Microhardness under strain. 2. Microhardness behaviour during stress-induced polymorphic transition in block copolymers of poly(butylene terephthalate)

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Abstract

In addition to homopoly(butylene terephthalate) (PBT) the microhardness technique was applied to its multiblock copolymers for examination of the stress-induced polymorphic transition. Drawn and annealed at 170°C for 6 h with fixed ends in a vacuum, bristles of poly(ether ester) (PEE) having PBT as hard segments and poly(ethylene oxide) (PEO) with mol.wt. 1000 as soft segments (PBT/PEO = 57/43 wt%) were characterized with respect to their microhardness (H) at various stages of tensile deformation. A sharp H-decrease (by 20%) in a narrow deformation interval (2-4%) due to the stress-induced $\alpha \rightleftharpoons \beta$ polymorphic transition is observed followed by an increase and decrease of H. The transition is registered at much higher relative tensile deformations (between 25 and 30%) in contrast to the case of homo PBT. This is explained by the presence of a very soft amorphous phase of PEO which deforms first. The same phase, distinguished by low viscosity in which the PBT crystallites are "floating", is the reason for the very low H-values measured (between 25 and 35 MPa, depending on the amount of α and β modifications). The stress-induced polymorphic transition in copolymers of PBT with PEO is demonstrated for the first time, supporting additionally the recently proposed concept of the microhardness depression effect.

Introduction

When polymers are crystallized from melt or solution, their crystalline region may exhibit various types of polymorphic modifications, depending on the cooling rate, evaporation rate of solvent, temperature, and other conditions. These crystal modifications are different in their molecular and crystal structures as well as in their physical properties. Many types of crystalline modifications have been reported [1].

Some polymorphic modifications can be converted from one into another by a change in temperature. Phase transitions can be also induced by an external stress field. Phase transitions under tensile stress can be observed in natural rubber when it orients and crystallizes under tension and reverts to its original amorphous state by relaxation [2]. Stress-induced transitions are also observed in some crystalline polymers, eg. poly(butylene

terephthalate) (PBT) [3,4] and its block copolymers with poly(tetramethylene oxide) (PTMO) [5], poly(ethylene oxide) (PEO) [6,7], polyoxacyclobutane [8], nylon-6 [9], poly(vinylidene fluoride) [10,11], polypivalolactone [12], keratin [13,14], and others. These stress-induced phase transitions are either reversible, where the crystal structure reverts to the original structure on relaxation, or irreversible, where the newly formed structure does not revert after relaxation. Examples of the former include PBT, PEO, and keratin.

Two crystalline phases of PBT can appear under tension and relaxation: the so called β -form and α -form, respectively [14,15]. The main difference in the molecular structure between the α and the β form lies in the methylene conformation.

X-ray diffraction patterns and infrared-Raman spectra show specific changes through this $\alpha \rightleftharpoons \beta$ transition [3-5,16-18]. The stress and strain dependence of the molar fraction of the β form, X_β , can be evaluated by quantitative analysis of the infrared spectra [16]. The characteristic behaviour of this phase transition observed in an uniaxially oriented sample is as follows: the X_β increases drastically above the critical stress f^* ; the fraction X_β is almost linearly proportional to the strain; the transition is reversible; and the stress-strain curve has a plateau at the critical stress f^* , that is, the curve is divided into three regions: the elastic deformation of the α phase (0-4% strain), the $\alpha \rightleftharpoons \beta$ transition (plateau region; 4-12% strain), and the elastic deformation of the β phase (>12% strain). These experimental results indicate that this stress-induced phase transition is a thermodynamic first-order transition.

It has been also pointed out [5] that in block copolymers of PBT and PTMO, the transition is smeared over a wide range of stresses due to the effect of the PTMO soft segments [5].

It is known [19,20] that the microhardness (H) technique is a simple, non-destructive method capable to follow the surface mechanical properties of polymers depending on processing conditions, heat treatment, microstructure characteristics, aging and other

physical treatments [20]. The crystal hardness H_c , has been shown to depend on the average thickness ℓ , of the crystalline lamellae [21]. In systems, however, where the degree of crystallinity w_c and ℓ remain constant, H_c , is a function of chain packing within the crystalline phase [22]. 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 [22].

