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New aspects of the *β–α* polymorphic transition in plastically deformed isotactic polypropylene studied by microindentation hardness

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Abstract The *β*–*α* polymorphic transition in plastically deformed isotactic polypropylene (iPP) was characterized by means of microindentation hardness. For this purpose microindentations were mapped onto the surface of the necking zone of a tensile loaded injection molded *β*-iPP ''dumb-bell'' specimen. Results evidence a sharp decrease of the *H*-values instead of the expected *H*-increase due to the *β*–*α* polymorphic transition. Far away from the necking zone an *H*-increase is detected. It is shown that the destruction of the starting isotropic spherulitic structure and the decrease of crystallinity in the necking zone gives rise to lower *H*-values. However, at larger distances from the neck, the emerging fibre structure induces a better chain orientation that results in a slight *H*-increase. Analysis of the isotropic and necked samples before and after their annealing using DSC and WAXS supports the assumption regarding the role of the microvoids in decreasing the hardness value.

Introduction

Polymer materials show a strong tendency to polymorphism presenting transitions from one polymorphic form to another that sometimes may be reversible [1]. The appearance of one or other crystalline modification depends on many factors, usually affecting the crystallization or recrystallization process. These include crystallization conditions (melt or solution temperature, rate of cooling, presence of specific nucleating agents, type of substrate, etc.), mechanical treatment (drawing, pressing, rate of treatment, a. o.) and reversible plastic deformation to observe the regeneration of the starting modification [1].

A good example in this respect is polypropylene (PP) because it appears in various modifications. For instance, in isotactic polypropylene (iPP) the *α*-form, the *β*-form normally referred to as ''hexagonal iPP'' and the *γ*-form, 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 detected [2]. The *α*-form is the most common crystalline phase of iPP and it is observed for, both, melt- and solution-crystallized samples prepared at atmospheric pressure. The *β*-phase spherulites, characterized by strong negative birefringence, have been sporadically obtained when iPP is crystallized in the 128–132 °C temperature range. Pure *β*-phase iPP can be obtained with the aid of crystalline nucleating agents. Crystallization in a temperature gradient is also an efficient route to produce oriented iPP samples with predominant *β*-crystallinity [3]. 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 vs. 180 °C, respectively), 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

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β- into the α-iPP form occurs via a melting-crystallization process [2].

In addition to crystallization of β-iPP in the α-form during heating [4, 5], if the sample was kept at ambient temperature prior to melting [5], the β–α transition can also be triggered by mechanical loading [5–8]. Recent studies indicate [6–8] that the β–α transformation is accompanied by a considerable increase in toughness. The toughness improvement was shown to depend on, both, molecular mass of the PP [9] and loading frequency [8, 10]. Differential scanning calorimetric (DSC) results reveal [8] that the β–α conversion changes locally in the stress whitened plastic zone caused by the mechanical loading. The level of conversion of the β–α transformation cannot be easily estimated by taking conventional DSC traces because of the following overlapping processes: (i) partial melting of the β-iPP, (ii) β–α recrystallization and (iii) melting of the resulting α-phase [5–8]. Modulated differential scanning calorimetry (MDSC) is a convenient tool to separate complex, overlapping thermal transitions [11]. Recently X-ray microdiffraction using synchrotron radiation has been employed to investigate the strain-induced crystalline modification in the plastic zone of an iPP β-phase [12]. This study evidenced that bulk β-iPP was gradually transformed into highly oriented, conformationally disordered, α-phase iPP as the strain was increased.

Although much effort has been invested to describe the various polymorphic modifications of PP, as well as to understand the reasons for their appearance or the transition to each other, many questions remain still open.

