Direct visualization of a strain-induced dynamic stress network in a SEBS thermoplastic elastomer with in situ AFM nanomechanics

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Thermoplastic elastomers (TPEs) may generate a residual strain after being stretched, which hinders their potential for use in high-performance materials. However, the mechanism of the residual strain formation has not been sufficiently elucidated thus far. Here, we used atomic force microscopy-based nanomechanical mapping to investigate a stretched TPE specimen consisting of poly(styrene-b-ethylene-co-butylene-b-styrene) with a content of 15 wt% styrene (SEBS-15). In the SEBS-15 polymer structure that maintained a strain of 0.5, hard-segmental (HS) amorphous domains aggregated by poly(styrene) segments deformed and became oriented parallel to the stretching direction, whereas soft-segmental rubbery domains aggregated by poly(ethylene-co-butylene) segments elongated, formed a stress network using the HS domains as junction points. Moreover, an in situ observation adopted for the stretched SEBS-15 revealed that HS domains therein underwent a relative displacement and partial separation that was influenced by the formed stress network, which was strongly related to the irreversible phenomena.

1. Introduction

The many advantages of elastomers make them applicable in a wide variety of fields, such as adhesives, seals, tires, and shoe soles.1,2) Conventional thermoset elastomers, such as vulcanized rubber, possess excellent mechanical properties because of their chemical crosslinked structure. After strain-induced deformation, thermoset elastomers can achieve almost complete elastic recovery. However, the irreversibility of permanent chemical cross-linking therein makes the material difficult to recycle, reprocess, or reuse.3) Currently, thermoplastic elastomers (TPEs) represent a desirable alternative to thermoset materials because of their high elastic deformation and advantages in terms of processing and recycling.4,5) Various methods have been conducted to improve the performance of TPEs using noncovalent interactions, such as hydrogen bonding,6,7) ionic bonding,8,9) and metal-ligand coordination.10) However, the residual strain in TPEs after deformation is still a significant obstacle to overcome to obtain tough TPEs that have the same performance as thermoset materials.

Structurally, TPEs can be classified into two categories, block copolymers and polymer blends, both of which have hard and soft domains in their polymer systems. In block copolymer (BCP)-based TPEs, hard segments and soft segments along the backbone chain of the polymers form via microphase separation, resulting in hard segmental domains and soft segmental domains, respectively. Soft-segmental rubbery domains (SS domains) elongate upon strain-induced deformation, while hard-segmental amorphous (sometimes crystalline) domains (HS domains) create physical cross-links needed for elastic recovery. To produce a tough TPE with a minimal residual strain, the polymer network of the TPE must achieve an almost complete recovery after deformation; thus, it is worth investigating the nanoscale structural changes in TPEs during deformation.

Many researchers studied the deformation of BCP-based TPEs using small angle X-ray scattering (SAXS),11–17) Fourier transform infrared spectroscopy,18–21) and transmission electron microscopy (TEM).15,22–27) They demonstrated that spherical HS domains in BCP-based TPEs were deformed and oriented from an isotropic structure upon stretching, which had a valid correlation to the stress relaxation and fracture of the stretched TPE. It was also confirmed by SAXS16) and TEM15) that a largely deformed lattice composed of HS domains undergoes affine deformation since the plane spacing increases proportionally. However, the distribution and evolution of the internal stress, which is a critical issue in deformed BCP-based TPEs, have not been determined by the test methods to date and need to be elucidated by direct and real-time visualization methods. In recent years, atomic force microscopy (AFM)-based nanomechanics have been developed to obtain nanomechanical mapping of soft materials, especially BCPs.28,29) This method enables the mechanical properties of the material surface, including the elastic modulus, adhesion, dissipation, and stiffness, to be simultaneously probed with nanometer resolution. We expect this measurement method to reveal the fundamental issues concerning the deformation mechanism of BCP-based TPEs.

In this paper, we focused on the strain-induced variation of microdomains in a TPE specimen consisting of a poly(styrene-b-ethylene-co-butylene-b-styrene) (SEBS) triblock copolymer. The morphological and mechanical evolution was obtained by in situ visualization with AFM nanomechanics. From elastic modulus mapping, an inhomogeneous distribution of the internal stress was observed during stretching, causing deformation, relative displacement, and partial separation of the phase-separated structure.

2. Experimental methods

2.1. Materials and sample preparation

A TPE sample resulting from hydrogenating a SEBS triblock copolymer (JSR Dynaron 8600P, styrene content = 15 wt%), namely, SEBS-15, was purified by reprecipitation from a toluene solution into methanol and dried under vacuum at
50 °C for three days to remove the residual solvent. The SEBS-15 film was prepared by a hot-press casting procedure.

