Microhardness under Strain. III. Microhardness Behavior during Stress-Induced Polymorphic Transition in Blends of Poly(butylene terephthalate) and Its Block Copolymers

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ABSTRACT: The microhardness (H) technique was recently applied to poly(butylene terephthalate)(PBT) and its multiblock copolymer of poly(ether ester)(PEE) type for examination of the stress-induced polymorphic transition. In the present study, these investigations are extended to blends of PBT and PEE. For this purpose, drawn and annealed with fixed ends at 170°C for 6 h in vacuum bristles of PBT–PEE, blends were characterized with respect to their microhardness at various stages of tensile deformation. H was measured under stress, with each step of deformation amounting 5%. The variation of H with strain (ε) shows 2 sharp stepwise decreasing values (by 40%). Each step is defined in a relatively narrow deformation (ε) range (2–5%) due to the stress-induced $\alpha \rightarrow \beta$ polymorphic transitions arising in PBT crystallites. The first polymorphic transition (at $\varepsilon = 2$–3%) is assigned to the PBT crystallites of the homopolymer (homoPBT). The second transition (at $\varepsilon = 25$%) is associated to those crystals within the PEE copolymer. From the observation of two distinct transitions, separated by a deformation interval of $\varepsilon = 20$% it is concluded that (1) homoPBT and the PBT segments from PEE crystallize separately (no cocrystallization takes place), and (2) the 2 species of PBT crystallites are subject to the external mechanical loading, not in a simultaneous manner, but in a two-stage process. In the deformation range between the 2 transitions ($\varepsilon = 2$–3% and 25%), it is pointed out that conformational changes are induced through stretching, mainly in the amorphous regions. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2271–2276, 1998

Key words: microhardness; poly(butylene terephthalate); blends; polymorphic transition; cocrystallization

INTRODUCTION

Thermoplastic elastomers are a special type of block copolymers exhibiting an extraordinary combination of reprocessability, elasticity, toughness, low-temperature flexibility, and strength at relatively high temperatures (frequently, approximately 150°C).[1,2] For these reason, they are now days of great commercial importance as engineering materials. The unique properties of these materials are mainly due to the existence of physical (temporary) network of crosslinks tying the polymer chains three-dimensionally.

In a systematic study of poly(ether ester) (PEE), thermoplastic elastomers based on poly-(butylene terephthalate)(PBT) as hard seg-

ments and poly(ethylene glycol) (PEG) as soft segments, the understanding of the deformation mechanism was attempted.[3-8] For this purpose, the relationship between the external (macro-) deformation ε and the microdeformation (at a morphological level expressed by the changes in the long spacing L) was followed within a wide deformation range by means of small-angle X-ray scattering (SAXS).[3-8] The affine and reversible increase of L at relatively low macrodeformation (up to $\varepsilon = 50-75\%$) is found to be related to reversible conformation changes in the intercrystalline amorphous regions in accordance with previous reports on polyethylene[9,10] and other thermoplastic elastomers.[1,2,11,12] At this level of deformation, there is no indications (from SAXS measurements) for any changes in the crystallites of PBT hard segments.[3-13]

One peculiarity of PBT crystallites is their ability to undergo a strain-induced polymorphic transition.[14-16] The α-form found in the relaxed material is transformed into the β-form when the sample is held under strain. There have been a number of attempts to determine the unit cell parameters for the 2 crystalline forms, and there is still some degree of controversy.[16-18] However, the general consensus is that in the α-form, the molecular chain in the crystal lattice 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 mechanism of the $\alpha \Leftrightarrow \beta$ transition, and this has been modeled for static and dynamic measurements.[19,20]

In preceding studies, we demonstrated that the microhardness technique is a very sensitive technique to detect structure changes, including polymorphic transitions in crystalline homopolymers and copolymers.[21-24]

Following the microhardness behavior during the strain-induced polymorphic transition of PBT differences for the 2 above-described systems were found. The common characteristic feature between PBT and its copolymer PEE is the relatively sharp (within 2–4% of deformation) drop in H (typically by 20–30% of the starting H value).[21-23] This drop appears at different deformation levels, as follows: for the PBT, it is between 5 and 8%[21]; for PEE, lies between 25 and 30%.[22,23] The observed very sharp change in H values (within 2–4% of external overall deformation) makes the microhardness method competitive with respect the sensitivity to other com-

monly used techniques as wide-angle X-ray scattering (WAXS), infrared (IR), and Raman spectroscopy and others for detection of the strain-induced polymorphic transitions in crystalline polymers.[13-15,25,26]

The study of the strain-induced polymorphic transitions by the microhardness technique offers the opportunity to gain additional information on the deformation behavior of more complex polymer systems, such as polymer blends. Since polymer blends are usually multiphase systems, the question arises concerning the way the independent phases react under the external load. In addition to the SAXS studies, the polymorphic transition will reflect the behavior of the crystalline phases, provided strain-induced polymorphic transition is available.

