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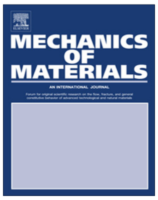

The role of dislocations in γ-iPP under plastic deformation investigated by X-ray line profile analysis

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ABSTRACT

Samples of γ-iPP were prepared by crystallization at elevated pressures using a specially designed pressure chamber. The γ-phase was subsequently investigated by dedicated in-situ X-ray diffraction experiments during deformation using synchrotron radiation. Parameters such as the crystallinity, the density of dislocations and the coherently scattering domain size (CSD-size) which in polymers corresponds to the lamella size, have been evaluated as a function of the strain by means of the multi-reflection X-ray line profile analysis (MXPA). Compared to the results for the α-phase, those for the γ-phase reveal an enhanced strength and a strongly reduced evolution of the dislocation density. The latter is explained in terms of a model comprising the formation of misfit dislocations.

1. Introduction

In semicrystalline polymers, the appearance of grown-in dislocations from solutiongrown single crystals is well established and has also been observed experimentally (Keith and Chen, 2002). However, the formation of dislocations under plastic deformation is discussed controversially. Two main mechanisms appear to be active during the deformation process, namely crystallographic slip on the one hand, and adiabatic melting and subsequent recrystallization on the other. Séguéla discussed these two processes pointing out that melting-recrystallization is not a necessity for plastic deformation but rather a consequence of chain unfolding, whereas crystallographic slip is present at all stages of deformation (Séguéla, 2007). In the case of crystallographic slip, dislocations may play a major role during the deformation process within the crystalline phase (Young, 1974; Galeski et al., 2010; Argon et al., 2005; Spieckermann et al., 2010, 2012). Wilhelm et al., 2004 proved for the first time that dislocations are present in melt-crystallized α-iPP (isotactic Polypropylene) and also that the amount of dislocations in α-iPP changes significantly under plastic deformation. For this purpose, a special X-ray diffraction method (multi-reflection X-ray Profile Analysis, MXPA) was adopted to semicrystalline polymers which has been successfully used in metal physics (Schafler and Zehetbauer, 2005; Ungár et al., 2001; Kerber et al., 2005). This method allows for a detailed analysis of the diffraction profiles which reveal microstructural parameters such as the dislocation density and the coherently scattering domain size (CSD-size) corresponding to the lamellae thickness in semicrystalline polymers (Spieckermann et al., 2010, see Section 4).

In this work MXPA has been used to investigate the evolution of the dislocation density and the CSD-size of the γ-phase of isotactic Polypropylene (γ-iPP) at different stages of plastic deformation. For this purpose iPP was subjected to a well defined pressure and temperature treatment in order to crystallize in the γ-phase, and subsequently mea-

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sured by means of a dedicated in-situ deformation X-ray diffraction setup using synchrotron radiation.

The crystal structure of the orthorhombic γ-form of iPP is characterized by a very unusual arrangement of the macromolecular chains (Turner-Jones, 1971; Thomann et al., 1996; Lotz et al., 1996). Instead of being arranged in a parallel manner as it is the case in most semicrystalline polymers, the structure contains sheets or bilayers composed of parallel helices. The bilayers are tilted at an angle of approximately 80° against each other and about 40° with respect to the crystallographic *b*-axis of the unit cell (Lezak et al., 2006). In order to crystallize in the orthorhombic crystal structure, a hydrostatic pressure of at least 200 MPa has to be applied to the sample (Mezghani and Phillips, 1998; Campbell et al., 1993). Another possibility is to use metallocene catalysts (Auriemma and Rosa, 2002; Perez et al., 1999), very low molecular weight samples (Lotz et al., 1991), high molecular weight samples with a controlled number of stereodefects (Cao et al., 2009), or PP copolymerized with 1–10 mol% 1-olefins (Hosier et al., 2003). Due to the unique structure of the γ-phase, the number of possible slip systems are restricted. Plane strain compression experiments of iPP samples with high γ-concentration demonstrated that there is no evidence of any crystallographic deformation mechanism within the crystalline component. These findings led to the conclusion that the critical resolved shear stress (CRSS) of the anticipated slip systems is too high to be relevant for plastic deformation resulting in a different deformation behavior, namely the interlamellar shear of the amorphous layers (Lezak and Bartczak, 2007). The results of this work are in accordance with the findings in this work and extends them by measurements of the dislocation density and coherently scattering domain size.