2.2. AFM measurements

The annealed specimen was cut into an ultrathin section with a thickness of 300 nm with an EM UC6 ultramicrotome (Leica Microsystems, Germany) at −120 °C to produce a sample for AFM investigation. The PeakForce Quantitative Nanomechanical Mapping (QNM) mode, together with a Multimode 8 AFM (Bruker, USA), was used to record elastic modulus maps at room temperature (∼25 °C). A Nanoscope V controller and Nanoscope software version 9.1 were utilized. The sample stage for in situ AFM visualization was established on a self-developed tensile unit based on a commercial sample holder. All quantitative measurements were carried out using a standard ScanAsyst-Air probe (Bruker, USA). The radius $R$ of the probe was evaluated by scanning a Nioprobe TipCheck sample (Aurora NanoDevices Inc., Canada) in QNM mode with a scan rate, scan size, and image resolution of 0.5 Hz, 400 × 400 nm², and 1024 × 1024 pixels, respectively, and the probe radius was determined to be ∼2 nm from the obtained height maps following the method in our previous report. The spring constant $k$ of the cantilever was measured to be ∼0.43 N m⁻¹ using the thermal tuning method. During a typical AFM nanomechanical mapping process, force-deformation curves (FCs), which were carried from the original deflection-displacement curves, were obtained by the AFM cantilever-probe tip assembly moving forward and backward along a randomly selected surface while measuring the relationship between the force and deformation. Meanwhile, the specimen was oscillated by the $Z$-piezo of an E-scanner (maximum scan area = 15 × 15 μm²) with frequencies, peak forces, and peak force amplitudes of 1 kHz, 0.5 nN, and 100 nm, respectively. The FCs were collected over an area with dimensions of 500 × 500 nm² at a digital resolution of 256 × 256 pixels. Topographical imaging and simultaneous mapping of the mechanical properties were extracted from each FC. During data analysis, Johnson–Kendall–Roberts (JKR) contact mechanics were applied to the retraction part of the FCs to account for the corresponding Young’s modulus $E$, as expressed by the following equation:

$$E = \frac{3(1 - \nu^2)}{4} \frac{1.27F_1}{\sqrt{R(\delta_0 - \delta_1)}},$$

where $\nu$ is Poisson’s ratio, $F_1$ (< 0) is the maximum adhesive force obtained in FCs, $\delta_0$ is the indentation depth when the adhesive and elastic restoring forces become equivalent, and $\delta_1$ is the indentation depth when the adhesive force encounters a maximum ($F_1$). For additional details on AFM nanomechanical mapping, please refer to our previous review paper. The abovementioned procedure to derive the local Young’s modulus was also applied to the macroscopically stretched specimens. In such cases, the modulus obtained in the stretched specimen no longer represented the “Young’s modulus” since it could only be defined in an unstretched state. Thus, hereafter, we refer to this as the “JKR modulus” in this paper.

2.3. Tensile tests

Tensile tests were performed using a Shimadzu EZ-S tensile tester (Shimadzu Corporation, Japan) at room temperature (∼25 °C). The SEBS-15 film with a thickness of ∼1 mm was cut into a dumbbell shape (20 mm gauge length and 2 mm width). The specimen was uniaxially stretched with a cross-head speed of 40 mm min⁻¹. The same experiment, repeated three times on different specimens, furnished similar results.

3. Results and discussion

3.1. Macroscopic tensile behavior of the SEBS-15

A typical strain–stress curve of SEBS-15 from a strain-rate controlled tensile test is shown in Fig. 1(a). Unsurprisingly, a residual strain (∼10%) was generated when the specimen recovered to zero stress after being stretched to a strain of 200%. The Young’s modulus of the specimen was calculated to be ∼3.2 MPa from the average slope of the elastic region of the stress–strain curves that corresponded to strains between approximately 2% and 4%.

Figure 1(b) shows the stress–time curve of the SEBS-15 that was stretched to 50% in a macroscopic view. During 12 h with a fixed 50% strain, the stress rapidly decreased at the beginning of relaxation (<1 h) and then slowly decreased with further relaxation. This stress-relaxation process, as elaborated above, indicates that some substantial structural evolution occurred as the stretching time increased, and it is speculated that such a structural evolution was related to the inability of the material to entirely elastically recover.

