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Structural investigation of the phase transformation in the plastic zone of a β-phase isotactic polypropylene by synchrotron radiation microdiffraction

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Abstract

X-ray microdiffraction with synchrotron radiation has been used to investigate the strain-induced crystalline modification transition in the plastic zone of a β-phase isotactic polypropylene (β-iPP). It was shown that the bulk β-iPP was gradually transformed into highly oriented, conformationally disordered (condis structure) α-phase iPP as the strain increased.

Keywords: Phase transformation toughening; Polypropylene; Synchrotron radiation microdiffraction

1. Introduction

The concept of phase transformation toughening has recently been applied to β-phase isotactic polypropylene (β-iPP) [1]. The improvement of mechanical properties during mechanical loading of β-iPP has been explained by the transition from β- to α-crystalline iPP (α-iPP), based principally on differential scanning calorimetry d.s.c. experiments [1–3]. The α/β-phase ratio was reported to depend on the magnitude of the strain [1–4] and should therefore vary across the plastic zone of a specimen with locally different strain magnitude. Experiments reported in this paper are aimed at establishing the structural basis for this assumption by a synchrotron radiation microdiffraction experiment.

2. Experimental

2.1. Materials preparation

β-iPP was produced by a selective nucleant and the plastic zone studied was created by static tensile loading of a deeply double-edge-notched (DDEN-T) specimen [1,3]. The thickness of the plastic zone varied between less than 0.1 mm (centre edge of the stress-whitened plastic zone) and ≈ 1 mm (bulk). A schematic picture of the fractured DDEN-T specimen used for the present study is shown in Fig. 1(a). A real specimen is shown elsewhere [3].

2.2. Microdiffraction

Experiments were performed at the European Synchrotron Radiation Facility (ESRF) microfocus beamline (ID13) using a wavelength of $\lambda = 0.078$ nm [5,6]. The beam size at the exit of a tapered glass capillary was about 4 μm full width at half maximum (FWHM). The sample was placed on a *x*/*y* translation stage and linearly scanned from the tip (centre of the process zone) into the bulk. Wide-angle X-ray scattering (WAXS) patterns were recorded with an image intensified Photonic Science LA CCD camera (90 mm converter screen diameter) at every 30 μm length. Data were digizited at video frequency and accumulated for 1 s per pattern. WAXS patterns obtained were practically undistorted. Data analysis was performed with the FIT2D program [7]. Small-angle X-ray scattering (SAXS) patterns were recorded for a 4 μm FWHM beam with an older generation Photonic Science LA CCD camera (110 mm entrance window) [8]. The lower limit in s ($s = 2\sin\Theta/\lambda$) was $s_{min} \approx 0.05$ nm^{-1}.

3. Results and discussion

Fig. 1(b) shows a series of selected WAXS patterns obtained at distances of 0.9 mm. All patterns have been

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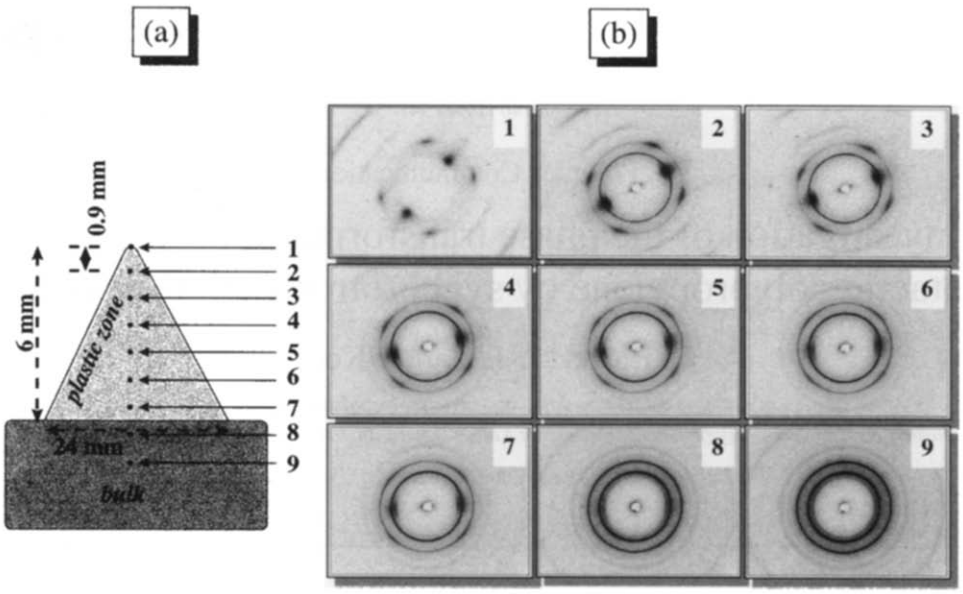