2. Experimental

2.1. Materials and sample preparation

The material used for crystallization was isotactic Polypropylene (iPP) of the type HD120MO from *Borealis* (www.borealisgroup.com) which was processed to cylinders with a diameter of 8 mm. From these cylinders, samples with the desired height (6–10 mm) have been cut using a *Struers Accutom-5* precision saw. The pressure of 200 MPa which is essential to crystallize the γ-phase was achieved by a self-designed pressure chamber (Fig. 1) mounted in an universal testing machine of the type *Shimadzu AG10-TA*. The computer-assisted control unit of the testing machine allowed for a constant hydrostatic pressure compensating the volume change of the specimen caused by melting and crystallization. A pressure of 200 MPa was applied on the sample and subsequently heated up above the melting temperature T_m to about 260 °C ($T_m = 245$ °C at $p = 200$ MPa Lezak et al., 2006) by means of a bandheater mounted around the casing of the pressure chamber and a heating rate of approximately 13 °C/min. The temperature was held for about 10 min above T_m and afterwards reduced to the crystallization temperature T_c of 200–210 °C held for 4 to 6 h.

2.2. Synchrotron measurement

The in-situ Wide Angle X-ray Scattering (WAXS) measurements during compression of the γ-sample were performed at the Synchrotron Light Source ELETTRA in Trieste, Italy (SAXS-Beamline 5.2L). A specially designed miniature compression machine mounted at the sample stage was used to deform the sample during the measurement. Diffraction profiles were recorded using a curved *INEL CPS-590* position sensitive detector covering an angle of 90°. That curvature is part of a circle with a radius of 500 mm with the sample located in the center. The beam had a size of 500 μm in the horizontal and 200 μm in the vertical direction with a photon energy of 8 keV which corresponds to a wavelength of CuK$_\alpha$ radiation of $\lambda = 0.154$ nm.

3. XPA-theory and evaluation

3.1. Profile analysis

The intensity profile of a diffraction pattern is composed of a strain effect caused by crystal defects such as dislocations and internal strains, and a size effect taking into account the limited size of a crystal. The Fourier coefficients for size and small strains being present simultaneously in the material read as follows (Warren and Averbach, 1950)

$$\ln A(L) = \ln A^S(L) + \ln A^D(L) \tag{1}$$

where L is the variable of the Fourier transformed, $A^S(L)$ and $A^D(L)$ are the size and distortion coefficients, respectively. The distortion coefficient calculated by Warren and Averbach (1950) reads as

$$A^D(L) = \exp\left(-2\pi^2 g^2 L^2 \langle \varepsilon_L^2 \rangle\right) \tag{2}$$

where $\langle \varepsilon_L^2 \rangle$ is the mean square strain and g is the length of the diffraction vector. Krivoglaz (1969) and Wilkens (1970) computed the mean square strain under the assumption that the peak broadening is primarily caused by the strain field of dislocations by introducing the dislocation contrast factor C. The contrast factors of the (hkl) planes can be averaged over their permutations for different crystal structures resulting in C, the average contrast factor (Ungár and Tichy, 1999)

$$A^D(L) = exp\left[-\left(\frac{\pi b^2}{2}\right)(g^2\,\bar{C})\varrho L^2 f\left(\frac{L}{R_e}\right)\right]. \tag{3}$$

The crystallite size distribution is calculated assuming a lognormal size distribution function within the formulation of the size coefficient of $A^S(L)$. In the case of an anisotropic crystal shape represented e.g. by a spherical ellipsoidal shape, the median of the size function depends on the (hkl) indices (Ribárik et al., 2001).

3.2. Pre-evaluation

Before the measured diffraction profiles can be evaluated, the peaks and/or phases have to be determined. By