3.2. Nanomechanical mapping of the unstretched SEBS-15

SEBS, a triblock copolymer consisting of hard poly(styrene) (PS) segments and poly(ethylene-co-butylene) (PEB) segments, always exhibits a phase-separated morphology, and its nanomechanical properties have been intensely studied. In a Young’s modulus map of a SEBS sample with a low PS component of 15%, sphere-like PS domains with a high modulus, namely, hard-segmental amorphous domains (HS domains), and PEB domains around the HS domains with a low modulus, namely, soft-segmental rubbery domains (SS domains), were observed in its microstructure. The corresponding Young’s modulus values can be estimated by the color bar placed at the right of Fig. 2(a). The histograms of the Young’s modulus distributions in Fig. 2(a) are shown in
of sample deformation and is affected by the tip radius and pushing force, could only be achieved from a very delicate operation. The Young’s modulus obtained from tensile testing reflected the initial elastic deformation of the SS domains. In the case of the Young’s modulus obtained from AFM, its value increased when the sample received additional deformation since the surrounding HS domains were involved when the SS domain deformed.

### 3.3. Deformation, relative displacement, and separation of poly(styrene) domains during the stress-relaxation process

AFM nanomechanics were utilized to reveal the nanostructural change that occurred in Fig. 1(b). Although the stress decreased rapidly during the initial stage upon stretching, which is considered to be appropriate for study, imaging during the initial stretching process was extremely difficult because the sample drifted substantially at the nanoscale. This situation eased approximately 3 h after the start of stretching, and we obtained clear images from 4 to 10 h. Figures 3(a) and 3(c) show JKR modulus maps of the SEBS-15 stretched 50% that was probed at almost the same region after 262 and 597 min. The double-headed arrows represent the stretching direction.

As shown in Figs. 3(a) and 3(c), HS domains deformed and oriented parallel to the stretching direction per a comparison with Fig. 2(a), which is a similar result to those reported by SAXS and TEM analyses. A two-dimensional fast Fourier transform algorithm implemented in ImageJ was utilized in the 8 bit grayscale images of 256 × 256 pixels converted from the modulus maps. The shape parameter, as shown in Fig. 3(e), is considered as the average separation distance of the HS domains. The HS domains in the unstretched SEBS-15 had a distance of approximately 23 nm regardless of the direction. Interestingly, in the stretched SEBS-15, the average distance of the HS domains in the stretching direction significantly increased to ~41 nm when the stretched state was maintained for 262 min and decreased from ~41 to ~38 nm at 597 min. At the same time, almost no change was observed in the average distance perpendicular to the stretching direction.

The modulus changes in the value and distribution of the sample during deformation are also worth discussing. The red histogram and black curve in Fig. 3(b) represent the modulus distribution in the SS domains only in Figs. 2(a) and 3(a) and indicate peak values of ~3.50 MPa and ~4.84 MPa, respectively. Such an increase in the JKR modulus indicates that the internal stress, as the resistance to the external force, forms in the stretched SEBS. In other words, the JKR modulus of a stretched specimen, measured by AFM-based nanomechanics, could reflect the evolution of the internal stress during stretching. Moreover, compared with the stretched sample, an increased proportion of the JKR modulus distribution in the stretched SEBS-15 occurred in the high modulus area, which was attributed to the formation of a so-called stress chain. In the microscopic view, a stress chain consists of SS domains within a deformed portion of the material that are held together to form a so-called stress network with HS domains as junction points. Therefore, due to the contribution of a stress network, the JKR modulus of some SS domains increased, resulting in a nonuniform distribution.
The red curve in Fig. 3(d) represents the JKR modulus distribution of the SS domains only in Fig. 3(a). Compared with the blue histogram, which represents the JKR modulus distribution of SS domains only in Fig. 3(c), a left shift of the peaks (from $\sim 5.7$ MPa to $\sim 4.8$ MPa) occurred with increasing stretching time, indicating a decrease in the JKR modulus in SEBS-15, which could also be concluded by the color change in Figs. 3(a)–3(c). A modulus decrease is consistent with the results derived from the tensile tests, as shown in Fig. 1(b). However, numerically speaking, the stress decrease in the SEBS-15 stretched 50% that was obtained in the macroscopic stress–time curve, as shown in Fig. 1(b), is $\sim 0.03$ MPa from 4 to 10 h, which is much less than the result obtained from AFM (decrease of $\sim 0.9$ MPa). Estimating the macroscopic stress value from the microscopic change of the JKR modulus in the tensile state will be carried out in a future work.

