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Strain-induced β-α polymorphic transition in iPP as revealed by microhardness

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The microhardness (H) technique was used for characterization of the β-α polymorphic transition in isotactic polypropylene (iPP). For this purpose the microhardness in the damage zone of a tensile loaded deeply edge-notched (DEN-T) β-iPP specimen was mapped. Mapping of H was performed, both along the loading direction (central) and close to the shorter fracture edge. Around half-length of the plastic zone a sharp increase of the H values in both cases was observed. The H increase is related to the $\beta \rightarrow \alpha$ polymorphic transition. Microvoid formation in the central part results in lower H values. However for the edge zone close to the top of the fracture surface unusually high H values (around 200 MPa) are obtained. The latter are explained in terms of the formation of microfibrils due to crazing during deformation which are characterized by very high molecular orientation as reported from X-ray analysis. © *1999 Kluwer Academic Publishers*

1. Introduction

A peculiarity of polypropylene is its large variety of crystalline polymorphic modifications arising from its ability to exist in different stereoregular forms. For instance, for isotactic polypropylene (iPP) the α-form (α-iPP), the β-form (β-iPP) and the γ-form (γ-iPP) are known [1]. In addition α-iPP is subdivided in α_1- and α_2-forms and another, mesomorphic form, often referred to as "smectic" is registered [1]. The presence of one or more forms in the polymer sample depends on the way of treatment determining the crystallization conditions as temperature, pressure, solvent etc. A polymorphic β-α transition is known to take place also under strain [1].

The α-form is the most common crystalline phase of iPP. It is observed for both melt- and solution-crystallized samples prepared at atmospheric pressure. Adequately annealed samples can melt at temperatures as high as 180 °C and their density is 0.94 g/cm^3. Some disorder is always present in the crystal structure of α-iPP [1].

The β-form is normally referred to as "hexagonal iPP" and was identified in 1959. β-phase spherulites, characterized by strong negative birefringence, could be sporadically obtained when iPP was crystallized in the 128–132 °C temperature range. Pure β-phase can be obtained with the aid of crystalline nucleating agents like, e.g., the quinacridone dye stuff Permanent Red E3B. Crystallization in a temperature gradient is also an efficient route to produce oriented iPP samples with predominant β crystallinity [2]. The growth rate of β spherulites is up to 70% faster than that of α spherulites. β-iPP is metastable relative to α-iPP ($T_m = 155$ °C vs. 180 °C), it has lower density (0.92 g/cm^{-3}) and is unstable upon stretching, which produces a transition to α-iPP or to the "smectic" form depending on whether the sample is processed above or below 60 °C. The unit cell of β-iPP is trigonal and it contains three isochiral helices with up-down statistics. Diffraction patterns display however a symmetry higher than trigonal (hexagonal) and are consistent with averaging effects produced by disorder or twinning. Transition of the β- in to the α-iPP form occurs via a melting-crystallization process [1].

In addition to crystallization of β-iPP in the α-form during heating (e.g., [3, 4]), if the sample was kept at ambient temperature prior to melting [4], the same β-α transition can also be triggered by mechanical loading [4–7]. Recent studies indicate [5–7] that this $\beta \rightarrow \alpha$ transformation is accompanied with a considerable increase in toughness. The toughness improvement was shown to depend on, both, molecular mass of the PP [8] and loading frequency [7, 9]. Differential scanning calorimetric (DSC) results reveal [7] that the $\beta \rightarrow \alpha$ conversion changes locally in the stress whitened plastic zone caused by the mechanical loading. The conversion grade of this $\beta \rightarrow \alpha$ transformation cannot be easily estimated by taking conventional DSC traces because of the following overlapping processes: partial melting of the β-iPP, β-α recrystallization and melting of the resulting α-phase [4, 7]. The modulated DSC (MDSC) is a proper tool to separate complex, overlapping thermal transitions [10].

In a very recent study [11] X-ray microdiffraction using synchrotron radiation has been used to investigate the strain-induced crystalline modification transition in

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the plastic zone of an iPP β-phase. It was shown that the bulk β-iPP was gradually transformed into highly oriented, conformationally disordered (condis-structure) α-phase iPP as the strain was increasing.

Although the DSC-experiments taken from the plastic zone suggest the presence of α-phase [6, 7, 10], the wide angle X-ray scattering (WAXS) [11] in the plastic zone does not show the characteristic α-iPP reflections [12]. Instead a rather disordered α-phase with a characteristic broad equatorial reflection is observed. This phase has been originally described as a smectic phase [13] though more recently as conformationally disordered (*condis iPP-co-iPP*) structure in view of the lack of a mesogen unit [14].