Fig. 1. (a) Schematic picture of the stress-whitened plastic zone of a DDEN-T specimen of β-iPP. The recording position of the WAXS patterns (1–9) are shown. Position 1 corresponds to the centre of the process zone. (b) WAXS patterns recorded at positions 1–9. Accumulation time per WAXS pattern is 1 s.

corrected for background by subtracting a pattern recorded without sample.

D.s.c. experiments taken from the plastic zone suggest the presence of α-phase [1–3]. The present data do not, however, show in the plastic zone the characteristic α-iPP reflections [9] but rather a disordered α-phase with a characteristic broad equatorial reflection (equator: $d \approx 0.59$ nm; first layer line: $d \approx 0.42$ nm). This phase has been originally described as a smectic phase [10] but more recently as a conformationally disordered (condis iPP, co-iPP) structure in view of the lack of a mesogen unit [11]. In the following the condis structure classification will be used.

At the very tip, i.e. the centre edge of the plastic zone (which can be considered as the process zone [1,3]; point 1) only the highly oriented fibre diffraction pattern of co-iPP is observed. There is no evidence for an additional amorphous phase at this point. It should be noted that well separated equatorial reflections of the α-phase [9,12] were not observed throughout the scan. Slight intensity fluctuations of the equatorial co-iPP reflection profile suggest at most a small fraction of α-iPP phase.

The pattern obtained at position 2 shows the co-iPP reflections plus the two strongest Debye–Scherrer rings of β-iPP [13–18] (2-10: 0.55 nm and 2-11: 0.42 nm; indexing corresponds to the simplest trigonal $P3_121$ cell [17]). This phase is associated with an amorphous halo indicating its semicrystalline nature. The two rings are only weakly textured. There is also evidence for central scattering (see below).

The fibre diffraction pattern of co-iPP rotates and disappears gradually as the bulk is approached while the β-iPP pattern gets stronger (Fig. 1(b)). Fig. 2(a–c) shows WAXS patterns recorded at the centre of the process zone and in the bulk. For comparison the major peak positions of co-iPP [19], α-iPP [9] and β-iPP [17] are shown. The co-iPP reflections are very broad and overlapping and have not been indexed.

The increase of β-iPP volume fraction from the centre of the edge of the process zone to the bulk has been determined by integrating the β-iPP (2-10) reflection and normalizing it to the background scattering derived from an area of the pattern which is free of reflections. This corresponds to a normalization to constant sample thickness. The result, shown in Fig. 3(a), suggests a rapid increase of β-phase fraction within about the first millimetre from the fracture plane or process zone, followed by a linear increase towards the bulk. As only co-iPP and β-iPP are present, the change in co-iPP volume fraction is assumed to be the inverse of the β-iPP volume fraction.