It was further found that a relative displacement of the HS domains occurs in the stretching direction. We measured the distance between the HS domains distributed parallel and perpendicular to the stretching direction at different relaxation times. In the direction parallel to the stretching direction, $L_1$ ($\sim 398$ nm) and $L_2$ ($\sim 250$ nm) in Fig. 3(a) were significantly shortened to $L_1$’ ($\sim 299$ nm) and $L_2$’ ($\sim 211$ nm) in Fig. 3(c); however, $L_3$ ($\sim 340$ nm) and $L_4$ ($\sim 377$ nm) in the direction perpendicular to the stretching direction maintained almost the same value as $L_3$’ ($\sim 339$ nm) and $L_4$’ ($\sim 374$ nm). The shrinkage in such a local area along the stretching direction, which should not have occurred during a fixed strain relaxation, indicates a nonuniform change in the polymer network inside the material. This conclusion could also be deduced from the previous discussion concerning the morphology of the HS domains. The average separation distance between the HS domains after stretching for 262 min ($\sim 41$ nm) indicated a 78% elongation compared with the unstrained HS domains ($\sim 23$ nm) at 50% of the macroscopic deformation, which indicated that other areas were stretched less than 50%.

Even though most of the microstructure in the stretched SEBS-15 maintained its morphology, some HS domains underwent a significant separation during the relaxation process, as observed by the marked dotted circles in Figs. 3(a) and 3(c); these areas indicate the same HS domains in the microstructure with a different stretching time. Structurally, a polymer network was formed by amorphous HS domains acting as junction points and rubbery SS domains bridging these junction points, also known as a bridge chain. When a macroscopic strain was applied, the bridge chains stretched first since the HS domains were relatively hard, which led to a local stress increase. A local stress can be transferred along a stress network in a polymer. Therefore, to relax the local stress, the stretched bridge chains consequently exerted a strong force on the HS domains and caused them to deform and separate at the weak junctions. The split HS domains formed new stress networks; that is, bridge chains that initially belonged to one junction point were allocated to two junction points. In addition, the chains that originally belonged to only one HS domain, a so-called loop chain, also could evolve into a bridge chain if the subordinated HS domain was separated into two new domains. The microstructure of the polymer was partially reformed by the deformation, separation, and reorganization of microdomains along with the stress network. The deformation of the domains was relatively easy to recover; however, the topological change caused by separation had a permanent impact on the material, and a residual strain was
from the original 500 in Fig. 4, we chose one HS domain, marked D1 in Fig. 3(a), continuous AFM observations over a short period. As shown separation of the poly(styrene) domain assimilation and simulation.42) explored in a future work that incorporates with data present. A dynamic stress network will be visualized and explored in a future work that incorporates with data assimilation and simulation.42)

3.4. Dynamic stress network observed during the separation of the poly(styrene) domain

We explored the details of the separation behavior through continuous AFM observations over a short period. As shown in Fig. 4, we chose one HS domain, marked D1 in Fig. 3(a), whose separation was observed as described above, and studied the structural evolution surrounding it at a time just before and after the separation. A small HS domain, marked as D2, grew in Figs. 4(a) to 4(b), which could be explained by the aggregation of PS segments, and continued to aggregate at the subsequent times shown in Figs. 4(c) and 4(d). This growth behavior increased the modulus of domain D2 and its surroundings containing the area between domains D2 and D1. Gradually, the SS domain in the interval of domains D2 and D1 was separated by the newly formed bridge chains between D1 and D2. This strain-induced structural evolution brought about the formation of a new connection between domains D2 and D1 inside the SS domain, which is referred to as a stress chain. There was also the effect of the stress chain between domains D1 and D3. For domain D1, the direction of the stress chain generated with domains D2 and D3 is shown by the arrow in Figs. 4(b)–4(e). Finally, in Fig. 4(e), under the effect of a continuous stress from two directions, domain D1 started to split into two smaller HS domains, domain D1.1 and D1.2, that moved away from each other. The aggregation and separation of the HS domains, subsequent generation of stress chains and dynamic changes in the stress network were observed for the first time herein.

4. Conclusions

By employing AFM nanomechanics, this work visualized the strain-induced evolution of the structure and mechanical properties of a SEBS-based TPE material. According to the nanoscale JKR modulus maps, microdomains in the stretched SEBS exhibited deformation, separation, and reorganization during the stress relaxation process. The stress network underwent a dynamic evolution that permanently changed the topological structure of the polymer. An atomic force microscope was used to continuously take images of the polymer microstructure during deformation, and this could be a powerful approach for understanding the continuous morphological changes of various materials under the action of external forces. Furthermore, with a combination of mathematical modeling, molecular dynamics simulation, and experimentation, the deterioration mechanism of polymer materials can be further investigated. These fundamental microscopic studies supply the theoretical basis for the development of high-strength polymer materials. Additional research on polymer morphology will be carried out in the future based on this new technique.

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