

Block Copolymer of *trans*-Polyisoprene and Urethane Segment: Shape Memory Effects

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ABSTRACT: Shape memory behaviors of *trans*-polyisoprene (TPI) segmented urethane copolymers were studied. Film specimens for cyclic loading tests were prepared from the polymer solution by casting, and tested at the loading temperature of 65°C. Results show that the recovery rates of the films depend on their TPI segment contents, while the fixity rate was measured to be close to 100% for each sample. The film containing 70% TPI segments was found to show a recovery rate of 85%. Two separated phases were clearly observed in the morphology of the films. The urethane

segments were organized into spherical domains acting as physical cross-links during the shape memory process. The continuous phase formed by the crystalline TPI segments serves as the reversible phase responsible for fixation of the temporary shape. The tensile and dynamic thermal properties of those films were also studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 879–885, 2006

Key words: shape memory effects; *trans*-polyisoprene; copolymer; morphology; tensile behavior

INTRODUCTION

Shape memory polymers are capable of changing their shape on exposure to an external stimulus. Thermoresponsive shape memory polymers are highly interesting when used as intelligent materials for biomedical applications. Their shape memory effect originates from thermal transition of polymer chains and from morphology of polymer systems.^{1–4} In block copolymers with the shape memory effect, domains of the switching segments are subjected to softening and hardening, upon heating above transition temperature and cooling below this temperature. The driving force of shape recovery is the elastic strain generated during the thermal deformation.

Shape memory polyurethanes consist of two separated phases—a reversible phase of soft segments and a fixed phase of urethane segments. Basically, the permanent shape of these polymers is fixed by physical cross-links, and the transition process is controlled by the melting temperature of the soft segments with crystalline structures.^{5–9} Recently, the shape memory polyurethanes have attracted immense attention because of their highly controllable properties. Their shape memory effects are found to strongly depend on properties of the soft segment employed, the molar ratio of the hard and soft segment, and the phase

separation related to polymerization processes.^{1,3} Recent developments connected with shape memory polyurethanes are the design of new polymer systems that are required for specific applications.

We have synthesized the *trans*-polyisoprene (TPI) segmented copolymer through the urethane-formation reaction of hydroxyl-terminated *trans*-polyisoprene (HTTPI) and toluene diisocyanate (TDI).¹⁰ HTTPI was derived from TPI by means of photochemical modification,^{10–13} and was found to be semicrystalline with an unchanged *trans* ratio.¹⁰ During crystallizing in solution, the polymer chains can be arranged into regular crystallites that seem to grow from lamellae [Fig. 1(A)]. In the copolymer, the urethane segments are capable of assembling into spherical domains [Fig. 1(B)], implying that there are strong interactions among the urethane segments. From the molecular mechanism of shape memory effects,¹ the TPI-urethane copolymer is expected to offer physically cross-linked shape memory materials with the switching molecule of TPI segment. It has been reported that the TPI segments show a decreased melting point below 60°C owing to the urethane segment introduced.¹⁰

In the present work, the shape memory effects of TPI-urethane copolymers are evaluated to examine the relationships between the shape memory properties and the copolymer compositions. The cyclic loadings tests were carried out at the loading temperature of 65°C. The results obtained are interpreted in terms of morphological structures as well as dynamic mechanical properties.

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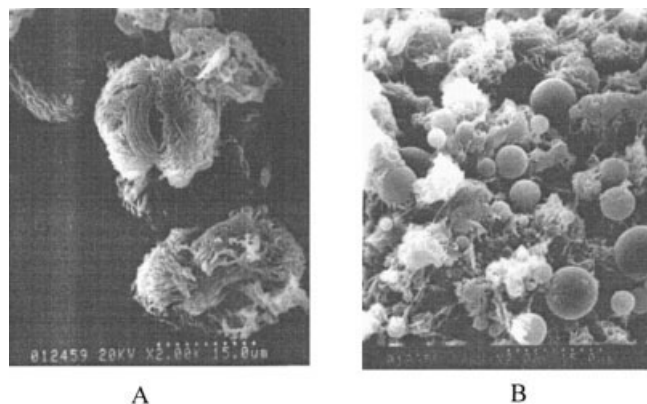


Figure 1 SEM photographs of HTTPI crystallites (A) and the morphology of the sample obtained from solution-growth crystallization of the copolymer (B).