The formation of highly oriented co-iPP is assumed to be related to the local plastic deformation [1–4]. Drawing experiments on oriented lamellae of the β-phase in plate specimens show the formation of α-phase with *c*-axis orientation at high draw ratios ($\lambda \approx 5$) [20]. The α-phase formation is assumed to be associated with a melting/recrystallization process. Such a process has also been proposed for the plastic deformation process [4,21]. The rotation of the co-iPP pattern seems to follow a first-order exponential decay (Fig. 3(b)). The physical origin of this rotation might be due to an instability in the crack growth prior to final fracture [1]. This could be associated with an offset deformation of the decreased ligament area and yields some offset orientation. We also note that the rotation of the co-iPP pattern and the change of β-iPP concentration are not well correlated as the volume fraction of the β-phase increases more rapidly within the first millimetre from the centre of the process zone and then levels off (Fig. 2(a)). As already indicated, the local β-iPP volume fraction has been

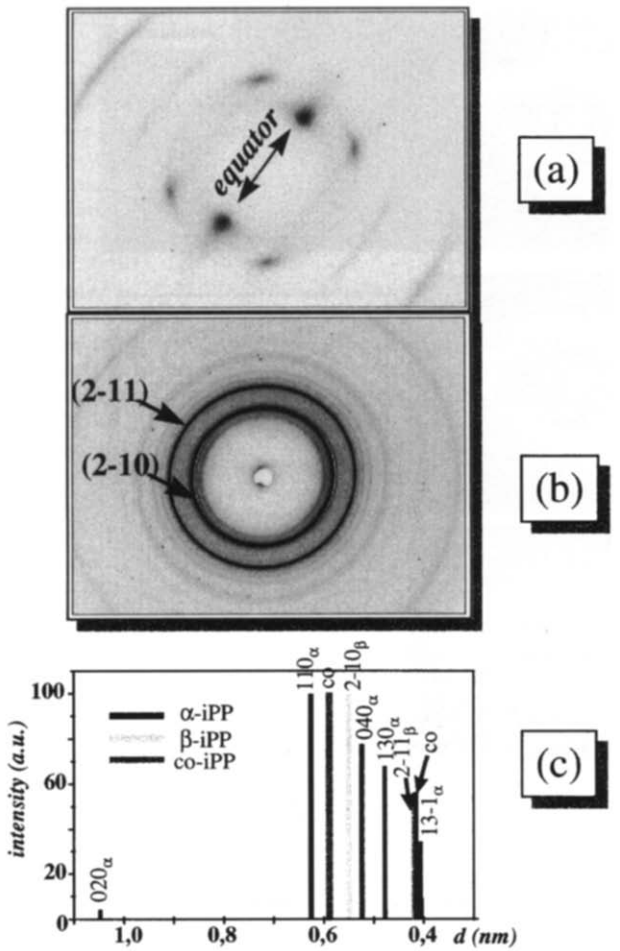

Fig. 2. WAXS pattern of (a) co-iPP recorded at centre of process zone and (b) β-iPP recorded in bulk zone together with Millers indices of strongest reflections. (c) Main peak positions of co-iPP, α-iPP and β-iPP. Indexing of β-iPP corresponds to the trigonal $P3_121$ cell (hexagonal setting)[17] . Reflections of every phase scaled individually to its strongest reflection (= 100).

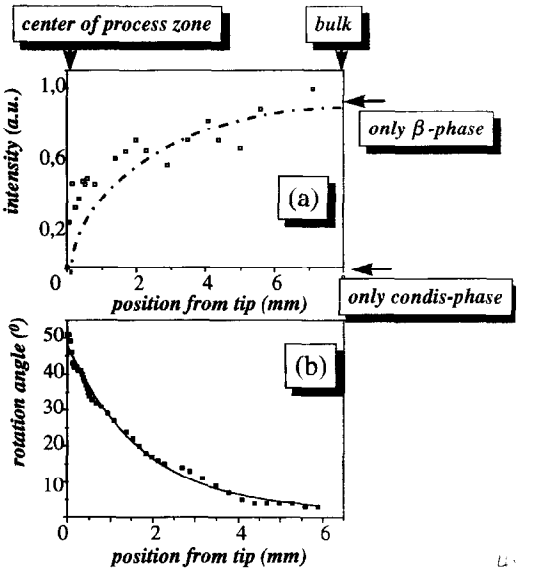

Fig. 3. (a) Variation of (2-10) reflection intensity of β-iPP as a function of position across the process zone. The intensity values (arbitrary units) have been scaled to 1.0 in the bulk and zero at the centre edge of the plastic zone (i.e. process zone). The line is only a guide for the eyes. (b) Variation of angle of rotation of the co-iPP equator from horizontal line. Line calculated for a first-order exponential decay.

related to the local magnitude of the strain in the plastic phase [2]. In order to check this scenario in more detail, in situ loading experiments of DDEN-T specimens combined with scanning diffractometry are required.

