Microhardness under strain. 1. Effect of stress-induced polymorphic transition of poly(butylene terephthalate) on microhardness

S. Fakirov*, D. Boneva*, F.J. Baltá Calleja, M. Krumova

Instituto de Estructura de la Materia, CSIC, Serrano 119. 28006 Madrid, Spain.

A.A. Apostolov

University of Sofia, Laboratory on Structure and Properties of Polymers
1126 Sofia, Bulgaria.

Keywords: poly(butylene terephthalate), microhardness, polymorphic transition.

Paper submitted to *J. Mater. Sci. Lett.*

June, 1997

*) Permanent address: University of Sofia, Laboratory on Structure and Properties of Polymers
1126 Sofia, Bulgaria

Poly(butylene terephthalate) (PBT) or poly(tetramethylene terephthalate) became the subject of much interest in the mid 1970s when three groups of workers [1-3] independently reported that it could crystallize in two distinct polymorphic forms. The α -form was found in a relaxed sample, whereas the β -form could only be observed when the sample was held under strain. There have been a number of attempts to determine the unit cell parameters for the two crystalline forms [3-6], and there is still some degree of controversy. However, the general consensus is that in the α -form the molecular chain is not fully extended, probably with the glycol residue in a *gauche-trans-gauche* conformation, whereas in the β -form the chain is fully extended with the glycol residue in the all *trans* conformation. There has been considerable interest in the mechanisms of the $\alpha - \beta$ transition, and this has been modeled for static and dynamic measurements [7,8].

The microindentation hardness technique provides a rapid evaluation of variations in surface mechanical properties of polymers affected by changes in processing or chemical conditions, heat treatment, microstructure and ageing [9]. In order to determine the irreversible contribution to deformation, static indentation, involving the formation of a local permanent surface impression is commonly used [10]. In polymers, such as polyethylene, displaying a lamellar morphology of stiff flat crystals intercalated by "amorphous" compliant layers, the microhardness (H) of such a system can be described by a simple additive model (parallel model) [11]:

$$H = H_c w_c + (1 - w_c) H_a \quad (1)$$

where H_c and H_a are the hardness values of crystalline and amorphous components, respectively, and w_c is the mass fraction of the crystalline phase. The crystal hardness, H_c , has been shown to depend on the average thickness ℓ , of the crystalline lamellae [12]. In systems, however, where w_c and ℓ remain constant, H_c , is a function of chain packing within the crystalline phase [13]. Crystal hardness – critical stress required to plastically deform the crystal – hence, reflects its response to the intermolecular forces holding the chains within the lattice and is a function of cohesion energy [13].

It has been demonstrated that microhardness is a technique capable of detecting polymorphic changes in polymers [14]. In particular the study of transition from the α - to the β -form in isotactic polypropylene (iPP) confirmed that the changes in H can be ex-

plained in terms of an additive contribution to the H of independent phase components H_c^α , H_c^β and H_a [14]. This approach opens up the possibility of characterizing iPP samples consisting of a mixture of α - and β -phases by means of H measurements.

The aim of the present study is to examine the influence of stress-induced polymorphic changes on the values of microhardness. While in the case of iPP [14] two samples comprising the α - or β -phase were characterized, in the present case it is aimed to follow the microhardness behaviour during the $\alpha - \beta$ polymorphic transition caused, for example by a mechanical field. For this purpose PBT was selected as a material known to undergo stress-induced polymorphic transition from α (relaxed) form to β (strained) form [1-3].

Bristles of commercial PBT with dia of about 1 mm were drawn at room temperature via neck formation (final dia about 0,5 mm and draw ratio of 3,4) and thereafter annealed at 200°C for 6 h with fixed ends in a vacuum oven.