EXPERIMENTAL

Films preparation

Synthesis of TPI-urethane copolymers by the two-shot process has been described elsewhere.¹⁰ In brief, HTTPI was dissolved in toluene, and a molar excess of toluene diisocyanate (TDI) was mixed with the solution. The urethane-formation reaction was carried out under the catalysis of DBTDL (dibutyltin dilaurate), followed by the reaction of chain extension with 1,4-butanediol at 80°C for 3 h. Films were prepared by casting the polymer solution onto a PTFE plate, and they were dried at 70°C for 24 h. To ensure relaxation, the film specimens were placed at room temperature for at least 2 weeks prior to tests.

Measurements

To study the bulk microstructure of the copolymer films, fracture surfaces of the specimens were required. The fracture surfaces were prepared under liquid nitrogen, and coated with gold using a Eiko IB3 coater. A scanning electron microscope (HITACHI S-520) was used to examine their morphology at 20 kV. Wide angle X-ray diffractograms (WAXD) of the films were recorded on a D/Max—III A diffractometer at a scanning rate (θ) of 4°/min. The wavelength of the beam applied was 1.5418 Å (Cu K α line).

The copolymer films were tested for tensile properties with an Instron 424 tensile tester, at room temperature around 25°C.

Shape memory effects of polymers were usually measured by cyclic loading tests.^{1,5,7} In our experiments, the tests were carried at the loading temperature of 65°C using an Instron 424 tensile tester equipped with a thermo-chamber. Plots of Figure 2 show the operating procedures of one cycle. The film sample was stretched at a rate of 10 mm/min to the strain of ϵ_m at 65°C (T_1). The elongated film was

cooled to 25°C (T_2) with the constant strain of ϵ_m , and stayed at this temperature for 5 min. The sample may exhibit a strain recovery ($\epsilon_m - \epsilon_u$) after the external load was removed. The cooled film was then heated to T_1 in 5 min, followed by maintaining for 10 min at T_1 to allow a substantial recovery of strain. The recovery rate (R_r) and the shape fixity (R_f) are defined as follows:

$$R_r = \frac{\epsilon_m - \epsilon_p}{\epsilon_m} \times 100\% \quad (1)$$

$$R_f = \frac{\epsilon_u}{\epsilon_m} \times 100\% \quad (2)$$

where ϵ_p is the residual strain of the film after one cycle is completed.

RESULTS AND DISCUSSION

Morphology of the films

The copolymer films show a complete micro-phase separation, with the urethane segments being well arranged into spherical domains (Fig. 3). The high degree of phase separation is believed to result from the difference in polarity between TPI and urethane segments. In the polyurethanes based on polar soft segments, various interactions can occur among the polymer chains, such as hydrogen bonding and dipole-dipole interactions.⁵ The interactions between hard and soft segments significantly influence the phase separation, and usually lead to a phase mixing.¹⁴ In the TPI-urethane copolymer, hydrogen bonding is only confined to the urethane segments, while there is no potential of strong interaction between the two segments. Consequently, the intermolecular interaction makes the urethane segments assemble and separate from the soft segments.¹⁴ It is noteworthy that the distinct phase separation usually favors the shape memory effects.¹

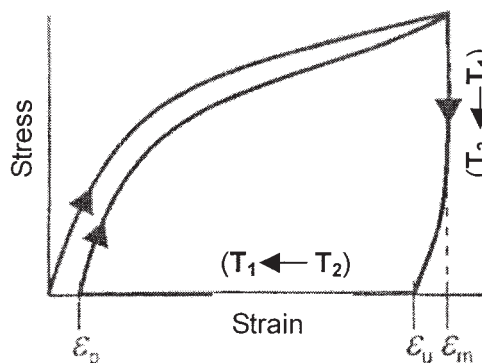


Figure 2 Cyclic tensile with loading at high temperature.

