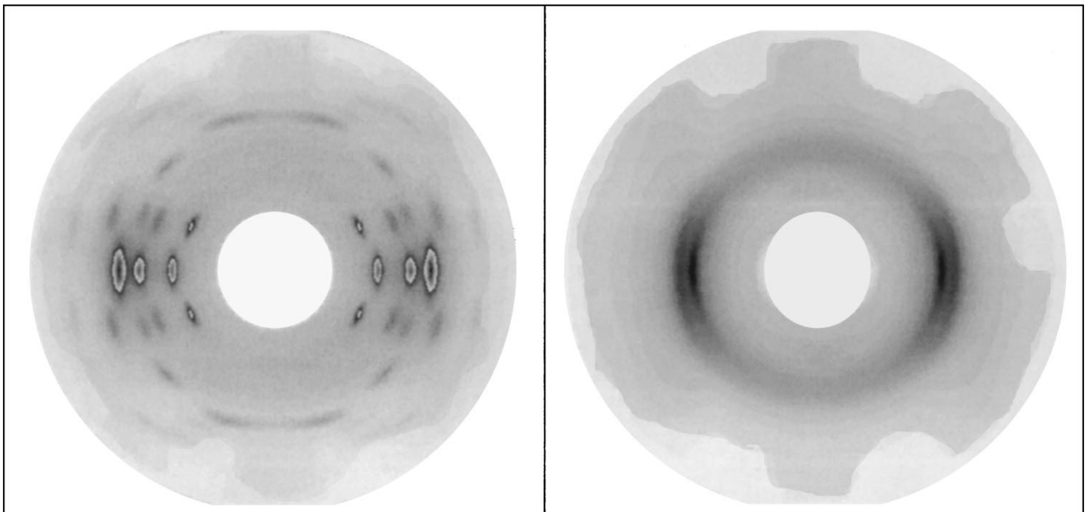
The well known pattern of the highly oriented crystalline polymers for the neat homopolymers PET and PA12 is observed (Fig. 1a and b, respectively). As expected, the typical texture pattern is much better expressed for the case of PET because of the more favourable crystallization conditions (see Table I).

It is important to note here that the orientation direction, i.e., the fibre axis (F.A.) is vertical being in the plane of the picture. This detail is significant for the interpretation of the subsequent WAXS patterns of the blend PET/PA12.

In Fig. 1c the WAXS pattern of the as extruded PET/PA12 blend is shown. There is no observable tendency of an uniaxial orientation of both the components in contrast to the case of the next stage of MFC manufacturing. After cold drawing one observes a very clear indication of orientation (Fig. 1d). Both components of the blend, the PET and the PA12, are oriented in the same direction, i.e., their chain axes are parallel being placed in the F.A. direction. In addition, in Fig. 1d one can see that the crystallinity of the two blend components is very poor.

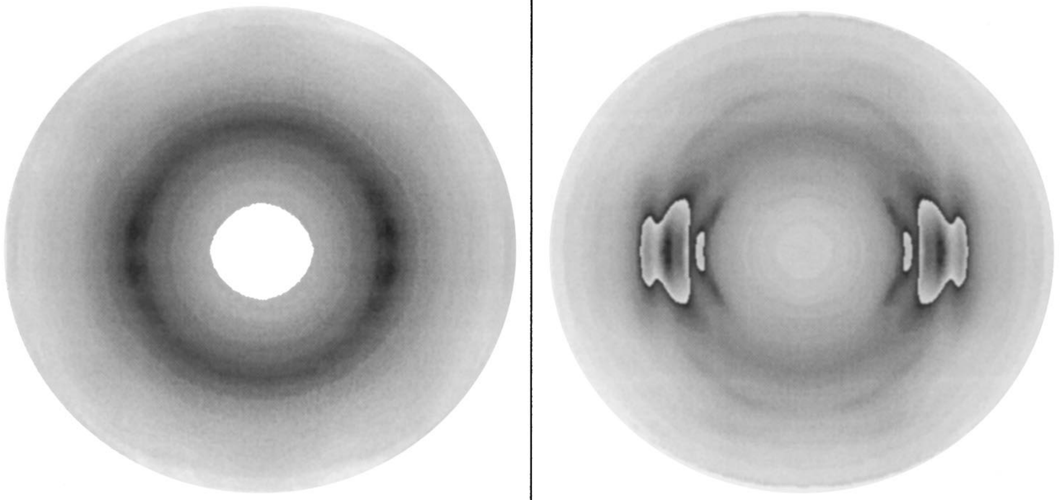
The situation changes drastically when the drawn PET/PA12 blend is subject to annealing at 220 °C for different durations (Fig. 1e and f). These changes concern primarily the crystallinity development. Proofs for highly oriented rather crystalline state, particularly for the case of PET, can be seen on these two pictures being comparable with those for the neat PET treated at the same conditions (Fig. 1a, Table I).

