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Strain-induced polymorphic transition in PBT and PBT/PEE blend as revealed by synchrotron radiation

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Poly(butylene terephthalate) (PBT) became the subject of main interest in the mid-1970s when several groups reported that it could crystallize in two polymorphic forms (see e.g. [1]). The α-form exists in a relaxed state whereas the β-form could only be found when the sample is under strain. Recently, the microhardness technique was used to follow this transition in homo-PBT [2] and its blends with poly(ether ester), the later being a copolymer of PBT and poly(ethylene glycol). For the blend a two-step transition was found at relative deformations $\varepsilon = 8$–10% and $\varepsilon = 25$–30% [3]. They were ascribed to the existence of two species of crystallites, differing in origin and perfection, coexisting in the sample. This assumption was proved by annealing of drawn blend samples at temperature between the melting temperatures of the two species of PBT crystallites. After cooling, one observes at the WAXS pattern PBT crystallites in isotropic state (arising from the low-melting population belonging to the copolymer) and highly oriented crystallites (arising from the homo-PBT). To the best of our knowledge there is no other report about the coexistence of two species of PBT crystallites in PBT/PEE blend being in isotropic and an oriented state in the same time [4].

WAXS is a common technique for observing polymorphic transitions. For this reason we decided to use the opportunity offered by the synchrotron for following minor changes in the WAXS patterns during the polymorphic $\alpha \rightarrow \beta$ transition in PBT and thus expecting to visualize the already observed by microhardness measurements two-step polymorphic transition in the PBT crystallites of a PBT/PEE blend.

Bristles from the blend were prepared by the following procedure. PBT (Celanex, Celanese Corp., USA) and a poly(ether ester) (PEE) thermoplastic elastomer (Arnitel EM 550, DSM, Holland), a copolymer of PBT as hard segments and poly(tetrahydrofuran) as soft segments, were cooled in liquid nitrogen and ground finely. The powder was dried for 6 h at 80 °C in vacuum. Blend of PBT/PEE in a ratio of 80/20 wt% was obtained and together with dry powder of neat PBT was subsequently used for preparation of bristles. They were prepared in a melt index instrument [4]. After the extrusion the bristles were drawn to $\lambda = 3.5$ at a draw rate of 5 mm/min and annealed for 6 h at 200 °C with fixed ends in a vacuum oven.

WAXS patterns were obtained from these bristles using synchrotron radiation generated at the beamline A2 of HASYLAB in Hamburg, Germany. The diffraction patterns were registered by means of a 2D image-plate detector. The sample-to-detector distance was set to 82 mm. The exposure time was between 10 and 30 s. An area of 900×900 pixels, each with a size of $176 \times 176\ \mu$m, was read out and used for data evaluation. A specially designed stretching machine which was mounted in the X-ray beam pathway allowed controlled elongation of the polymer bristles. Here and hereafter ε is defined as

$$\varepsilon = 100(l - l_0)/l_0 \qquad (1)$$

where l_0 and l are the initial and the actual polymer length of the bristle, respectively, as measured between two marks placed close to the irradiated zone of the polymer bristle. After increasing the strain to the next step a diffraction pattern was recorded under stress. Then, the polymer bristle was released, the detector plate was exchanged and the corresponding pattern in the relaxed state was taken followed by the next measurement under stress at higher deformation.

In order to evaluate the presence or absence of the α- and β-form, the position of the near meridional (-104) reflex on the WAXS image was considered. On the basis of the crystalline data of the two forms [2] it may be easily calculated that reflex is situated at $2\theta = 30.45$ deg for the α- and at 27.42 deg for the β-form and a wavelength $\lambda = 1.5$ Å of the synchrotron radiation used. Since the normal to the lattice plane (-104) makes an angle of 9 deg with the chain axis [3], the bristle was tilted toward the image plate to approx. 7 deg in order to register the (-104) reflex. From the position of this reflex at every elongation a conclusion was drawn about the existence of a certain crystalline form (or both forms if this reflex is split).

In Fig. 1 are shown the WAXS patterns of the homo-PBT and the blend at various deformations, both samples cold drawn up to 3.5 x.