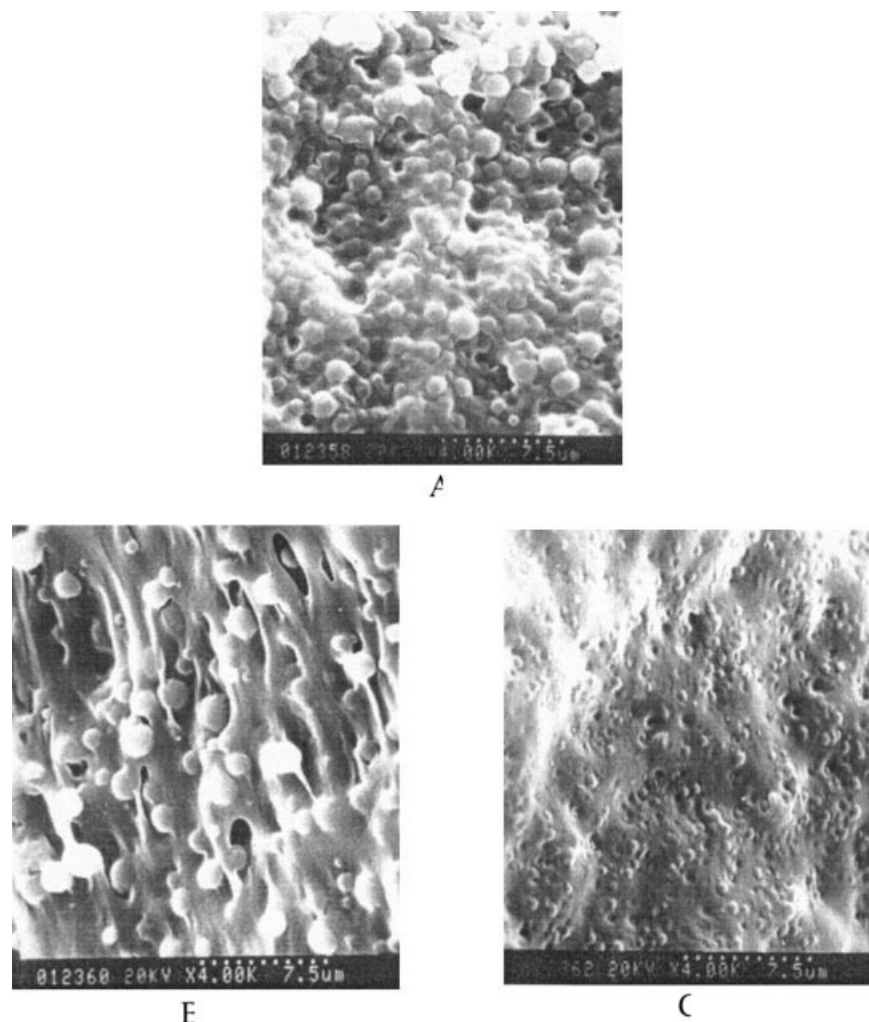


Figure 3 Scanning electron micrographs of the films. The soft-segment content: (A), 30%; (B), 50%; (C), 70%. \bar{M}_n of the starting HTPI was 2.4×10^4 .

When the TPI content is increased over 50%, TPI segments begin to form a continuous phase in which the urethane domains are uniformly dispersed [Fig. 3(B)]. Of interest, some of the dispersed domains are found to be interlinked by bundles of TPI. This structure is believed to result from the assembling of the urethane segments that are actually connected to different TPI segments. The urethane domains can serve as physical net points, and are responsible for fixation of the original shape during the shape memory process.

Figure 4 shows the WAXD patterns of the films with different TPI contents. The sharp diffraction peaks confirm crystalline structures of TPI segments. The strength of these peaks increases with an increase in the content of TPI. It has been reported that any other diffraction signals exclusive of that of TPI were not detected for the copolymer samples.¹⁰ The result indicates that the urethane domains are amorphous.