This peculiarity of the microhardness technique makes it possible to distinguish between polymorphic modifications of the same polymer as convincingly demonstrated for polypropylene [23]. In a very recent study [24] on PBT, known as a polymer capable to undergo a reversible stress-induced polymorphic transition [3-5,15-18], it was demonstrated that the microhardness technique can also be applied successfully for detecting and following this transition. The observed very sharp change in H-values (within 2-4% of external overall deformation) makes the method competitive with respect to the sensitivity of such other commonly used techniques as wide-angle X-ray scattering (WAXS), IR- and Raman spectroscopy, and others [3-5,15-18]. Furthermore, by means of the additive law

$$H = \sum H_i \varphi_i \quad (1)$$

where H_i and φ_i are the hardness and the weight fraction of each component and/or phase of the system, it was possible to evaluate the H-value of completely crystalline PBT comprising crystallites of the β -modification.

The aim of the present study is to examine the microhardness behaviour during the stress-induced polymorphic transition of PBT in its block copolymers, for some of which this transition is very smeared [5]. An additional reason for performing this work is the fact that the copolymers of PBT with poly(ethylene oxide) (PEO) and/or polycarbonate (PC) were not so far studied with reference to polymorphic transitions. The very detailed structural characterization of the copolymers with PEO [25-30] is expected to shed more light on the understanding of the microhardness behaviour.

Experimental

Materials

The starting material represents a polyblock poly(ether ester) PEE comprising PBT as hard segments and PEO with a molecular weight of 1000 and polydispersity of 1.3, according to gel permeation chromatography analysis [25], as soft segments in a ratio of 57/43 wt%. The synthesis was carried out on a semicommercial scale as described elsewhere [32]. The BFSA-2 stabilizer was chosen since it leads to the best mechanical properties of PEE in comparison to five other stabilizers keeping at the same time a comparatively high relative viscosity of 1.66. The sample was shaped as a bristle, drawn at room temperature to five times its initial length, and then annealed with fixed ends for 6 h in vacuum at a temperature of 170°C. The initial material used for measurements was highly oriented with a dominating α -modification of PBT (see Table 1).

Techniques

A Siemens diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation was used to obtain wide-angle X-ray scattering (WAXS) equatorial and meridional diffractograms of drawn and annealed samples at selected deformation stages. The X-ray diffractograms were also used to estimate the relative degree of crystallinity. It is known that the true value for the degree of crystallinity of oriented polymers cannot be obtained from the WAXS patterns unless a randomization of the orientation is undertaken [33]. We have derived “relative crystallinity” values from the equatorial scan ($2\theta = 12 - 36^\circ$) taken in the transmission mode. These values should be considered only as an indication of the expected trend in the crystallinity development. Thus, to determine “relative crystallinity”, w_c (WAXS), the amorphous peak (the shape of which is determined by the WAXS patterns of molten PBT) is fitted to the diffraction curve so that it intersects at some points near its maximum with crystalline minima; the area under the amorphous curve is subtracted from the total diffraction pattern to yield I_c , the portion of the diffraction attributable to the crystalline regions. The crystallinity w_c is computed as the ratio of the integrated area under the crystalline peaks to the total integrated area I_t under the WAXS scan ($\Sigma I_c / \Sigma I_t$).

Microhardness was measured at room temperature using a Leitz tester adapted with a square-pyramidal diamond indenter. The H values were 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 [20]. A loading cycle of 0.1 min was used. Loads of 150 mN and 250 mN were employed to eliminate the instant elastic contribution. The value of H for each deformation was derived from an average of 10 indentations.

Deformation measurements up to 80% overall relative deformation ε , after which the sample breaks, were performed by means of a stretching device. The elongation ε is defined as $\varepsilon = \frac{\ell - \ell_0}{\ell_0}$ where ℓ_0 and ℓ are the starting length and the length of the sample after a given deformation, respectively. The indentation anisotropy $\Delta H = 1 - (d_{\parallel}/d_{\perp})^2$ was also determined.

Although the stress-induced $\alpha \rightarrow \beta$ polymorphic transition in PBT is well documented, comparative WAXS measurements were carried out on the same samples in the same deformation range.

