Plasticity and X-ray Line Profile Analysis of the Semicrystalline Polymer Poly(3-hydroxybutyrate)

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Abstract. The evolution of the microstructure during compressive deformation of the biodegradable polymer poly(3-hydroxybutyrate) (P3HB) was investigated in-situ via X-ray diffraction using synchrotron radiation. Flow curves were measured in-situ together with X-ray profiles for several degrees of deformation. The profiles were analysed using Multi-Reflection X-ray Line Profile Analysis (MXPA) adapted by the authors for semicrystalline polymers providing lamella thickness, crystallinity, and the presence and density of dislocations as a function of the deformation. In contrast to previous investigations in crystallised isotactic polypropylene (α-iPP), P3HB does not exhibit a deformation induced increase of the dislocation density which suggests mechanisms other than dislocations to be involved in plastic deformation of P3HB.

1. Introduction

In a previous paper on α crystallised isotactic polypropylene (α-iPP) [1] it has been demonstrated that the use of Multi-Reflection X-ray Profile Analysis (MXPA) as developed by Ungár and co-workers [2, 3] allows for the proof of the existence of dislocations in semicrystalline polymers. It was also possible for the first time to measure the density of dislocations quantitatively, which in the case of α-iPP was found to increase with increasing plastic deformation.

In general, the mechanical properties and particularly the yield stress of semicrystalline polymers seem to be governed by the size of the crystalline lamellae rather than by the crystallinity [4]. For the mechanism related, Flory and Yoon [5] and Balta-Calleja and Cruz [6] suggested that plastic deformation in semicrystalline polymers is driven by localised melting and recrystallisation under adiabatic conditions. However, this concept is not able to account for the specific change in yielding behaviour for larger lamella thicknesses as it was observed experimentally in semicrystalline polyethylene [4]. Contrary to this concept, Argon et al. [7] suggested that the mechanisms in question involve dislocations i.e. by the thermally activated generation of dislocations on the surfaces of nano-sized lamellae, and by a dislocation half-loop mechanism for larger lamellae. One strategy to shed more light on this problem is to investigate other types of semicrystalline polymers especially by means of MXPA which is capable of analysing the presence and density of dislocations on the one hand, and the lamella thickness on the other.
Recently the polyester poly(3-hydroxybutyrate) (P3HB) produced by microorganisms experienced some attention of the industrial community due to its high biodegradability. As the mechanical properties and the processibility are comparable to those of polypropylene (PP) this material qualifies for a number of future applications especially for medical and agricultural purposes.

From a scientific point of view, P3HB is particularly interesting for MXPA measurements because unlike many other semicrystalline polymers (a) its crystal system is simple orthorhombic and (b) its wide angle X-ray scattering (WAXS) pattern shows a large number of high intensity peaks [8], which is important for the efficiency of the MXPA. Moreover, the lamella thickness of P3HB is as small as 7 nm which should strongly affect the mechanical properties, and/or the generation dynamics of dislocations in case of their existence. Furthermore, there is only little data in the literature on the evolution of the microstructure of P3HB during deformation. Therefore the experiments presented in this paper aim at the presence of dislocations and potentially related deformation mechanisms in P3HB.

2. Experiments

2.1. Sample Preparation

P3HB rods were purchased from Goodfellow Cambridge Limited. For compression tests cylindrical samples with a height of 10 mm and a diameter of 6 mm were machined.

![Figure 1. Compression true stress-true strain curve of P3HB for strain rates of $\dot{\varepsilon}_t = 4 \times 10^{-3}$ s$^{-1}$ (– – –) and $\dot{\varepsilon}_t = 4 \times 10^{-4}$ s$^{-1}$ (—). After yielding a small softening is followed by a strong hardening beyond $\varepsilon_t \approx 0.7$ (vertical line).](image1)

![Figure 2. Compression true stress-true strain curve of P3HB for cyclic loading-unloading of an in-situ MXPA-measured sample. The large opening of the cycles is an indication for strong activity of the amorphous phase.](image2)

2.2. Mechanical Experiments and In-situ Diffraction Experiments

Uniaxial compression tests were carried out at room temperature on a Shimadzu AG50 deformation machine. Geometric stress-strain correction of the compressed samples was ensured by a video extensometer capturing the maximum bulging diameter with a digital camera. The curves resulting from deformation at two different strain rates are shown in figure 1.