During the last two decades it was demonstrated that hardness tests provide a rapid evaluation of the variation in surface mechanical properties of polymers affected by changes in processing or chemical conditions, heat treatment, microstructure and ageing [15]. In order to determine the irreversible contribution to deformation, static indentation, involving the formation of a local permanent surface impression is commonly used [16]. Indentation hardness testing is also finding an increased usage in the investigation of the microstructure of semicrystalline polymers at various morphological levels [17–21]. It has been also demonstrated that microhardness is a technique capable of detecting polymorphic changes in polymers [22]. In particular, the study of the transition from the β- to the α-form in iPP confirmed that the changes in H can be explained in terms of an additive contribution to the H of independent phase components H_c^{α}, H_c^{β} and H_a, the latter being the hardness of the amorphous phase [22]. This approach opened up the possibility of characterizing iPP samples consisting of a mixture of α- and β-phases by means of H measurements. Microhardness was recently applied to poly(butylene terephthalate) (PBT), its multiblock copolymers and their blends [23–25] for examination of the stress-induced polymorphic transition. Following these investigations an attempt to observe the reversible variation of microhardness under strain was undertaken as well [26].

The aim of the present study is to use the microhardness technique in order to gain a deeper insight on the strain-induced $\beta \rightarrow \alpha$ transformation in iPP and thus to complement and correlate recent MDSC [10] and X-ray [11] investigations.

2. Experimental

2.1. Materials

1 mm thick β-iPP sheets were prepared as described in an earlier work [7]. A stressed deeply edge-notched (DEN-T) specimen was prepared in tensile fracture at room temperature using crosshead speed of $v = 1$ mm min^{-1}. Fig. 1 schematically shows the stressed whitened damaged zone together with its process and plastic constituents. This designation agrees with the works on fracture used for ductile polymers (e.g. [6]).

The plastic zone is nearly symmetrical as shown on the photograph of Fig. 1. However, such a symmetry is more an exception than a rule. Frequently the triangle depicted on the photograph has three different sides. In a recent publication [11] on the X-ray study of a β-iPP sample prepared in the same way as in the present investigation, the plastic zone of the sample was schematically presented as symmetrical which does not correspond to the real case. Such a drawing is misleading and makes difficult to understand the actually observed change in the chain-axis orientation with the development of the plastic zone. Fig. 2 schematically shows the actual shape and dimensions of the sample used in this work for the microhardness measurements.

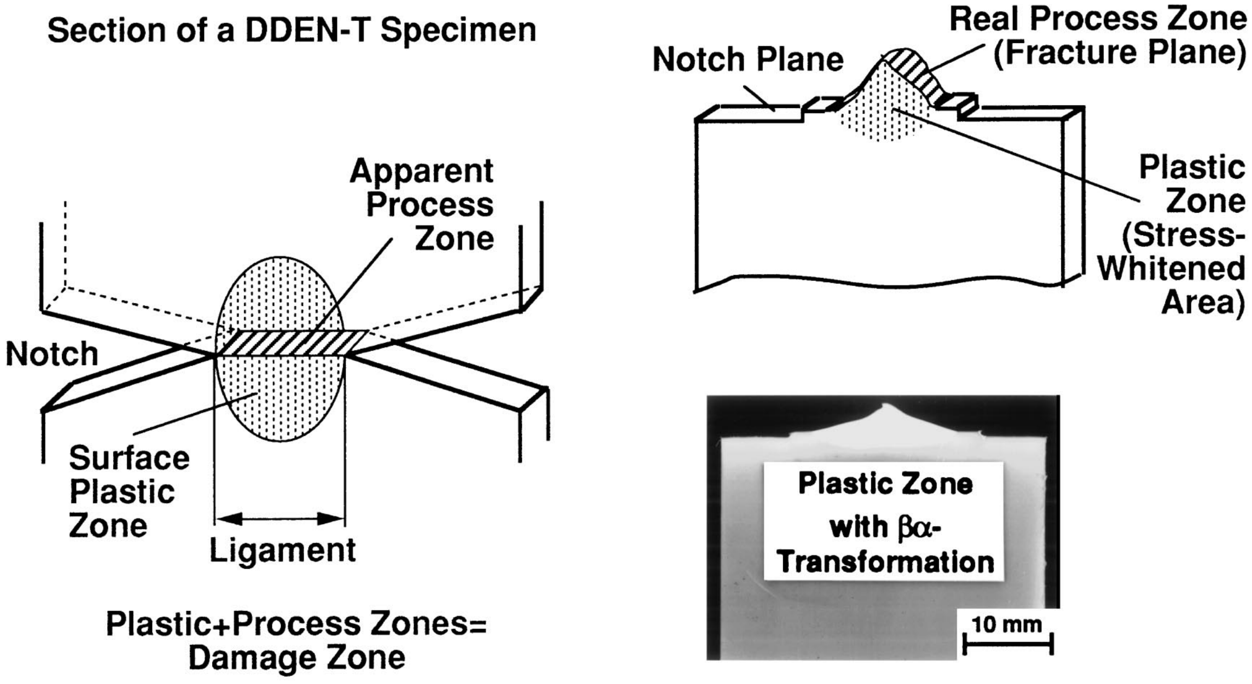

Figure 1 Schematics of deformation in a fractured DDEN-T specimen of β-iPP and photograph of the plastically deformed region.