Tensile behaviors at room temperature

Figure 5 shows the tensile behavior of the copolymer films at room temperature. Each curve has an upper yield point, instantly followed by a necking step where the strain increases at the constant stress. The necking step is a behavior of cross section contraction,

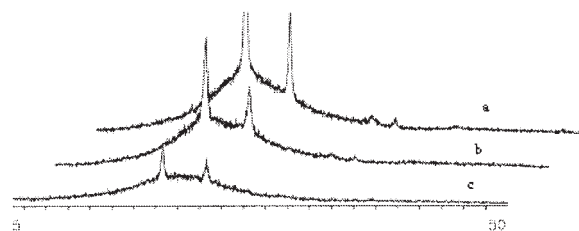


Figure 4 X-ray diffraction profiles of the copolymer. Soft-segment content: (A), 70%; (B), 50%; (C), 30%. \bar{M}_n of the starting HTPI was 2.4×10^4 .

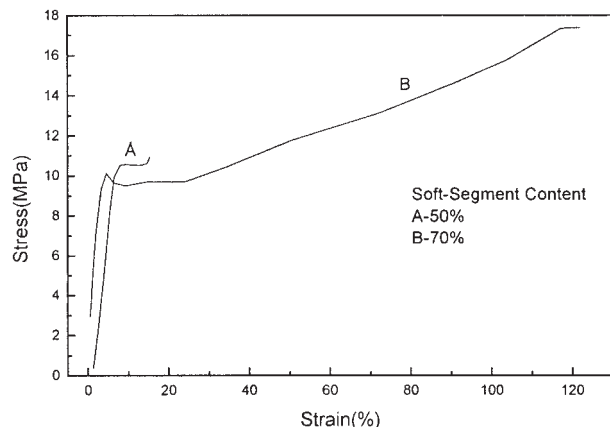


Figure 5 Tensile curves of the films at 25°C. \bar{M}_n of the starting HTTPI was 3.2×10^4 .

and always occurs in the tensile process of semicrystalline polymers. Here, the necking property is attributed to the crystalline TPI. It is known that during the necking step, polymer chains are oriented in the direction of extension, and the crystallites are changed in the sequence of distortion, orientation in the stretching direction, and recrystallization afterwards.¹⁵ Thereby, the deformation after the upper yield point is irreversible when the stress is unloaded.^{15,16} Figure 5 shows that the upper yield points of the copolymer films appear at low strains below 10%. This result implies that at room temperature, the film underwent a large strain and is unlikely to exhibit shape recovery.

The results shown in Figure 5 indicate that the tensile properties of the films strongly depend on their composition. The film with 70% soft segments has a long strain-hardening process after the necking, whereas the film with 50% soft segments breaks shortly after the necking step. The micrographs clearly show that a notable difference between the two films is the remarkable change in the sizes of the dispersed domains. The dimension decreases from 4 to 0.4 μm as the TPI content increases from 50 to 70% (Fig. 3). Such a reduction may bring about a sharp change in the surface effects. Especially, another film with 30% soft segments shows a typical brittle breakage: it breaks at the highest stress without any upper yield point (The tensile curve is not presented here). As depicted in Figure 3(A), its morphology consists of accumulated urethane spheres coalescing by TPI. Consequently, the tensile behaviors of the copolymer films are related to their microstructures that can readily evolve with the ratio of soft and hard segments.

