Microhardness under strain. 4. Reversible microhardness in polyblock thermoplastic elastomers with poly(butylene terephthalate) as hard segments

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Abstract

The microhardness (H) technique was recently applied to poly(butylene terephthalate) (PBT) and its multiblock copolymers for examination of the stress-induced polymorphic transition. Following these investigations the present study attempts to observe the reversible variation of microhardness under strain. For this purpose bristles of drawn and annealed (at 160°C in vacuum) poly(ether ester) (PEE) were characterized with respect to their microhardness at various stages of tensile deformation. H was measured under and after loading (σ) in deformation steps of 5% each. In accordance with previous results on PBT and PEE, H values at $\sigma \neq 0$ show a sharp drop (by 40%) in a relatively narrow deformation interval ($\epsilon = 10\text{-}15\%$), owing to the stress-induced $\alpha \rightleftharpoons \beta$ polymorphic transition. The hardness measurements at $\sigma = 0$ show a continuous decrease of H with a remaining strain. H values at $\sigma = 0$ corresponding to plastic deformation up to 5% are much higher than the corresponding ones taken under stress at an overall deformation between 10 and 25%. The higher H-values are explained by the regeneration of the starting α modification characterized by a higher H-value. Results reveal that in materials characterized by high and reversible deformability it is possible to observe a reversible microhardness behaviour provided the strain-induced structural changes are reversible.

Introduction

In a series of preceding studies we investigated¹⁻³⁾ the microhardness behaviour of various polymers under strain. The systems selected: homo poly(butylene terephthalate) (PBT)¹⁾, its multiblock copolymers with poly(ethylene glycol) (PEG)²⁾ and the blends of PBT with the same copolymers being thermoplastic elastomers of poly(ether ester) (PEE) type³⁾ – are characterized by the unique ability to undergo a strain-induced polymorphic transition. Such a behaviour is related to the peculiarity of PBT which can crystallize into two distinct polymorphic forms⁴⁻⁶⁾: the α -form which is found in the relaxed sample, and the β -form which can only be observed when the sample is held under strain. There have been a number of attempts to determine the unit cell parameters for the two crystalline forms though there is still some degree of controversy⁷⁻⁹⁾. Nevertheless, it is generally accepted that in the α -form the molecular chain within the crystal lattice is not fully extended, probably with the glycol residue in a *gauche-trans-gauche* conformation. On the other hand, 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 mechanism involving the $\alpha - \beta$ transition, and this has been modeled for static and dynamic measurements^{10,11)}.

In the last two decades the value of microhardness as a technique capable to detect a variety of morphological and textural changes in crystalline polymers has been amply emphasized leading to an extensive research^{12,13)}. This is so because micro-indentation hardness is based on plastic straining and consequently is directly correlated to molecular and supermolecular deformation mechanisms occurring locally at the polymer surface. These mechanisms critically depend on the specific morphology of the material.

It has been demonstrated that microhardness is a technique capable of detecting polymorphic changes in polymers¹⁴⁾. In particular the study of the transition from the α - to the β -form in isotactic polypropylene (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 phase¹⁴⁾. This approach opened up the possibility of characterizing iPP samples consisting of a mixture of α - and β -phases by means of H measurements.

Following the microhardness behaviour during the strain-induced polymorphic transition of PBT, differences for the three above described systems were found. The common characteristic feature among PBT, its copolymer PEE and the blend PBT/PEE is the relatively sharp (within 2-4% of deformation) stepwise decrease in H (typically by 20-30% of starting H value)¹⁻³). This drop appears at different deformation intervals: for the PBT the sharp decrease occurs between 5-8%¹), for PEE it appears between 25-30%²). For the blends one observes two sharp decreasing steps with increasing strain. The first 20% decrease of the starting H-value coincides with the deformation interval typical for the homo PBT. The second decrease, amounting another 10% drop in H – coincides with the interval observed for the PEE. The observed extremely sharp change in H-values (within 2-4% of external overall deformation) makes the microhardness method competitive, as concerns sensitivity, with other commonly used techniques such as wide-angle X-ray scattering (WAXS), IR- and Raman spectroscopy, and other methods employed for detection of the strain-induced polymorphic transitions in crystalline polymers^{4-6,15,16}).

Owing to the capability of thermoplastic elastomers to undergo large (up to a couple of hundred %) deformations which are to a great extent (up to 50%) reversible – the aim of the present study is to examine the microhardness behaviour of these systems at different deformation levels, both, while maintained under stress, and after removing the stress. In this way one may expect to observe reversibility in the microhardness values in so far the polymer structure is restored after removing the stress.