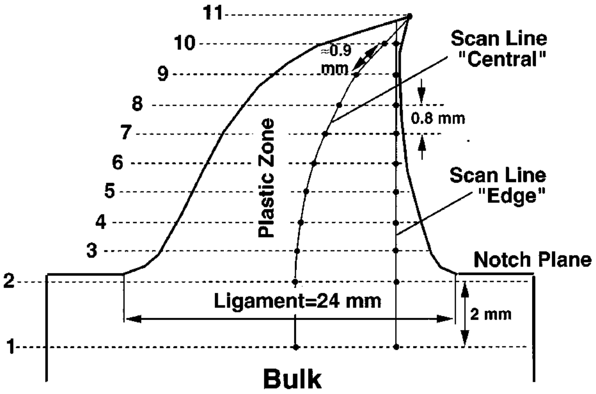

Figure 2 Real shape of the β-iPP sample used for microhardness measurements. The black points denote the location of indentation for the two series of measurements, along the central and the edge line.

2.2. Techniques

Microhardness was measured at room temperature using a Leitz tester adapted with a square-pyramidal diamond indentor. The H value was derived from the residual projected area of indentation according to $H = kP/d^2$, d being the length of the impression diagonal, P the contact load applied and k a factor equal to 1.854 [16]. A loading cycle of 0.1 mm was used. Loads of 98 and 147 mN were employed to eliminate the instant elastic contribution. About 10 indentations were averaged for each hardness value.

Two series of indentations were performed: (i) one series along the "central" part of the plastic zone and (ii) the second series along the "edge" of the the plastic zone, see (Fig. 2).

3. Results and discussion

The variation of H as a function of the distance l from the bulk zone (Fig. 2) to the top of the fracture surface (point 11 in Fig. 2) is shown for the two series of measurements in Figs 3 and 4, respectively. One sees common features but also essential differences between these two curves (Figs 3 and 4). The starting H value for both series of measurements, is the same ($H \sim 50$ MPa). In both cases, H first remains constant, then slightly increases with l and, for $l \sim 6$ mm, H suddenly increases.

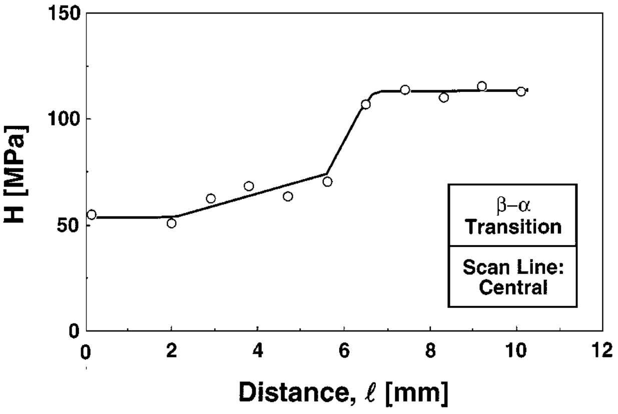

Figure 3 Dependence of microhardness H as a function of distance l from the bulk along the central line (Fig. 2).

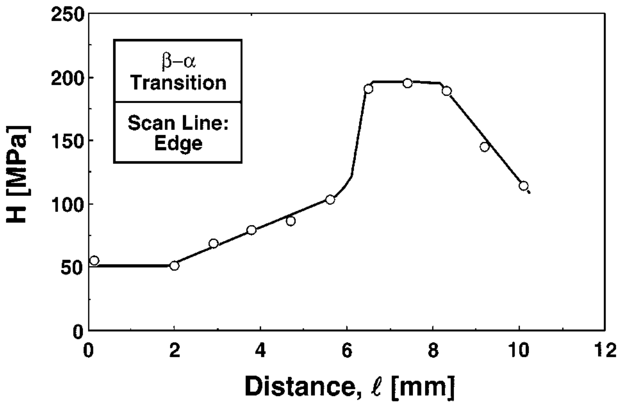

Figure 4 Dependence of microhardness H as a function of distance l from the bulk along the edge zone (Fig. 2).