The aim of the present study is to investigate, by means of the microhardness technique, the deformation behavior of a blend of PBT and PEE thermoplastic elastomer, the latter being a copolymer of PBT and PEG. This system is attractive not only because the 2 polymers have the same crystallizable component, but also because the copolymer, being an elastomer, strongly affects the mechanical properties of the blend. It should be mentioned that these blends are well characterized by differential scanning calorimetry (DSC), SAXS, dynamic mechanical thermal analysis (DMTA), and static mechanical measurements.[27]

EXPERIMENTAL

Materials

PEE was prepared on a semicommercial scale[28] using PEG of molecular weight 1000 (PEG-1000) in PBT-to-PEG weight ratios of 49/51. For the preparation of the blend, both the homopolymer PBT and PEE were cooled in liquid nitrogen and finely ground. PBT was blended with PEE in a weight ratio of PBT-to-PEE = 51/49. Bristles of the blend were prepared according to the following procedure. A capillary rheometer, flushed with argon and heated to 250°C, was loaded with the dried powdered material. The melt obtained was kept in the rheometer for 5 min and then extruded through the capillary (diameter of 1 mm). These bristles were annealed for 6 h at 170°C in vacuum.

Techniques

Microhardness was measured at room temperature using a Leitz tester adapted with a square-
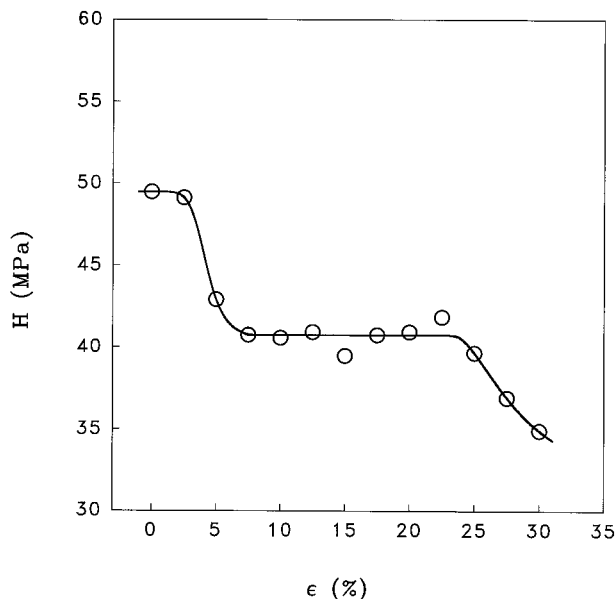
Figure 1 Variation of microhardness with increasing relative deformation ε of the blend PBT/PEE = 51/49 wt % (with PEE of PBT/PEG-1000 = 49/51 wt %).

pyramidal diamond indenter. The H values were derived from the residual projected area of indentation according to $H = kP/d^2$, with d being the length of the impression diagonal; P, the contact load applied; and k, a factor equal to 1.854.[29] A loading cycle of 0.1 min was used. Loads of 147 and 245 mN were employed to eliminate the instant elastic contribution. Each measurement was derived from an average of 10 indentations.

Measurements up to 30% overall relative deformation ε (where fracture occurs) were carried out by using a stretching device. The deformation ε is defined as $\varepsilon = \dfrac{l - l_0}{l_0}$, where l_0 and l are the starting and a given length of the sample, respectively. In accordance with the preceding measurements of microhardness under strain[21-23] in the present case also, a deformation step of $\varepsilon = 5\%$ was used.