Although the stress-induced $\alpha - \beta$ polymorphic transition in PBT is well documented, comparative wide-angle X-ray scattering (WAXS) measurements of the samples were carried out in the same deformation range at which the H measurement are performed. In addition, the size of the coherently diffracting domains (crystal size) D_{hkl} in the (100) and (010) and ($\bar{1}$ 04) directions ("c"-axis) during stretching, was calculated from the integral breadth of the equatorial reflexions according to $\delta\beta \sim 1/D_{hkl}$ [15].

For this purpose a Siemens diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation was used, in the transmission mode. By means of a sample holder for a single fiber which allows a stepwise increase of the strain, both, equatorial (in the range $2\theta = 10$ to 30°) and meridional reflexions (in the range $2\theta = 25$ to 35° where the ($\bar{1}$ 04) reflection for the two modifications is situated), were taken at selected deformations.

To determine the degree of crystallinity, w_c (WAXS), a standard procedure was used. The amorphous peak (which was determined by the WAXS 0pattern of molten PBT) was subtracted from the total diffracted area to yield I_c , the diffraction portion attributed to the crystalline regions. The value of w_c (WAXS) was computed as the ratio of the integrated area under the crystalline peaks to the total integrated area I_t under the WAXS scan ($\Sigma I_c / \Sigma I_t$). This technique has the advantage, in contrast to calorimetry or density measurements, that is applicable to samples which are under strain. Nonetheless, for

the sake of comparison, differential scanning calorimetry was also used for the unstrained sample of PBT. Very narrow and sharp melting peaks were obtained showing a degree of crystallinity of 44,2% which is very close to that obtained from WAXS.

Microhardness was measured at room temperature using a Leitz tester adapted with a square-pyramidal diamond indenter. 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 [10]. A loading cycle of 0.1 min was used. Loads of 147 and 245 mN were employed to eliminate the instant elastic contribution. 10 indentations were made for each point.

H measurements under strain up to 20% relative deformation (ε) were performed using a stretching device. The deformation ε is defined as $\varepsilon = \frac{\ell - \ell_0}{\ell_0}$ where ℓ_0 and ℓ are the starting and a given length of the sample, respectively. The indentation anisotropy $\Delta H = 1 - (d_{\parallel}/d_{\perp})^2$ was also derived. In order to evaluate the contribution of each polymorphic phase to the total H -value it was necessary to know their mass fraction at the different deformation stages as required by the additive law (eq 1). For this purpose the data of Tashiro et al [16] obtained by IR study of the $\alpha - \beta$ transition were used. It was previously shown [16] that just in the transition deformation interval ($\varepsilon = 4-16\%$) the relationship between ε and the amount of the β -phase is linear.

The values obtained are summarized in Table 1. The variation of strain on the H value is also presented graphically in Fig 1. One can see a very well defined decrease in the H -values (from 150 to 120 MPa) in a rather narrow deformation interval (ε between 5 and 8%). Before this drop of H ($\varepsilon = 0-5\%$) the microhardness has a relatively constant value of about 150 MPa typical for semicrystalline PBT [17]. After reaching its lowest value ($H = 118$ MPa) around $\varepsilon = 10\%$, H starts to increase almost linearly up to 190 MPa with the further rise of deformation up to $\varepsilon = 20\%$ when the sample breaks.

Fig 2 shows the WAXS radial scans of the ($\bar{1}04$) reflection of PBT taken at different stages of tensile deformation. One can see that the angular peak position for the relaxed and slightly deformed ($\varepsilon = 5,3\%$) samples is the same ($2\theta = 31.5^\circ$) in contrast to the samples deformed at higher strains ($\varepsilon = 12.9$ and 21.2%) for which the maximum is shifted to lower angles ($2\theta = 28$). The observed change in the peak position is in agreement with

former reports [1-3] and demonstrates that in the deformation interval between $\varepsilon = 5$ and 12% a stress-induced polymorphic transition takes place.