For the case where measurements were done in the central part, for $l > 6$ mm, $H = 120$ MPa, Fig. 3). In case indentations were placed along the edge, H reaches values of nearly 200 MPa and finally, for $l > 8$ mm H decreases down to 120 MPa (Fig. 4). It also seems important to note that this sudden increase in the H values takes place in a very narrow distance interval of the plastic zone, i.e. less than 10% of the total length.

Previous DSC [4, 5, 10] and WAXS [11] studies indicate that the starting bulk iPP material shows the β-polymorphic form. For this modification [22] a H value of 90 MPa was reported which is higher than that found in the present work (Figs 3 and 4). One can explain this difference by the fact that H also depends on the degree of crystallinity w_c [15, 16]. For this reason the H values in these two cases cannot be compared without taking into account the value of w_c.

The fact that H does not immediately increase with the initial deformation (point 2, Fig. 3) as does with larger strains (points 3 and 4, Fig. 3) can be related to cavitation formation during deformation. The ocurrence of microvoids has been evidenced by scanning electron microscope [10]. Light scattering through these microvoids within the plastic zone is responsible for the "whitening" effect, usually termed to "stress-whitening." It is not yet fully understood how far and to what extent this microvoiding is an effect of a polymorphic transformation. Nevertheless, this "side effect" is exploited for the production of microporous films [27, 28].

The sharp H increase in the two cases (Figs 3 and 4) can only originate from the $\beta \rightarrow \alpha$ polymorphic transition of iPP. The H different values before and after the polymorphic transformation are related to the various crystalline densities of the polymorphic phases: 0.92 g/cm^3 for the β-modification and 0.94 g/cm^3 for the α-phase [1]. This conclusion is supported by a former investigation of the two modifications of iPP [22] as well as by the well documented relationship between H and crystal density [15].

By comparing the above two series of measurements (Figs 3 and 4) two interesting questions arise:

(a) How can one explain the drastic H decrease in the edge (Fig. 4) when one approaches the fracture zone (points 10 and 11, Fig. 2)? A possible explanation could be that the material flow during deformation is not homogeneous in the whole plastic zone. To this conclusion leads the final shape of the plastic zone (Fig. 2) as well as the visual observation of the transparent test samples after breaking where families of parallel, but assymetric with respect to the two edges, refractive lines are observed. Obviously, due to inhomogeneous material flow the material close to the edge and to the fracture top surface did not experience the required stress during deformation for the $\beta \rightarrow \alpha$ phase transition to take place as completely as possible.

(b) The second question concerns the H numerical value for the indentation done near the edge immediately after the $\beta \rightarrow \alpha$ transition. The 200 MPa value is notably higher than the reported for the two fully crystalline modifications, $H_c^\beta = 119$ MPa and $H_c^\alpha = 143$ MPa [22]. Both values were obtained via extrapolation. On the other hand, the value of $H_c^\alpha = 200$ MPa (Fig. 4) is in good agreement with recent calculations of the hardness for iPP crystals of infinite thickness in the α-form [29].

This unusually high H-value for PP could also originate from the inhomogeneous character of the material flow during deformation. If one takes into account that while the deformation in the central part close to the bulk (Fig. 2) creates microvoids [10], in the opposite place of the sample, (i.e. at the edge between the plastic zone surface and the fracture surface (Fig. 2)) the deformation results in crazing with formation of microfibrils. In this case the value of $H = 200$ MPa could be acceptable since according to a recent [30] report the microhardness of glassy polystyrene microfibrils is, at least, twice the value of the bulk polymer. This finding is consistent with the occurence of highly oriented polymer chains within craze fibrils [31]. In fact, in the present case one deals with an α-phase characterized as conformationally disordered but remaining highly oriented throughout the plastic zone (stress whitened region produced by static loading of a DEN-T specimen). Its volume fraction increases towards the edge of the plastic zone (fracture plane or process zone) as concluded from microdiffraction synchrotron radiation experiments [11].

The conclusion about the very high packing density originating from both, the orientation and the presence of the polymorphic modification with the highest density for iPP [1] is also supported by the reported value for the microhardness of infinitely large iPP crystals of $H_c^\alpha = 230$ MPa [29]. This value was derived from the extrapolation of the H_c vs. lamellae thickness l_c dependence [29].

It is important to note that according to the above mentioned microdiffraction structural investigation [11] in the plastic zone of a sample prepared in the same way, the $\beta \rightarrow \alpha$ transformation takes place gradually, in contrast to our present more abrupt transition (Figs 3 and 4). This finding suggests that the microhardness technique is a sensitive method for the characterization of the polymorphic transitions in crystalline polymers. It presents some advantages in comparison to the scattering or spectroscopic techniques because it is not averaging the bulk radiated material but offers local surface characteristics.

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