RESULTS

Figure 1 shows the dependence of the microhardness on the external deformation for the PBT/PEE blend. One sees that H drops sharply from 50 to 40 MPa at the very beginning of stretching (around $\varepsilon = 2$–3%) keeping the value up to $\varepsilon = 25\%$. Based on previous studies[13-15,25,26] and on our recent results,[21-23] this sharp drop in H

(Fig. 1) can be assigned to the $\alpha \rightarrow \beta$ polymorphic transition in PBT crystallites. A further increase of deformation from $\varepsilon = 5\%$ to $\varepsilon = 25\%$ does not cause any pronounced changes in H. Such a constances of H suggests that no transitions take place in this deformation interval. The next transition starts at $\varepsilon = 25\%$ and seems to be completed in a rather narrow deformation interval amounting $\varepsilon = 5\%$ (between $\varepsilon = 25$ and 30%) (Fig. 1). The occurrence of 2 distinct transitions, taking place in quite different deformation ranges ($\varepsilon = 5\%$ and $\varepsilon = 25\%$), suggests that the PBT crystallites that are present in the blend differ significantly in their response to the external mechanical load. DSC and X-ray results show the existence of the following 2 types of PBT crystallites: those of the homoPBT, and those of the PBT segments from the polyblock PEE.[27,30] One can assume that the first strain-induced polymorphic transition arises from the homoPBT crystallites, and the second one, appearing at higher deformation range, can be assigned to PBT crystallites belonging to PEE. This assumption is supported by the curves presented in Figure 2, where the
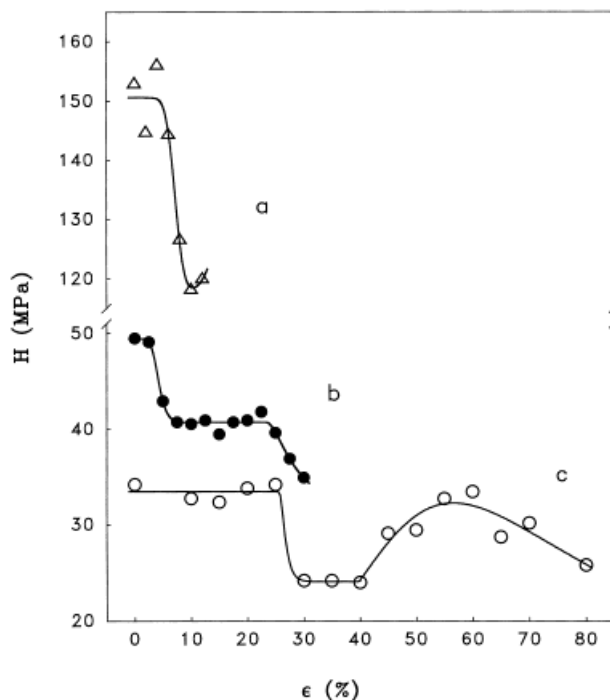

Figure 2 Variation of H with relative deformation ε for a)—homoPBT [21], b)—blend PBT/PEE = 51/49 wt % (with PEE of PBT/PEG-1000 = 49/51 wt %) (from Fig. 1) and c)—multiblock copolymer PEE with PBT/PEG = 57/43 wt % [22]. For better visual presentation a different scale for samples b) and c) is used.

results from the present study (Fig. 1) are replotted together with the previous data for homo-PBT[21] and its multiblock copolymer PEE.[22]

One can see the fairly good agreement in the deformation range for the blend and the homo-PBT, on the one hand [Fig. 2(a) and (b)], and the blend and the copolymer on the other [Fig. 2(b) and (c)]. In the first case, the strain-induced polymorphic transition is observed at deformations around $\varepsilon = 5\%$ and, in the second case, at ε around 25% [Fig. 2(a) and (b) and (b) and (c), respectively].

Comparison of the curves presented in Figure 2 for homoPBT (top), the blend (middle), and the copolymer of PBT with PEG (bottom) allows one to draw the following conclusions. The first drop in H at around $\varepsilon = 5\%$ (Fig. 1) originates from the strain-induced polymorphic transition in the crystallites comprising only homoPBT segments. The second step in H at around $\varepsilon = 25-30\%$ is related to the strain-induced polymorphic transition in the PBT crystallites comprising PBT segments from its multiblock copolymer PEE.

Another striking observation in Figure 2 is the fact that the numerical value for experimentally measured H of the blend [Fig. 2(b)] is much lower than the calculated one according to additivity law using the values for the homoPBT and the copolymer PEE [Fig. 2(a) and (c), respectively]. One possible explanation could be due to the presence of 2 types of PBT crystallites differing significantly in their perfection, as demonstrated earlier.[27] The second one could be related with the strong influence of the crystal surface free energy on H.[31,32] The latter would contribute to the decrease of the crystal hardness particularly because of more defective PBT crystallites arising from the PEE copolymer.