In-situ WAXS measurements during plastic deformation were performed in transmission setup at the SAXS-Beamline 5.2L of Sincrotrone ELETTRA Trieste. For this purpose a specially designed miniature compression machine was used. The stress-strain curve of a cyclic loading-unloading experiment is depicted in figure 2. The photon energy used was 8 keV which corresponds to a wave length of CuK$\alpha$ radiation of 0.154 nm. The incident beam had a spot size...
of 200 μm × 500 μm on the sample. The photon flux amounted to $5 \cdot 10^{11}$ photons mm$^{-2}$s$^{-1}$. The WAXS spectra were recorded with a linear position-sensitive detector (1024 channels, type PSD 50 of Braun, Munich, Germany) at a distance of 370 mm between the detector and the specimen. To ensure sufficient statistics for a reliable evaluation of the WAXS profiles, at least $10^4$ counts were collected in the maxima of the diffraction peaks. The recorded profiles were evaluated by means of the Multi-Reflection X-ray Line Profile Analysis (MXPA) [2, 3]. The evaluation procedure followed three steps, starting with the background determination and peak separation. After this a pre-fit of the components of the average dislocation contrast factor was done by evaluation of the modified Williamson-Hall plots. These values were then used as starting values for the evaluation with the program CMWP-fit [9, 10]. Details of this procedure are given in the papers by Wilhelm et al. [1] and Kerber et al. [11].

3. Results and Discussion

Surprisingly the change of the profile broadening induced by plastic deformation found in P3HB seems to be very small. Earlier investigations of X-ray line broadening in α-iPP [1] revealed a strong deformation induced increase of the broadening. This could be related to the formation of dislocations while the coherently scattering domain size (CSD) (which is also responsible for an important part of the broadening) remained nearly constant. Nevertheless the CSD was found to correspond very well to the lamella size of α-iPP as determined by DSC or SAXS [12, 13]. In the present investigation of P3HB, a stronger scattering for the CSD in comparison with α-iPP is found which results in a CSD between 6-11 nm. The broadening related to dislocations, however, does not seem to be affected by deformation (figure 4). Although in absolute terms the initial dislocation density turns out to be even higher in P3HB ($6.5 \cdot 10^{16}$ m$^{-2}$) than in α-iPP ($3.8 \cdot 10^{16}$ m$^{-2}$[1]) it does hardly change as a function of the compressive strain applied (figure 4). This contrast to the observations in α-iPP indicates that in P3HB a different deformation mechanism is active. Different explanations may account for the unexpected behaviour of P3HB:

(i) The dislocation density is high enough to accommodate the crystallographic slip, and generation and annihilation of dislocations may be in balance.

(ii) Intralamellar slip occurs with a mechanism other than dislocation motion, e.g. localised adiabatic melting [5] without mobilisation of dislocations.
(iii) Interlamellar processes are responsible for the main part of the deformation due to a high stiffness of the crystallites. In this case the lamellar crystallites would fragment before crystallographic slip occurs. Like mechanism (ii), also this mechanism would not involve dislocation motion.

As the interaction between dislocations in polymers is expected to be low [4] the hardening curve in figure 1 cannot be used to decide between the three processes. The opening of the cycles shown in figure 2 increases with deformation. According to Hiss et al. [14] this can be attributed to the viscoelastic properties of the amorphous phase. The strong reduction of the crystalline volume fraction plotted in figure 3 is in accordance with this observation, since it suggests a stronger influence of the amorphous phase on the relaxation and deformation behaviour of the material. Both observations support the occurrence of mechanisms (ii) and (iii). In particular, the considerable amount of kinematic hardening which can be seen in figure 2, and the marked brittleness of the bulk material hint at the formation of cracks as suggested by mechanism (iii).

Nevertheless, the real reasons for the occurrence of a deformation mechanism in P3HB, which is different to that operating in α-iPP remain unclear. Future measurements of the deformation induced texture might prove useful in order to identify possibly activated slip systems. Transmission and/or scanning electron microscopy should give insight in how far fragmentation of the crystallites occurs with deformation.

4. Summary and Conclusions
With the present experiments, using the method of Multiple X-ray Profile Analysis, for the first time the existence of dislocations in melt-crystallised P3HB was shown. A considerable initial dislocation density of $6.5 \times 10^{16} \text{m}^{-2}$ was found. However, a deformation-induced change in the dislocation density has not been observed in P3HB which suggests one of the following microstructural deformation mechanisms to occur: (i) a balance of dislocation annihilation and generation, (ii) deformation-induced adiabatic melting, and (iii) brittle fragmentation of the lamellae.

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