In a preceding report we tried [13] to describe the transition of β–α modification in a plastically deformed isotactic PP (up to failure) trough the neck region, using the microindentation technique. In accordance with expectation, a significant increase in the microhardness values after necking (due to the higher crystalline density ρ_c of the α modification, ρ_c^{α} as compared to that of the β modification, ρ_c^{β}) was observed [13]. In the present paper we attempt to complement the above study by measuring microhardness of plastically deformed iPP samples before failure occurs [13]. However in the present work, a different situation arises, as the microhardness (H) in the necking zone is significantly lower than that in the isotropic (non-stretched) part, regardless of the well documented facts [12, 13] that after necking the higher density crystallites of the α modification dominate [2, 5]. A similar drastic decrease in hardness with draw ratio, corresponding to the first stages of plastic deformation, has been recently found both, α- and β-iPP samples [14]. The aim of the present investigation is to discuss the observed H decrease of iPP during the β–α polymorphic transition through the necking zone in the light of DSC and X-ray observations.

Experimental section

Materials and sample preparation

Commercial iPP Dalpen BE 50 (Now Borealis, Linz, Austria) with a M_w = 1000 kg/mol and melt flow index MFI = 0.3 dg/min (determined at T = 230 °C and a load of 2.16 kg) was injection molded in order to prepare ''dumbbell'' test samples. Further details to the iPP including β-nucleant along with the injection molding conditions are given elsewhere [15, 16]. The specimens were subjected to drawing until neck formation at its failure using a Zwick tensile test machine at ambient temperature and a deformation rate of 2 mm/min.

Techniques

Microhardness

The microindentation hardness (H) of the sample surface was measured using a microindentation tester with a Vickers square-based diamond indenter. The hardness value (in MPa) was derived from the residual projected diagonal impression, using $H = kP/d^2$, where P is the applied force in N, k is a geometrical constant equal to 1,854, and d is the length of the projected indentation diagonal in μm. Loads of 0.25 and 0.50 N and a loading cycle of 6 s were used. As schematically shown in Fig. 1, the microindentation measurements started on the isotropic part of a ''dumbbell'' sample, passing through the necking zone and also performed on different places along the neck (up to 20–25 cm). Since the necking zone (about 2 mm width) is thinner than the isotropic part, one had to keep the sample surface horizontal to the XY-stage by placing a wedge underneath the sample.

DSC

Samples of the isotropic and the necked parts of the materials were analyzed by means of a differential scanning calorimeter (DSC 821e device of Mettler–Toledo) at 20 °C/min heating rate. For the calculation of the degree of crystallinity, w_c, the commonly used equation $w_c(\text{DSC}) = (\Delta H_{\text{exp}}/\Delta H_{\text{id}}$, where ΔH_{exp} and ΔH_{id} are the experimentally measured melting enthalphy and that of the 100% crystalline sample, respectively. For ΔH_{id} of the β- and α-modifications, the values $\Delta H_{\text{id}}^{\alpha}$ = 177.0 J/g and $\Delta H_{\text{id}}^{\beta}$ = 168.5 J/g were taken [17]. The same values were recently proposed by Li et al. [18].

WAXS

Wide-angle X-ray scattering (WAXS) photographic patterns were recorded on a Siemens X-ray diffractometer

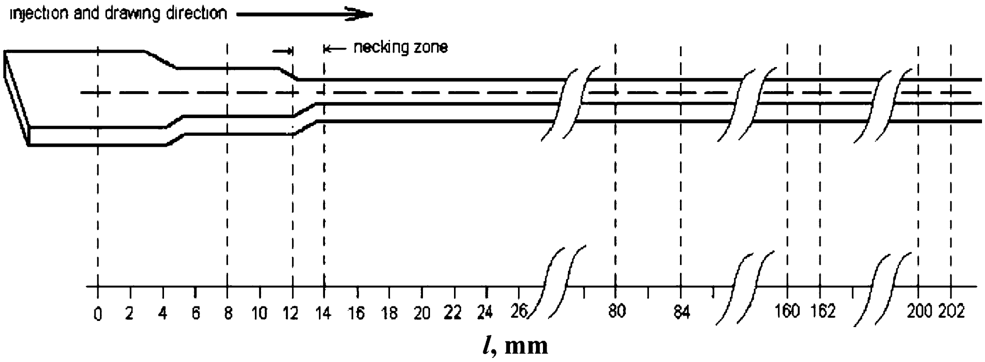

Fig. 1 Schematics of the isotropic and necked zones of the ''dumb-bell'' samples illustrating schematically the location of the microindentations