One can see that the copolymer films exhibit relatively low elongations at break, in comparison with the polyurethanes consisting of polar soft segments. Elastic properties of those materials partly come from the phase mixing that is caused by the interaction between the soft and hard segments.¹⁷ In this copoly-

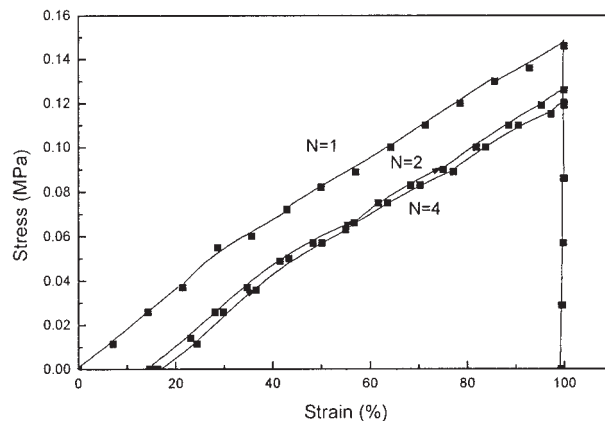


Figure 6 Cyclic loading behavior of the copolymer film with 70% soft segment. \bar{M}_n of the starting HTTPI was 3.2×10^4 .

mer film, the urethane domains should be weakly bonded with the TPI matrix. Debonding may take place in response to a relatively low stress and create craters at the interfaces, leading to a low elongation.

Shape memory effects of polymers generate from their morphology and thermal transition of the chains. Knowledge of the morphology of the films and their tensile behaviors at room temperature may help in understanding the shape memory behaviors.

Shape memory properties

The tensile cyclic plots of the film with 70% soft segment are shown in Figure 6. N marked on the plot refers to the number of cycles. Various strains pertinent to the cyclic loadings are plotted against N , as shown in Figure 7. The sample that that underwent the first cycle is found to have a recovery rate of 85% and a strain fixity (ϵ_u) close to 100%, at ϵ_m of 100%. In addition, the recovery rates remain constant with in-

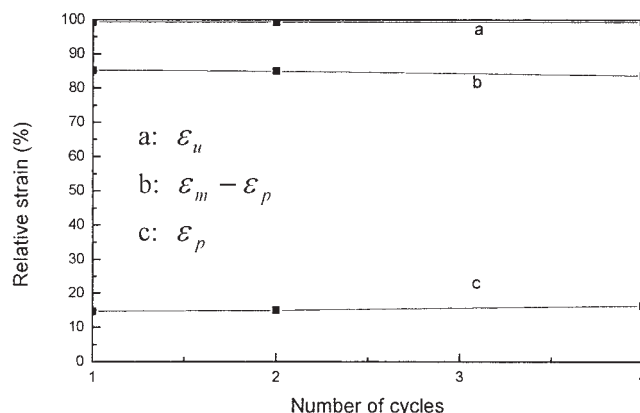


Figure 7 Cyclic dependence of various strains for the copolymer film with 70% soft segments. $\epsilon_m = 100\%$. \bar{M}_n of the starting HTTPI was 3.2×10^4 .

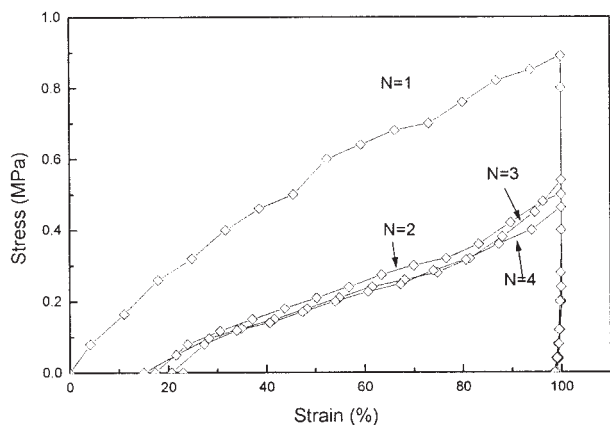


Figure 8 Cyclic loading behaviors of the copolymer film with 50% soft segment. M_n of the starting HTPI was 3.2×10^4 .

crease in cycles. The unloading curves at different cycles almost overlap.

Figure 8 shows the loading behavior of the film containing 50% soft segments at ϵ_m of 100%. The film also shows good shape memory effects at the first cycle (Fig. 9). However, the recovery rates slightly change with the number of cycles. When $N = 4$, the recovery rate is decreased to 80% but the fixity rate keeps constant. For the film with 30% soft segment, a poor shape memory behavior can be clearly observed (Figs. 10 and 11). The recovery rate is lower than 35% at ϵ_m of 50%. Nevertheless, the film also retains high shape fixity.