The fact that the abrupt drop in the H-value (Fig 1) coincides with the well documented $\alpha - \beta$ transition just in the deformation interval between 4 and 10-12% [2] shows that the observed changes in H-values (Fig 1) are related exclusively with the stress-induced polymorphic transition. Thus, the starting value of $H = 155$ MPa should be typical for PBT containing the crystalline α -phase and the lower value of $H = 118$ MPa can be assigned to PBT comprising in addition the crystalline β -phase. The observation that $H^\alpha > H^\beta$ is related obviously to the fact that the α -modification is distinguished by a denser packing of chains as can be concluded from the ideal crystal densities. According to the comparison [4] of the published crystalline polymorphic structures the volume of the unit cell for the α -phase varies between 260.0 and 262.8 Å³ and that of β -phase – between 268.9 and 285.0 Å³ [4]. As mentioned above, it has been demonstrated [13] that in cases when w_c and ℓ do not change, the crystallites hardness H_c depends exclusively on the chain packing within the crystalline phase. In this way one can explain why $H^\alpha > H^\beta$, although other factors acting in the same direction can also exist.

The obtained strong increase on H after completing the stress-induced polymorphic transition (from 118 up to 150 MPa) can be explained by the additional orientation of chains in amorphous regions which results in an additional densification of the total structure. As a matter of fact this densification effect should take place during the earlier stages of deformation where the indentation anisotropy also increases (Table 1). However, in this case it is compensated by the effect on H of the stress – induced polymorphic transition. Furthermore, it is hardly to expect that the observed increase in H-values after the polymorphic transition (Fig 1) is due to an increase of crystallinity during stretching since such a change cannot be found in the diffractograms of the WAXS (Table 1).

Let us come back to the most interesting part of Fig 1 – the deformation range in which the $\alpha - \beta$ transition occurs. The experimentally measured values of H allow one to calculate the H^β value provided the mass fraction of the crystallites of β -type is known.

For this purpose let us present eq. 1 in the following form:

$$H = H_c^\alpha w_c^\alpha + H_c^\beta w_c^\beta + [1 - (w_c^\alpha + w_c^\beta)] H_a \quad (2)$$

where $w_c^\alpha + w_c^\beta = w_c$ are the mass fractions of α - and β -crystallites, respectively. Making use of the observation [16] that in the transition interval a linear relationship between the deformation ε and the amount of β -phase obtained as a result of $\alpha - \beta$ transition exists, we can evaluate the w_c^β at each deformation stage in the deformation interval 4–16% (Table 1). For the hardness of the amorphous phase the value $H_a = 54$ MPa [17] was taken. The values of H_c^α for each strain were defined for the corresponding crystal thickness value using the expression:

$$H_c = H_c^\infty / (1 + b/l_c) \quad (3)$$

where $H_c^\infty = 369$ MPa is the hardness value for infinitely large PBT crystals and the $b = 15$ Å, as found in ref 17.

Assuming that the amorphous phase does not crystallize further during this deformation interval, as it is done for similar analysis in [16] and proven by WAXS in the present case (as can be concluded from the values of w_c in Table 1), one obtains for H_c^β values between 100 and 190 MPa. It is noteworthy, that all the H_c^β -values can be grouped into 3 ranges (Table 1): a) in the deformation range before starting the stress-induced polymorphic transition, $H_c^\beta = 150$ –190 MPa; b) in the range where the transition is completed ($\varepsilon = 10$ –12%), $H_c^\beta \approx 110$ MPa; c) in the range of larger deformations after completing the transition, $H_c^\beta = 150$ –180 MPa. One can assume that the most reliable values are those around 120 MPa for the following reasons. In the first group the amount of the β -modification is relatively low (below 10%); the higher H_c^β -values in the deformation range above $\varepsilon=14\%$ (Fig 1) can be hardly related to the β -phase. One can assume that the calculated increase of H_c^β in this deformation interval (Fig 1) originates from the increase of the measured overall H due to the additional orientation of the amorphous phase giving rise to H_a . Such an assumption is supported by the systematic change in the indentation anisotropy ΔH as can be concluded from Table 1. For this reason one can accept for H_c^β the value of 122 MPa. In fact, this value corresponds to the microhardness of fully crystalline PBT comprising crystallites only of the β -type. For comparison, let