Results

The microhardness, the degree of crystallinity and the percentage of α and β -phase are summarized in Table 1. The dependence of the microhardness H on the deformation ε for drawn and annealed bristles of PEE (PBT/PEO = 57/43) is plotted in Fig 1. One can see that the H variation presents several regimes depending on the stress applied. At the lowest deformations (ε up to 25%) H is nearly constant (~ 33 MPa) and thereafter, in a very narrow deformation interval ($\varepsilon = 2-3\%$) the H -value suddenly drops by 30% reaching the value of 24 MPa which is maintained in the ε -range between 30 and 40%. With further ε increase (between 40 and 60%) H then increases up to nearly its starting value followed by decrease again to 25 MPa for $\varepsilon \sim 60$ to 80%.

The most striking change in the H behaviour is the sharp decrease at $\varepsilon = 25-27\%$. Taking into account the recent similar study on homo-PBT [24] where a similar change has been observed (a drop in H by 20%) due to the well documented stress-induced polymorphic transition in PBT, one can assume that in the present case also the same

transition takes place.

The fact that the $\alpha - \beta$ polymorphic transition in the PEE under investigation occurs at a much higher deformation (around $\varepsilon = 27\%$) in comparison to the homo-PBT where it was observed at ε between 5 and 10% [24] can be explained by the peculiar behaviour of the thermoplastic elastomers.

In a preceding study [25-31] we showed that the deformation of PEE with varying PBT/PEO ratio deformed in the 25-50% range is related to the conformational changes in the amorphous regions, the crystallites remaining untouched. The stretching and relaxation of these amorphous segments causes an affine and reversible change of the measured X-ray long spacing [25-31]. With further increase of deformation (for PEE with compositions as in the present case – starting at $\varepsilon = 25-30\%$) the external load is transferred to the crystallites contributing to the observed polymorphic transition (Fig 1, [24]).

The drop in the microhardness is due to the fact that the β -phase has a lower density in comparison to the α -phase [34] as concluded in our previous study [24].

Additional support of the assumption concerning the stress-induced polymorphic transition around $\varepsilon = 27\%$ can be found in our WAXS study on the same samples in the same deformation interval.

Fig 2 illustrates the radial (near meridional) scans of the $(\bar{1}04)$ reflection of PBT taken from drawn and annealed PEE (PBT/PEO = 57/43) at various tensile deformations. One sees that up to $\varepsilon = 12\%$ the angular position of the $(\bar{1}04)$ peak remains unchanged. The same is also true for the diffractogram taken at $\varepsilon = 28.8\%$ though, in contrast to the previous ones here one sees indication for another peak at a lower angle ($\sim 27^\circ$). This tendency is very well defined on the diffractogram taken at $\varepsilon = 58.8\%$ where the intensity of the new peak is higher than that of the starting one. This observation on PEE is in accordance with previous [17,35,36] WAXS studies of homo-PBT during the stress-induced polymorphic transition.

Similar changes can be found on equatorial scans of drawn and annealed PEE (PBT/PEO = 57/43) taken at various tensile deformations. Some of the diffractograms are presented in Fig 3. Once again, the drastic changes, both with respect to the peak shape and peak angular position, can be detected at $\varepsilon = 28.8$ and 58.8% . These diffrac-

tograms (Fig 3) were used for evaluation of the “relative crystallinity” w_c (WAXS) at various stages of sample deformation (Table 1) since calorimetry or density measurements cannot be used for strained samples.

Let us come back to Fig 1 and follow the H variation as a function of ε . The observed H increase resulting in a restoration of the initial microhardness cannot be related to a regeneration of the α -phase, distinguished by a higher microhardness H^α , because the sample is under stress. In order to explain the observed H increase one has to remember a peculiarity of the system: – PEE is a physical network where the crystallites are the cross-links. In addition, the crystallites are embedded in a soft amorphous matrix, i.e. they are “floating” in a relatively low-viscosity matrix. During the deformation the network will stretch further depending on the relative “softness” of the various components of the system. The stretching of the amorphous segments restricts the mobility of the crystallites and makes the system harder. In other words, the decrease of H caused by replacement of crystallites of a higher H by others of lower H is compensated by this hardening effect caused by stretching of the network.

In addition to the assumed hardening of the noncrystalline phases, in the same direction simultaneously acts the crystallization of the PEO soft segments in PEE in the same deformation range.