(type D 500) using Ni-filtered CuK$_\alpha$ radiation. This analysis was performed on the isotropic and necked parts of the samples prior and after annealing at 120 °C for 6 h in vacuum.

Results and discussion

Crystallinity changes during the polymorphic transition

Figure 2 illustrates the microhardness variation as a function of the distance *l* from the isotropic part of the sample along the drawing direction (see Fig. 1). The *H* data before the necking starts scatter around a value near to 100 MPa, in agreement with previous results reported for iPP, characterized for the β crystalline modification [13]. When crossing the necking zone microhardness rapidly drops reaching a constant, though much lower value of about 20 MPa. At larger distances from the necking zone (between 20 and 200 mm) *H* increases significantly, remaining again nearly constant. The *H* increase can be related to the better orientation of the chains in these parts of deformed material, resulting in a more dense chain packing. The *H* values measured in the neck region are much smaller than those on the isotropic part. This observation contrasts seriously to previous findings where the opposite situation was observed [13]. In addition, it should be mentioned that on the necked region of the sample an indentation anisotropy is observed, which is not presented in Fig. 2.

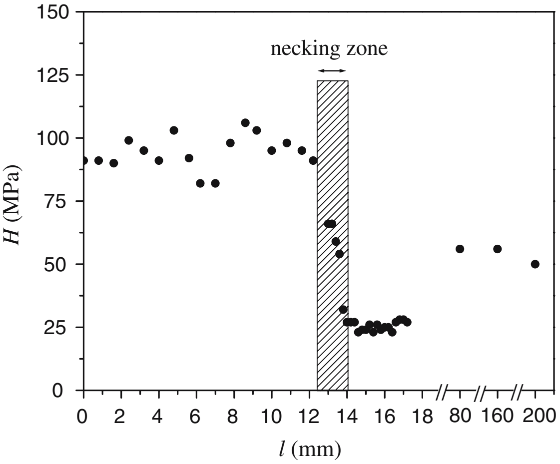

Fig. 2 Dependence of microhardness *H* as a function of the distance *l* along the drawing direction covering the isotropic (left) and the necked (right) parts of the sample (Fig. 1)

Investigations on the deformation mechanism of iPP carried out in the past [19–22] revealed that the change from the isotropic spherulitic to the fiber structure is discontinuous, showing a sudden change in long period, molecular orientation and morphology. In a very recent study [14] the deformation of β-iPP in the necking zone has been shown to involve various structural mechanisms, such as lamellar separation, microvoid formation, fibrillation and other nano-mechanical processes that contribute to a notable decrease of the microscopic density [14]. The necking process (draw ratio λ up to 5), thus, assumes drastic morphological changes involving an important decrease of crystallinity owing to the destruction of the starting isotropic structure. This transition has been recently discussed by Li and Cheung [23] in support of the mechanism of necking involving local melting of the starting structure and recrystallization in a fibrous one [24].

Comparison of experimental and calculated hardness values

It is now well established that the microhardness of semicrystalline polymers obeys the additivity law, [25]:

$$H = w_c H_c + (1 - w_c) H_a \tag{1}$$

in which H, H_c, and H_a are the microhardness values for the polymer and of the crystalline and amorphous phases, respectively, and w_c is the degree of crystallinity.