DISCUSSION

From the above results, one may ask what could be the reason for the different behavior of the 2 types of crystallites with respect to their two-step response to the external mechanical field. Before answering this question let us recall some structural peculiarities of the system under investigation.

1. The present blend contains the same crystallizable component in both the homopolymer and the copolymer. In other words, the PBT crystallites can arise as a result of complete cocrystallization, that is, formation of uniform crystallites with simultaneous participation of PBT from both the homopolymer and the copolymer as found for PEE containing 75–91 wt % PBT.[30]

2. For reasons related to the length of the crystallizable blocks in the PEE copolymers,[27] the more frequent case is that of partial cocrystallization, that is, formation of (continuous) crystals consisting of 2 spatially not separated, crystallographically identical populations of crystallites, differing in their size, perfection, origin, and time of appearance.[27] Such type of cocrystallization is observed when the PBT–PEE blends are drawn and thereafter annealed at a temperature lying between the melting temperatures of the 2 species of crystallites.[27]

3. The third possibility of crystallization is when no cocrystallization takes place, that is, formation of 2 types of PBT crystallites comprising only segments either from homoPBT or only from PEE.

The microhardness data presented in Figure 1 strongly suggest that, in the present case, one deals with the third case for the following reasons: If PBT crystallites would result from complete cocrystallization, one should expect 1 single strain-induced polymorphic transition in the whole deformation interval. In case of partial cocrystallization, one should observe a more or less continuous polymorphic transition between the deformation ranges typical for the homoPBT and the PEE.

The experimental results of Figure 1 show 2 rather sharp transitions separated from each other by $\varepsilon = 20\%$. This finding supports the assumption that for the blend under investigation, one deals with crystallographically identical, but spatially separated, 2 species of crystallites differing in the origin of the PBT segments.

The conclusion about the lack of cocrystals in the present PBT–PEE blend helps to better understand the observed mechanical behavior of the system.

The finding of Figure 1 that the 2 species of crystallites respond to the mechanical field subsequently, first, the homoPBT crystallites, and, later, those arising from PEE, means that the homoPBT crystals are probably dispersed within PEE in such way that they experience the mechanical field from the very beginning of loading. Even more, one can assume that in the blend, some internal stress and/or strain preexists since

the strain-induced polymorphic transition starts even at lower deformations (about $\varepsilon = 2-3\%$; Fig. 1) than in the case of homoPBT where $\varepsilon = 5\%$.[21]

After the well-pronounced mechanical response of the homoPBT crystallites, one observes conformation changes (stretching) only of the amorphous intercrystalline layers, as concluded from previous SAXS measurements.[3-8] These processes dominate up to deformations of about $\varepsilon = 25\%$ when the applied stress is also undergone by the crystallites arising from the PEE copolymer (Fig. 1).

Thus, the observation of 2 sharp, well-defined, strain-induced polymorphic transitions, clearly separated in the deformation scale, convincingly demonstrates that the 2 populations of PBT crystallites differing in their origin undergo the mechanical loading not simultaneously but in 2 subsequent steps, as follows: first, those comprising homoPBT (at $\varepsilon = 2-3\%$), followed by crystallites belonging to PEE (at $\varepsilon = 25\%$).

CONCLUSIONS

The systematic variation of microhardness under strain performed on (1) homoPBT,[21] (2) its multiblock copolymer PEE,[22,23] and (3) on blends of both of them (the present study) is characterized by the ability of these systems to undergo a strain-induced polymorphic transition. The possibility accurately to follow the strain-induced polymorphic transition, even in complex systems, as polymer blends allows one to make conclusions concerning also such basic phenomena as that of cocrystallization. In the present study of the PBT−PEE blend, 2 distinct, well-separated (with respect to the deformation range), strain-induced polymorphic transitions arising from the 2 species of PBT crystallites are observed. From this observation, it is concluded that (1) homoPBT and the PBT segments from the PEE copolymer crystallize separately, that is, no cocrystallization takes place; and (2) the 2 types of crystallites are subjected to the external load, not simultaneously but in a subsequent manner.

In summary, the microhardness technique, being a simple and sensitive method, allows one to derive conclusions not only about the micromechanical properties of polymers but also on structural and kinetics characteristics,[32] including polymorphic transitions and the occurrence of cocrystallization or other details responding to the applied mechanical field.

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