The subject of this study, the PEE, is well characterized mainly by use of small-angle X-ray scattering (SAXS) in the same deformation regime¹⁷⁻²²). In addition to these morphological investigations¹⁷⁻²²) the recent²⁾ study of the strain-induced polymorphic transition by microhardness in PEE will shed additional light in the understanding of the stress- and strain-induced structural reorganization of this new class of polymeric materials.

Experimental

Materials

The starting material is a polyblock poly(ether ester) PEE comprising PBT as hard segments and PEG with a molecular weight of 1000 and polydispersity of 1.3, according to gel permeation chromatography analysis²³⁾, as soft segments, in a ratio of 75/25 wt%. The synthesis was carried out on a semicommercial scale as described elsewhere²⁴⁾. 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 1.66²⁵⁾. The sample was shaped as a bristle, drawn at room temperature to six times its initial length, and then annealed with fixed ends for 6 h in vacuum at a temperature of 160°C.

Techniques

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 1.854¹²⁾. A loading cycle of 0.1 min was used. Loads of 147 mN and 245 mN were employed to eliminate the instant elastic contribution. Each measurement represents an average of 10 indentations.

Measurements up to 70% overall 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. In accordance with previous studies, in the present case, microhardness under strain¹⁻³⁾ was also measured after deformation steps of $\varepsilon = 5\%$. The main difference is that in previous measurements the deformation was increased continuously without relaxation. In the present study the sample was unloaded and let to relax after each H measurement under stress before the next H measurement without stress ($\sigma = 0$) was performed. Then the sample was stretched again at the subsequent deformation step and H was measured again. It should be noted that beyond some overall deformation (typically $\varepsilon > 20\%$) the unstressed sample shows some residual (plas-

tic) deformation amounting about 50% of the strain ε under stress. The same deformation cycle has been used for SAXS measurements aiming at morphological characterization of these PEE^{17–22}).

Results

Fig 1a shows the H values as a function of the deformation under stress and Fig 1b the H values taken after removing the tensile stress on the sample. In accordance with the common practice¹²⁾ the H values in the direction perpendicular to the draw direction ($H_{\perp}$) have been used and further designated by H. They correspond to the plastic deformation of the oriented polymer material under the indenter.

After the initial H increase, as a result of the first loading (unloading) cycle ($\varepsilon = 5\%$), a drastic decrease of hardness (by 50%) is observed (Fig 1a). With further increasing deformation under stress (in the range $\varepsilon = 20\text{--}70\%$) H shows a very slight increase and a final decrease (Fig 1a). The initial strong H decrease in the deformation range 5–10% is much larger than the observed one for homo PBT¹⁾, for its copolymers (PEE)²⁾ or blends³⁾ where it amounts to 20–30% of the starting H values. There is another important difference between the present results and the previous ones^{1–3)}. In particular for PEE²⁾ – the H-decrease takes place at much lower deformation. This is typical for the homo PBT¹⁾ but not for PEE where this occurs in the range $\varepsilon = 25\text{--}30\%$. Such a difference in the microhardness behaviour of PEE could be related to the rather different deformation regime in both cases. While in the previous studies^{1–3)} deformation continuously increases maintaining the sample constantly under stress, in the present case the PEE sample was let to relax ($\sigma = 0$) after each deformation step ($\varepsilon = 5\%$).

It is worth noting that the H values for the homo PBT¹⁾ are at least twice higher in comparison to its copolymers²⁾ or blends³⁾. This observation is related to the specific role played by the soft-segment phase during deformation. This subject is discussed in detail in a preceding study^{26,27)} and is behind the scope of this investigation. In the present case the interest is focused on the relative difference between H_c^{α} and H_c^{β} and not on their absolute values; even more because the experimentally obtained H values contribute not

only the two crystalline modifications but also the two amorphous phases arising for the hard (PBT) and soft (PEG) segments.

For the poly(ether-esters) under investigation it was shown that beyond a given deformation range, depending on the ratio hard/soft segments, but typically above ($\varepsilon = 20\text{--}25\%$) the observed overall deformation under stress is only partially reversible (usually about 50%)^{17–23}. This means that the remaining deformation under stress is a consequence of a plastic deformation. In Fig 1b the microhardness H as a function of the residual plastic deformation is plotted.