If the crystalline phase is present into two polymorphic modifications, Eq. 1 can be rewritten as:

$$H = w_c^\alpha H_c^\alpha + w_c^\beta H_c^\beta + (1 - w_c^\alpha - w_c^\beta) H_a \tag{2}$$

For the isotropic iPP material before the neck, where the β modification prevails, one can write:

$$H = w_c^{\beta} H_c^{\beta} + (1 - w_c^{\beta}) H_a \tag{3}$$

For the necked region where the α modification emerges:

$$H = w_c^{\alpha} H_c^{\alpha} (1 - w_c^{\alpha}) H_a \tag{4}$$

If one assumes that before and after necking the crystallinity remains constant: $w_c^{\alpha} = w_c^{\beta} = w_c$ one should expect a higher overall microhardness after necking because it is known that $H_c^{\beta} < H_c^{\alpha}$ [13], owing to the difference of the crystalline densities for the β and α modification ($\rho_c^{\beta} = 0.92$ g/cm^3 and $\rho_c^{\alpha} = 0.94$ g/cm^3 [2, 5]).

Let us try to examine the assumption regarding the destructive role of necking on the level of crystallinity. Figure 3 illustrates the DSC traces of a sample from the isotropic zone (before drawing) and from the plastically deformed region (at two different places with respect to the necking zone). Analysis of the normalized heat of fusion ΔH evidences a significant decrease of the degree of crystallinity after necking. Using the above reported values, ΔH_{id}^{α} and ΔH_{id}^{β}, for the ideal heat of fusion of each modification and applying the equation $w_c = \Delta H_{exp}/\Delta H_{id}^{\alpha}$, one obtains for w_c^{β} and w_c^{α} values of 49% (for the isotropic region) and 29%, (for the necked region), respectively; and $w_c^{\alpha} = 39\%$ for the plastically deformed region further away from the necking zone.

In order to calculate the overall microhardness for the samples with predominant β or α-phase one can proceed as follows: By using Eqs. 3 and 4, the values $H_c^{\beta} = 119$ MPa, $H_c^{\alpha} = 143$ MPa [26], and $H_a = 50$ MPa (average value between two previously reported values of 30 MPa [27] and 90 MPa [28]) together with the above w_c data one obtains for the isotropic and for the necked regions values of 84 and 77 MPa, respectively. The fact that the calculated value $H^{\beta} > H^{\alpha}$ reveals the relevant role of the crystallinity. If one neglects the destructive role of the necking process on the crystallinity (i.e. if one assumes $w_c^{\alpha} = w_c^{\beta}$), then the obtained value for H^{α} would be 95 MPa, i.e. $H^{\beta} < H^{\alpha}$ as previously observed [13].

The above-suggested explanation to justify the sudden hardness decrease at the β–α transition of iPP is supported by the annealing experiments reported below.

Influence of annealing on the microhardness

If one allows the isotropic and the necked regions of the sample to recrystallize under the same conditions one may expect that both regions would reach similar values of degree of crystallinity (although one may expect a higher w_c-value for the oriented material). DSC analysis can give