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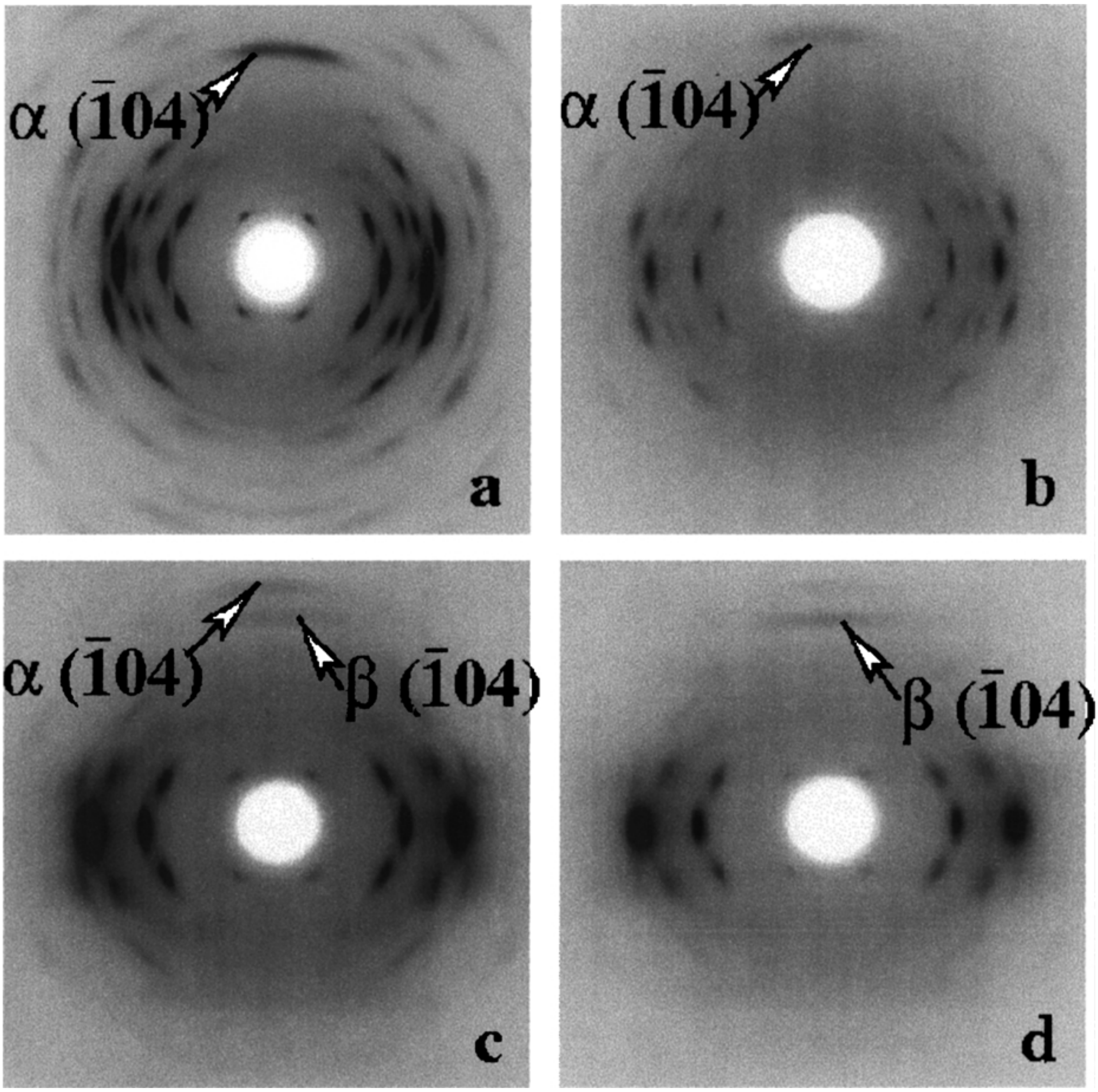

Figure 1 WAXS patterns of the drawn homo-PBT and the drawn blend at various deformations: (a) PBT at $\varepsilon = 0$; (b) blend at $\varepsilon = 0$; (c) blend at $\varepsilon = 10\%$ and (d) blend at $\varepsilon = 27\%$.

Fig. 1a shows the pattern of the oriented PBT at $\varepsilon = 0$. As demonstrated the angular position of the transition sensitive reflection (−104) shifts from 30.45 to 27.42 deg 2θ after the $\alpha \rightarrow \beta$ transition (the X-ray wavelength $\lambda = 1.5$ Å) [5, 6]. Since in the present case the (−104) reflex is situated at the larger angle one can conclude, in accordance with expectation, that the PBT crystallites are in α-form.

Fig. 1b shows the pattern of the oriented blend at $\varepsilon = 0$. Again one observes (−104) in position typical for the α-form.

The situation is completely different when WAXS pattern is taken from the same blend (Fig. 1b) but at $\varepsilon = 10\%$, where the (−104) reflex splits to two reflexes (Fig. 1c). The outer one preserves its position (as in Fig. 1a and b) whereas an inner one appears at $2\theta = 27.42$ deg. Having in mind the results of the microhardness measurements [3] where it was demonstrated that in this deformation interval the polymorphic transition takes place in the crystallites arising only from homo-PBT, whereas those from PEE remain unaffected, these results (Fig. 1c) shown that in the blend sample two populations of crystallites coexist. What is more, when the blend sample is strained ($\varepsilon = 10\%$) the two species of PBT crystallites are even presented in two different polymorphic modifications: these arising from the homo-PBT are in β-form and the others, arising from the PEE-in α-form.

Finally, Fig. 1d displays the WAXS patterns of the same blend taken at $\varepsilon = 27\%$. One sees the strong (−104) reflex of the β-form whereas the (−104) reflex of the α-form is only slightly indicated. Thus, at this relatively high deformation the crystallites arising from the PEE also undergo $\alpha \rightarrow \beta$ transition and in this way almost all crystallites in the blend are transformed in the β-form.

It can be concluded from the study of the strain-induced polymorphic transition by WAXS from synchrotron that in the PBT/PEE blend two populations of PBT crystallites coexist differing mainly in their origin, i.e. there is no complete cocrystallization as assumed earlier [4].

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