One immediately sees that this curve has a completely different shape and position in comparison to that measured under stress. Indeed a continuous decrease of the H values in the entire rather narrow remaining deformation interval is observed (plastic deformation between 0 and 20%). The most interesting observation here is that the H -values for plastic deformations above 5% (corresponding to overall deformations ε between 25 and 70%) are very close to each other (Fig 1b) and small in magnitude (close to or even smaller than the lowest values measured under stress, Fig 1a). In contrast to this group of H values, the ones corresponding to plastic deformations smaller than 5% are larger than the H -values measured under tensile stress ($\sigma \neq 0$). The arrows indicate the sequence of the measurement, i.e. after which deformation under stress the relaxed H -values were taken.

Discussion

Our preceding studies^{1–3}) on homo PBT¹⁾, its multiblock copolymers with PEG²⁾ as well as its blends with PEE having PBT as hard segments³⁾ have convincingly demonstrated that the observed strong decrease in H values measured under strain is related to the $\alpha \rightarrow \beta$ strain-induced polymorphic transition of PBT. The deformation ranges in which this transition takes place particularly for homo PBT¹⁾ and its copolymers²⁾ coincide fairly well with the reported ones for PBT^{4–6)} and its copolymer with poly(tetramethylene oxide)¹⁵⁾ as revealed by WAXS, IR- and Raman spectroscopy. For this reason the observed strong decrease in H values of PEE taken under stress with increasing overall deformation

could be attributed to the $\alpha - \beta$ strain induced polymorphic transition in PBT.

Most interesting are the H-data measured in a relaxed state ($\sigma = 0$) and their plot as a function of the remaining deformation during the measurements (see Fig 1b). In addition to the continuous decrease of H with increasing plastic strain the most striking observation is that the H-values for residual plastic deformation up to 5% are much higher than the rest of values. These values are in fact even higher than the H-values measured under strain (compare the H values under strain ($\varepsilon = 5-15$ (Fig 1a) with those after relaxation (Fig 1b). In contrast, when the residual plastic deformation exceeds 5% (for the steps with higher than 25% overall deformation) the H-values are very low.

The occurrence of these two groups of values (below and above 5% residual deformation) can be explained by the strain-induced $\alpha - \beta$ polymorphic transition in PBT. It is well known¹⁻⁶⁾ that up to 5% deformation the α polymorphic modification characterized by higher microhardness H_c^α predominates in the samples¹⁻³⁾. The observation that $H_c^\alpha > H_c^\beta$ is related to the fact to the α -modification is distinguished by a denser packing of chains as can be concluded from the ideal crystal densities. According to the comparison⁷⁾ 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 ⁷⁾. It has been shown ¹²⁻¹⁴⁾ that in cases when the degree of crystallinity and crystal size 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 $H_c^\alpha > H_c^\beta$, although other factors acting in the same direction can also exist. Furthermore, for 12-15% deformation (for homo PBT)¹⁾, the $\alpha - \beta$ transition is essentially completed (see Fig 1a) and the samples show predominantly the β polymorphic modification, which has a lower microhardness $H_c^\beta < H_c^\alpha$ ¹⁻³⁾. However, after removing the load ($\sigma = 0$) the samples contract (for example, after $\varepsilon = 5-10\%$, the deformation is around 1%) and after $\varepsilon = 15-20\%$ the plastic deformation is around 3%. In all these cases the plastic deformation is less than 5%, i.e. the α modification should predominate with its higher H values. This finding suggests that the H-increase observed after relaxation, in comparison to the stressed cases (provided the plastic deformation does not exceed 5%), is related to the regeneration of the initial α modification due to the reversibility of the $\alpha \rightleftharpoons \beta$

polymorphic transition (see the scheme of Fig 2).

The results obtained in Fig 1 are not only in favour of the reversibility of the strain-induced polymorphic transition⁴⁻⁶⁾ but also allows one to speak about reversibility of microhardness. The latter is possible in cases when, as a result of some treatment, it is possible to regenerate the starting structure of the polymer as in the present case. The reversibility of the microhardness further emphasizes that this mechanical property depends primarily on the structure of material.

Summarizing, it can be concluded that as a result of our systematic studies of the microhardness behaviour of strained materials it was demonstrated¹⁻³⁾ that this technique is sensitive enough for the detection of strain-induced polymorphic transitions. The results of the present report show that in materials characterized by high and reversible deformation ability it is possible to observe a reversible microhardness value provided the strain-induced structural changes are reversible too.

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Figure captions

Fig 1 Dependence of microhardness H on strain ε : a) H measured under stress ($\bullet$), b) H measured after relaxation (Δ), starting H value ($\blacksquare$). The residual plastic deformation is reached after removing the tensile stress.

Fig 2 Scheme illustrating the reversible $\alpha - \beta$ transition in the PBT crystals.

Fig. 1

Fig. 2. Scheme illustrating the reversible α - β transition in the PBT crystals