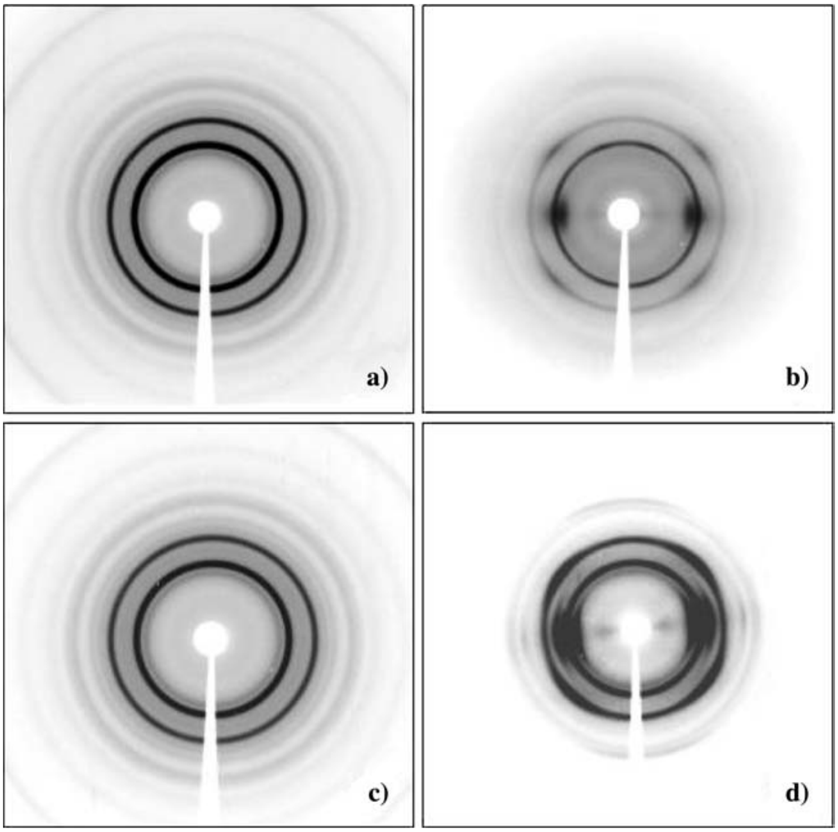

Fig. 3 WAXS patterns of the isotropic (**a**, **c**) and necked (**b**, **d**) parts of iPP samples before (**a**, **b**) and after (**c**, **d**) annealing

us an idea about the crystallinity values reached for w_c^α and w_c^β. Again by means of Eqs. 3 and 4 one may evaluate the expected H^α- and H^β-values. These experiments provide further evidence as regards to which extent the decrease of crystallinity may reduce the microhardness value.

If the observed hardness decrease (Fig. 2) would prevail after annealing, this could mean that the increasing contribution of the higher crystalline density from the α modification to H cannot compensate the lowering effect of the microvoids and other structural defects. Let us next qualitatively discuss the structural changes introduced through annealing, as revealed by the wide-angle X- ray scattering data obtained. Fig. 3 illustrates the high degree of orientation introduced into the necked part (Fig. 3b) as compared with the isotropic region (Fig. 3a). One sees that annealing at 120 °C results in an increase of crystallinity, specially in the drawn, zone where the α modification dominates (see Fig. 3d). On the other hand, in the non-stretched (isotropic) zone, where the β modification predominates, the intensity of the reflections apparently does not change after annealing (Fig. 3b).

The conclusion regarding the crystallinity increase after annealing is also supported by the DSC analysis of the annealed samples. Using the approach described above for the case of the non-annealed samples and the cited data for ΔH_{id}^β and ΔH_{id}^α the following values for w_c^β and w_c^α are now obtained after annealing: $w_c^\beta = 52\%$ and $w_c^\alpha = 58\%$. The crystallinity values after annealing are, thus, clearly higher than those measured before annealing, particularly for the necked part.

Let us next calculate the H^β and H^α values after annealing, using the w_c data derived from the DSC measurements. As expected, these values are higher than those for the unannealed samples because of the additional crystallization during the annealing process.

Finally, it is worth comparing the calculated H^β- and H^α-values with the measured ones after annealing. Figure 5 illustrates the dependence of H as a function of distance l along the drawing axis (see Fig. 1). From these data we conclude: (i) that after annealing H^β practically remains constant (the H-values scatter in the interval 75–100 MPa for the both cases, compare Figs. 4 and 5) and (ii) that this average value (showing less scattering of data) is preserved after necking (Fig. 5). In other words, in contrast to expectation, the microhardness of the necked part is practically the same as that of the isotropic one regardless of the fact that w_c^α is much higher after annealing. In addition, the measured H^α-value is significantly lower than the calculated one ($H_{cal}^\alpha = 108$ MPa against $H_{exp}^\alpha = 88$ MPa). These two observations could be explained by taking into account the decreasing effect of microvoids and other irregularities from the necked region to the overall microhardness. The occurrence of microvoids arising during the deformation is well documented for many polymers [27, 29] and particularly for iPP (in Ref. [14] and [23]).