The formation of oriented microvoids at high uniaxial drawing ratios ($\lambda > 3$) of iPP films is known to accompany the β/α-phase transformation [22,23]. This results in a characteristic SAXS pattern with a central streak [21]. Diffuse light scattering experiments also suggest the formation of microvoids in the stress-whitened zone of β-iPP [20,23]. Finally, scanning electron microscopy pictures from the fracture surface of a DDEN-T specimen directly show that the β/α-transformation is associated with microvoiding [3]. The SAXS patterns observed in the present case also agree to the formation of microvoids. Both shape and orientation of the patterns were found, however, to depend on their taking position as shown in Fig. 4. At the centre of the process zone a central streak (taken as zero position) is observed. The bulk pattern (at 6.3 mm distance) in Fig. 4 is, in contrast, symmetrical. A long period due to a lamellar morphology [22] could not be detected which might be due to the limited resolution of the SAXS camera. SAXS patterns observed at intermediate positions do not resemble patterns observed at different draw ratios of β-iPP foils [22]. They rather appear to be composed of a mixture of the two patterns observed at the extreme (i.e. bulk and process zone) positions. Thus the pattern observed at the 1.8 mm position can be simulated by adding the patterns at the beginning (0) and end (6.3 mm distance) of the scan and rotating the sum by $\phi = 25°$ (Fig. 4). The rotation angle is similar to the one derived from the WAXS data at the corresponding position (Fig. 3). This may be explained by the formation of a local concentration of anisotropic microvoids which is proportional to the local volume concentration of co-iPP. The anisotropy of the central streak suggests that the microvoids are expanded in the direction of the macroscopic strain. The SAXS pattern will then correspond to the sum of scattering from the lamellar morphology of β-iPP and the scattering from microvoids. The rotation of the microvoid pattern may be due to the same mechanism as discussed above for the WAXS patterns.

Pure co-iPP existing at the center of the process zone appears to be free of microvoids. This cannot be derived from the SAXS patterns as the positional correlation with the WAXS patterns has not yet been established. A close-up of selected WAXS patterns shown in Fig. 5 supports, however, this conclusion as SAXS scattering can be observed close to the beamstop. Thus the pattern recorded at the very tip (Fig. 5(a)) does not show practically any SAXS