us remind that for the α -phase this value amounts to $H_c^\alpha = 287$ MPa [17] which is considerably higher than H_c^β found in the present measurements. What could be the reason for this relatively large difference in the microhardness of the two polymorphic phases? In addition to the above mentioned difference in the unit cell volumes leading to lower H_c^β values there are at least other two factors acting in the same direction. It should be stressed, as outlined above, that the packaging density will be the only H-determining factor in case the crystal sizes remain constant as well as the crystal mass fraction. This is not the case in the present study at least with respect of crystal sizes as can be seen from the data presented in Table 2. A significant decrease (up to 2-3 times) of crystal sizes in the (100) and (010) directions has been found (Table 2). This observation is in a very good agreement with the results of Ward et al [18]. Even more, in addition to the smaller crystal sizes found after the polymorphic transition, the above authors concluded that in order for such small crystals to be stable they should be poorly connected to the bulk polymer [18]. Both outlined peculiarities of the β -phase will contribute to a decrease of H. In order to estimate the contributions of crystal size to the H-value it is convenient to recall that recent measurements on polyamide 6 showed that a decrease in the crystal size from 106 Å to 33 Å results in a reduction in the overall microhardness by 20% keeping the crystalline mass fraction constant [19].

In conclusion, in the present work we have shown that microindentation hardness allows to follow the strain-induced polymorphic transition in PBT. The observed rather sharp change in the H-values (within 2-4% of external deformation) makes the method competitive with respect to sensitivity to other commonly used techniques such as WAXS, IR, Raman spectroscopy and others [1-7,16]. Furthermore, by applying the additive law it was possible to calculate the H-value of completely crystalline PBT comprising crystallites of β -type as $H_c^\beta = 122$ MPa. The technique can be used for examination of stress induced polymorphic behaviour of PBT in its copolymers and blends. These studies are in progress.

Acknowledgements

The authors are grateful to DGICYT, Spain (Grant PB94-0049) for the support of this investigation. The partial support of DFG, Germany (Grant DFG-FR 675/21-1) is also highly appreciated. One of us (S.F.) deeply appreciates the tenure of a sabbatical grant from DGICYT, Spain.

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Figure captions

Fig 1 Effect of deformation ε on the microhardness H of PBT.

Fig 2 Radial scans of the $(\bar{1}04)$ reflection of drawn annealed PBT bristles taken at various tensile deformations ε .

Table 1 Microhardness H , indentation anisotropy, X-ray crystallinity, percentage of α and β modifications [16] and crystal hardness of PBT stretched at various strains.

Property	Strain, ε (%)										
	0	2	4	6	8	10	12	14	16	18	20
$H_{\perp}$ (MPa)	152.9	144.8	156.0	144.4	126.6	118.2	120.2	125.7	133.7	144.4	193.5
ΔH^{25}	-0.0338	0.0071	0.0656	0.1603	0.2026	0.3799	0.2461	0.4059	0.3796	0.2460	0.4054
w_c (WAXS) (%)	47	47	48	48	49	50	50	50	49	47	46
α -phase (%)	43.0	40.3	38.9	34.2	30.5	26.6	21.6	17.9	16.3	-	-
β -phase (%)	4.0	6.7	9.1	13.8	18.5	23.4	28.4	32.1	32.7	-	-
H_c^{β} (MPa)	193.7	137.6	179.2	155.3	93.1	100.6	122.4	147.3	181.5	-	-

Table 2 Crystal size, D of PBT stretched at various strains.

Crystal size ($\text{\AA}$)	Strain, ε (%)			
	0	5.3	12.9	21.2
$D_{(100)}$	84.1	51.9	36.9	36.8
$D_{(010)}$	132.5	109.3	43.7	37.2
$D_{(\bar{1}04)}$	40.8	44.9	40.75	49.5

Fig 1

Fig 2