It is convenient to stress here that the density-diluting effect of the microvoids created during necking cannot be overcome by the three following factors acting in opposite direction regarding the overall microhardness, namely: (i) the higher crystalline density of the α modification ($\rho_c^\alpha > \rho_c^\beta$), (ii) the high density of chain packing due to the high molecular orientation in the necked part (compare Fig. 3b, d), and (iii) the increased crystallinity in the necked part after annealing (58% against 29%, Fig. 3b, d).

In conclusion, the above findings confirm that the microhardness change through the β–α polymorphic transition, in the necking zone, is rather abrupt favoring the concept of local melting of the initial isotropic lamellar morphology in the neck and recrystallization into the highly oriented microfibrillar structure. At larger distances

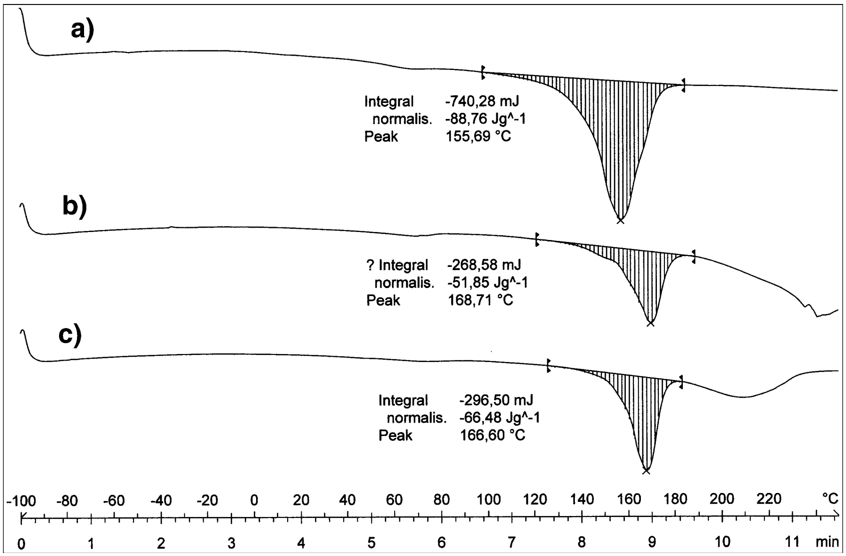

Fig. 4 DSC traces of three parts of iPP ''dumb-bell'' samples: (**a**) isotropic (unstretched) zone; (**b**) stretched zone closer to the necking boundary; (**c**) stretched zone further apart from the necking boundary

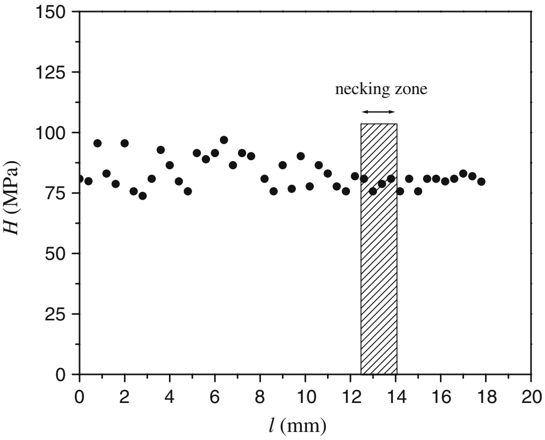

Fig. 5 Dependence of microhardness *H* as a function of the distance *l* along the drawing direction covering the isotropic (left) and the necked (right) parts of the sample after annealing

from the necking zone the emerging fibre structure is shown to give rise to a slight *H* increase. The present measurements thus indicate that the microhardness technique is a sensitive method to reveal polymorphic transitions in semicrystalline polymers.

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