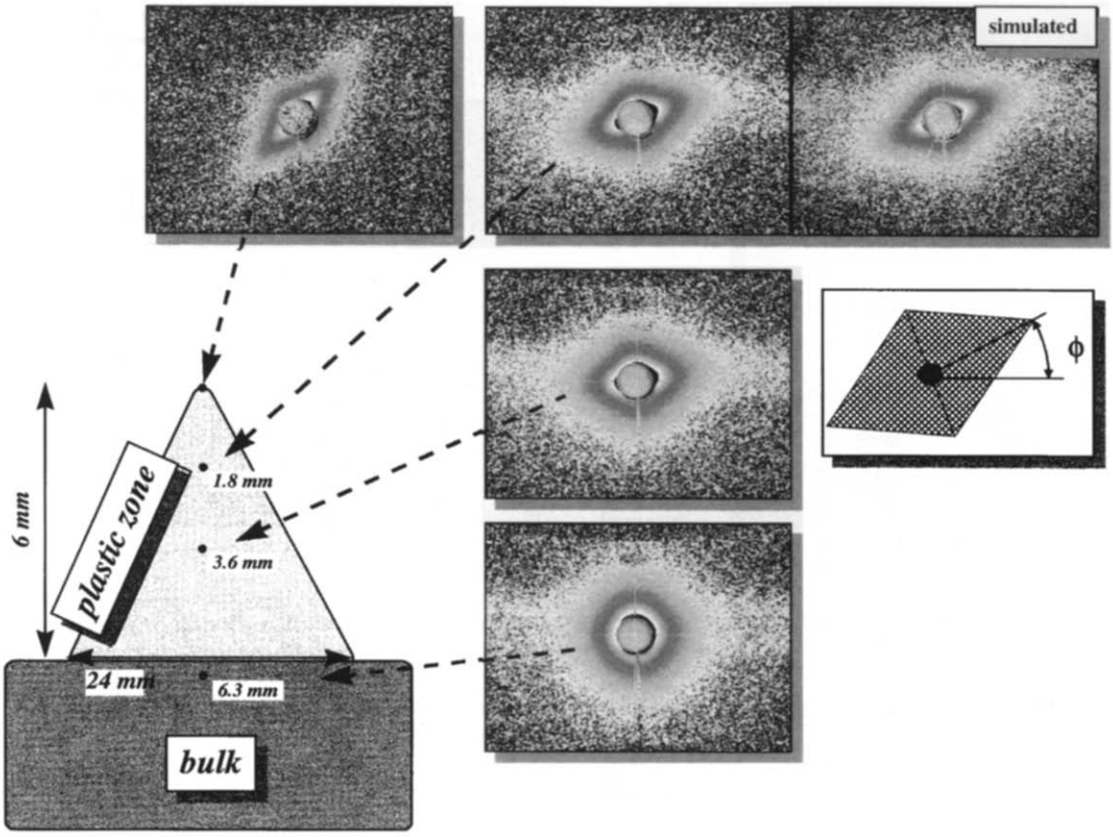

Fig. 4. SAXS patterns obtained at selected positions (logarithmic scale). Their positions are indicated relative to the first observed SAXS pattern from the process zone. The pattern at 1.8 mm was simulated by adding the patterns at 0 and 6.3 mm and rotating the summed pattern by $\phi = 25°$.

scattering at the beamstop while the pattern recorded 0.78 mm below (Fig. 5(b)) shows a strong SAXS signal. This suggests that the microvoids collapse in the pure co-iPP phase. Evidently, this point has to be investigated in more detail. In principle the beamstop size (here ≈ 0.5 mm diameter) could be reduced much further so that combined WAXS/SAXS experiments could be recorded with the same detector.

4. Conclusions

The present WAXS results agree with d.s.c. experiments suggesting a gradual increase of α/β-ratio as a function of the overall strain [1–4]. In addition, the α-phase was characterized as conformationally disordered (condis iPP). This condis iPP phase remains highly oriented throughout the plastic zone (stress-whitened region produced by static loading of a DDEN-T specimen) and its volume fraction increases towards the edge of the plastic zone (fracture plane or process zone). The use of a microbeam allowed us, in particular, to observe a practically pure condis iPP phase at the centre of the process zone. The formation of microvoids during the phase transformation also results in a characteristic SAXS pattern which overlays the SAXS pattern of β-iPP.

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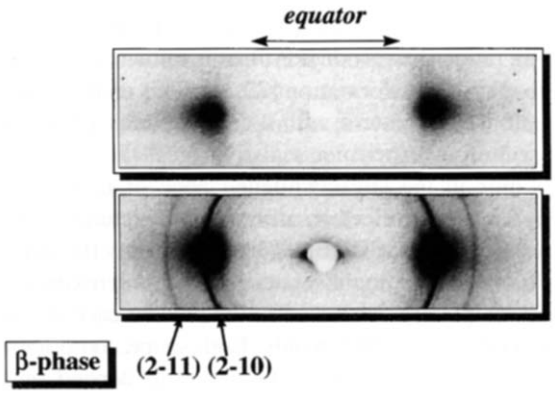

Fig. 5. Close-up of WAXS pattern recorded at (a) the centre edge of the plastic zone (pattern rotated so that equatorial scattering horizontal), and (b) 0.78 mm below centre edge of plastic zone

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