As shown in Fig 3, the scattering curves at $\varepsilon = 28.8\%$ and $\varepsilon = 58.8\%$ are different from the previous ones. Their shape indicates overlapping of two independent reflections from two different cells. The lower-angle one (15.5°) arises from the β modification of PBT-segments in PEE as a result of the polymorphic transition, as shown in former studies [36,24]. The higher-angle one belongs not only to (100) and ($1\bar{1}1$) of PBT ($\theta = 22.6$ and 24.6°) but also to the planar zigzag modification of poly(ethylene oxide) under tension [6,7], reflections (010) and ($\bar{1}10$). These two reflections are approximately at the same angular position and, for this reason, are not separated [6]. For the next, higher deformation of 58.8% (Fig 3) the PBT-reflections becomes weaker and larger and together with the PEO-reflections they all merge in one large reflection at approximately $2\theta = 24^\circ$. The zig-zag modification of PEO, formed at high tensile deformations [37] is expected to show a higher microhardness H_c , due to its higher crystal density [6,37]

in comparison to the H_c of the usual (7/2) helix modification of PEO, existing without tensile deformation.

The subsequent decrease of H in Fig1 down to again 25 MPa at the highest deformation ($\varepsilon = 60\text{--}80\%$) can be explained by a partial destruction of crystallites due to the pulling out of hard segments. This mechanism has been demonstrated by SAXS [25-30] and WAXS [31] measurements. The introduction in this way of defects in the crystallites may induce a decrease in their H value.

In addition to the gradual decrease of perfection of the crystallites in the deformation range 60–80%, the changes in the overall orientation have the same effect on the H as can be concluded from the microhardness anisotropy plotted in Fig 4. Up to $\varepsilon = 50\text{--}55\%$ a nearly linear continuous increase of the anisotropy is observed followed by a tendency to a leveling off. As shown in previous studies [25-31] the external deformation at this stage is related mostly to slippage of microfibrils or their assemblies as well as possible splitting between fibrils. But it does not arise anymore from conformational changes contributing to the improvement of the overall deformation.

Discussion

A characteristic feature of the material under investigation is its very low microhardness – between 25 and 35 MPa depending on the crystalline modification present. These values are up to 5–6 times lower than those for semicrystalline homo-PBT regardless of the crystalline modification. Even more, the obtained values for H of PEE (Table 1, Fig 1) are about twice lower than the amorphous hardness, H_a , of PBT, being 54 MPa [38]. This means that there should be other factors responsible for the very low H -values of the copolymer.

It is generally accepted [19,20] that microhardness is primarily determined by the crystalline phase, which in the case of polymers is always dispersed in an amorphous matrix. In the present case the PBT crystallites are embedded in a two-phase amorphous matrix, the amorphous PBT segments and the soft PEO segments. The latter are distinguished by very low viscosity at room temperature – PEO of mol.wt 1000 melts around 30°C and being incorporated in a polymer chain its T_m is even lower – around 0°C [39].

This means that during the first H decrease (see Fig 1), PEO is in a molten state. It is worth mentioning that for the same reason the observed stress-induced polymorphic transition cannot arise from PEO, even though basically it is known that PEO is capable to undergo such a transition [6,7].

By means of the additive hardness law (eq 1) one can try to evaluate the contribution of the soft segments amorphous phase to the overall microhardness. For a four phase system as in the present case (two crystalline modifications and two amorphous phases), eq 1 can be presented in the following way:

$$H = \varphi \left[H_c^\alpha w_c^\alpha + H_c^\beta w_c^\beta + (1 - w_c^\alpha - w_c^\beta) H_a \right] + (1 - \varphi) H_{soft} \quad (2)$$

where φ is the mass fraction of the hard PBT segments, w_c^α and w_c^β – the degree of crystallinity values of both α and β modifications of PBT, H_c^α and H_c^β – their microhardness values, $\varphi (1 - w_c^\alpha - w_c^\beta)$ – the mass fraction of amorphous PBT with a microhardness H_a , and $(1 - \varphi)$ – the mass fraction of the soft segments having a microhardness H_{soft} .

If we assume for H_c^β the value of 122 MPa which was recently obtained from the study of the stress-induced polymorphic transition in homo PBT by microhardness [24], then the calculations of H for both cases, before the stress induced polymorphic transition ($H = 34$ MPa) and after this transition ($H = 24$ MPa) would lead to negative values of H_{soft} –112 and –70 MPa, respectively, which are of course not physically acceptable.