Quite different is the situation with the PA12 component. Two peculiarities can be observed: (i) its scattering



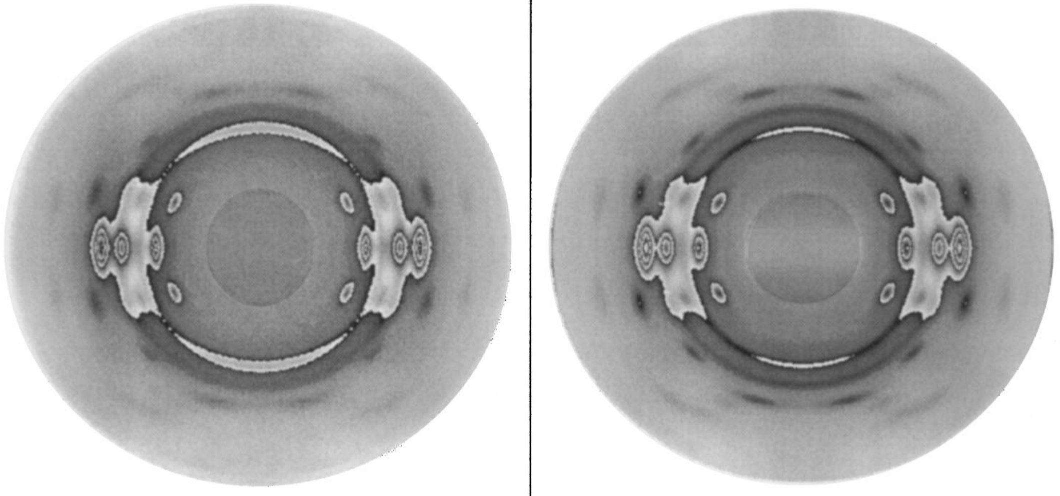
(a) PET — drawn and annealed

(b) PA12 — drawn and annealed



(c) AE — PET/PA12 as extruded

(d) CD — PET/PA12 cold drawn



(e) 220–12 — annealed 12 h

(f) 220–24 — annealed 24 h

Figure 1 WAXS patterns taken with synchrotron radiation from: (a) drawn and annealed neat PET; (b) drawn and annealed neat PA12; (c) PET/PA12 as extruded (AE); (d) PET/PA12 cold drawn (CD); (e) PET/PA12 annealed at $T_a = 220\,^\circ\mathrm{C}$ for 12 h (220-12); (f) PET/PA12 annealed at $T_a = 220\,^\circ\mathrm{C}$ for 24 h (220-24) (for more details concerning sample preparation see Table I). In every subfigure the fibre axis of the material is vertical. Visualisation is performed using a repeated gray scale. Thus high intensity peaks appear as if presented in a contour plot.

pattern is closer to that of crystalline polymers being in anisotropic state, and (ii) is some orientation is observed it is in a direction perpendicular to the starting one displayed in Fig. 1b and d.

4. Discussion

The observation that PA12 does not crystallize any more in oriented state after thermal treatment of the drawn blend at 220 °C is not surprising. Let us recall that the melting temperature of PA12 is $T_\mathrm{m} = 183$ °C (compared to 265 °C for PET). This means that during the thermal treatment at 220 °C PA12 was in a molten state and its crystallization takes place only during the subsequent cooling down to room temperature of the blend. Actually, this is the purpose of such a thermal treatment at $T_\mathrm{m}^\mathrm{PA12} < T_\mathrm{a} < T_\mathrm{m}^\mathrm{PET}$ in order to transform the PA12 component into an isotropic state and in this way to produce a MFC. Such an isotropisation is well documented for other crystallizable polymers as PA6 and poly(buthylene terephthalate) (PBT), in blend combinations as PET/PA6 [8], PET/PBT [8] and PET/PA6/PBT [8, 10]. In all these cases the low melting component after melting crystallizes in a completely isotropic state as can be concluded from its circular iso-intensity WAXS reflections [8–10].

The same situation was expected also in the case of the PET/PA12 blend after thermal treatment above T_m of PA12. The careful inspection of the WAXS patterns after melting, displayed in Fig. 1 shows, in addition to the dominating tendency to isotropisation (compare Fig. 1b with Fig. 1e and f) also a slight tendency to orientation (Fig. 1e and f).

What is striking in this case is the fact that the orientation is completely different from the starting one (compare Fig. 1b with Fig. 1e and f). One should expect that after melting of PA12 at 220 °C it will crystallize in a completely isotropic state, similarly to the case of PA6 and PBT [8–10] or if oriented—the chain axis should be placed parallel to those of the oriented PET as reported for other [3–5] and PA6-matrix [6] systems. Fig. 1e and f show that this is not the case—the main chain direction in the crystallites of PA12 is placed perpendicular to the initial orientation direction, i.e., it is perpendicular to the main chain direction of PET molecules in the microfibrils. In other words, after melting of PA12 the subsequent crystallization takes place with reorientation of the chain axis.

5. Conclusions

A quite unusual situation is observed in a drawn PET/PA12 blend (60/40 wt %) when after melting of PA12 at a temperature below (20–25 °C) the melting temperature T_m of PET the subsequent crystallization during cooling takes place with drastic (up to 90° with respect to the initial chain orientation) reorientation of the PA12 chains.

Obviously, one deals with transcrystallization when the well documented PET microfibrils [8–10] play the role of a nucleating agent similarly to the glass and other reinforcing fibres [3, 4, 6] in the common composites. The significant difference between the two cases—the classical composites and the MFC—is that in the second case the PET microfibrils do not only favour the crystallization, but they also affect the orientation of the matrix chains during the transcrystallization in such a way that they are placed perpendicular to the chains direction of PET, i.e., perpendicular also to their own orientation direction before melting. To the best of our knowledge such a transcrystallization with reorientation is reported for the first time.

More detailed investigation of this interesting observation, including the a more detailed texture analysis, a study of the effect of blend ratios, the chemical composition of the blend, thermal treatment conditions, etc. is in progress.

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