For this reason one has to revise the deformation mechanism during microhardness determination commonly used for complex systems comprising components having T_g values above room temperature. For these purpose it is convenient to remember the structural peculiarity of the system under investigation. The fact that PBT crystallites are “floating” in a matrix of low viscosity has important consequences on the microhardness behaviour. By floating in a liquid of low viscosity, the crystallites of PBT as well as the PBT amorphous phase cannot respond properly to the external stress to demonstrate in this way their inherent microhardness, but they are doing this mostly via the response of the liquid matrix.

Quite a similar situation was recently observed [40] by studying the microhardness behaviour of thermoplastic elastomers of poly(ether ester carbonate) type comprising PBT as hard segments (60 wt%) and PTMO and aliphatic polycarbonate (PC) as soft

segments. In those cases the microhardness depression (difference between calculated from eq.(2) and measured value) $\Delta H = 35\text{--}55$ MPa was similar to the depression estimated in the present case and H_{soft} was evaluated to be between -90 and -140 MPa, depending on the amount of PC in the soft phase.

Obviously in both cases the contribution of the soft segment phases–PEO– or PTMO– based to the overall mechanical resistance against the external stress takes place via their viscosity. In contrast to the other soft amorphous solids the viscosity of these soft phases is not high enough to be characterized by means of microhardness (for which a residual indentation impression should be formed). For this reason such low–viscosity liquids exhibit a microhardness decreasing effect. The latter is the higher the lower the viscosity of the liquid–like phase (component).

Conclusions

Summarizing it can be concluded that in addition to the recent study on stress-induced polymorphic transition in homo PBT by means of the microhardness technique, in the present case it is demonstrated that this method can be successfully applied for the same purpose to copolymers of PBT. A relatively sharp (within 2–4% of deformation) drop in H is observed but in contrast to homo PBT it occurs at much higher deformations (between 25 and 30%). This difference, as well as the following increase and decrease of H , are related to the structural peculiarities of thermoplastic elastomers – presence of a soft amorphous phase which first deforms, and the existence of a physical network.

The very low H values obtained for PEE are related to the fact that the PBT crystallites are “floating” in an amorphous matrix characterized by a low viscosity.

The observed stress induced polymorphic transition in a multiblock of PBT with poly(ethylene oxide) is reported for first time.

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Figure captions

Fig 1 Microhardness H vs overall relative tensile deformation ε of drawn and annealed PEE (PBT/PEO = 57/43) bristles.

Fig 2 Radial scans of the $(\bar{1}04)$ reflection of drawn and annealed PEE (PBT/PEO = 57/43) bristles taken at various elongations ε (the ε -values are given in the respective diffractograms).

Fig 3 Equatorial scans of drawn and annealed PEE (PBT/PEO = 57/43) bristles taken at various elongations ε (the ε -values are given in the respective diffractograms).

Fig 4 Indentation anisotropy ΔH vs overall relative tensile deformation ε at measured loads of: (O) – 0.15 N and (Δ) – 0.25 N.

Table 1 Microhardness, “relative crystallinity” and crystal modifications of block copolymers of PBT (drawn 500% and annealed at 170°C) at different strains.

Property	Strain (%)																
	0	5	10	12	15	20	25	30	35	40	45	50	55	60	65	70	80
H_α MPa	34.2	26.6	32.7	–	32.4	33.8	34.2	24.2	24.2	27,0	29.1	29.5	32.7	33.5	28.7	30.2	15.8
w_c (WAXS) (%)	37	32	33	29	–	–	–	25	–	–	–	–	–	22	–	–	–
α -phase (%)	33.9	27.9	28.1	24.3	–	–	–	15.55	–	–	–	–	–	7.3	–	–	–
β -phase (%)	3.1	4.1	4.9	4.7	–	–	–	9.45	–	–	–	–	–	14.7	–	–	–

FIG. 1. Microhardness H versus overall relative tensile deformation ϵ of drawn and annealed PEE (PBT/PEO = 57/43) bristles.

FIG. 2. Radial scans of the (104) reflection of drawn and annealed PEE (PBT/PEO = 57/43) bristles taken at various elongations ϵ (the ϵ values are given in the respective diffractograms).

Fig. 3

Fig. 4