TPI-urethane copolymer is considered as a typical shape memory polymer with the transition temperature being the melting point. The TPI segment not only serves as the switching molecule but also enables the fixation of the temporary shape. As the stretched film is cooled from the loading temperature to room temperature, TPI segments begin to recrystallize un-

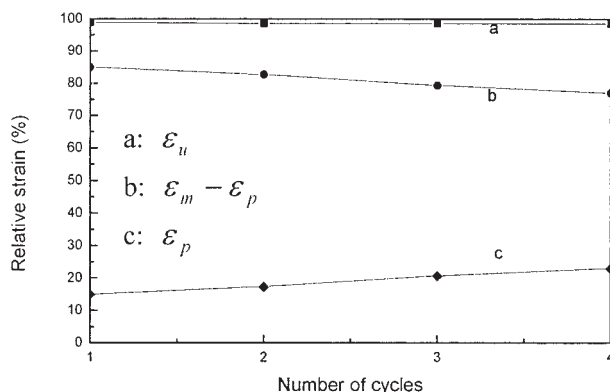


Figure 9 Cyclic dependence of various strains for the copolymer film with 50% soft segment. $\epsilon_m = 100\%$. M_n of the starting HTPI was 3.2×10^4 .

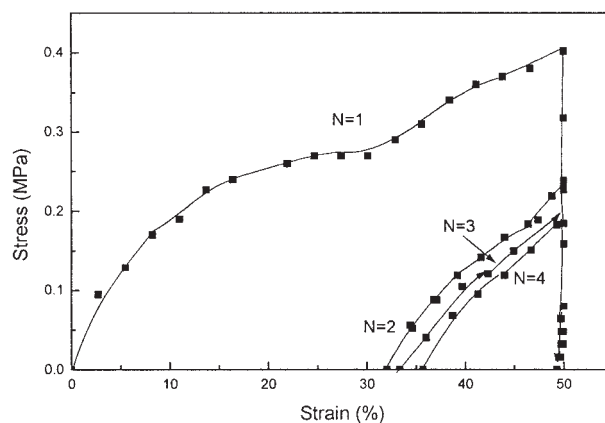


Figure 10 Cyclic loading behaviors of the copolymer film with 30% soft segment. M_n of the starting HTPI was 3.2×10^4 .

der the stress. The crystallites reformed can prevent the polymer from immediately reforming coil-like structures and from spontaneously recovering the original shape.¹ The good shape fixity observed for our films implies that the strain-induced crystallization of TPI is promptly initiated.

Features of the loading behaviors

The loading curve mentioned earlier actually reflects their tensile behavior at 65°C. As expected, the necking step disappears from the loading curves, confirming the melting of TPI crystallites at this temperature. Under this condition, the physical cross-links of the hard domains play an important role in the tensile process. Figure 6 shows that the film with 70% soft segment exhibits a linear tensile behavior at 65°C, *i.e.*, an elastic deformation takes place. It is known that the elastic deformation is defined in terms of isotropy.

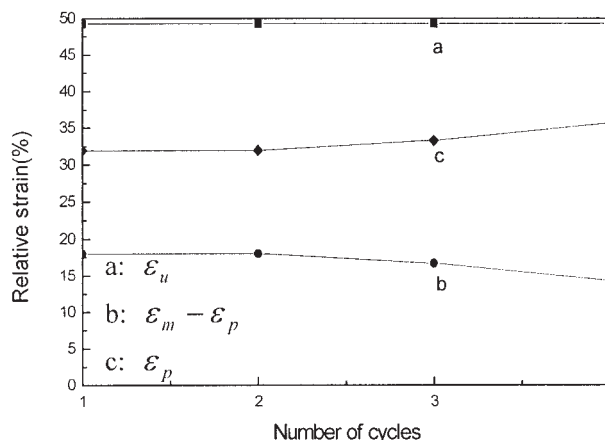


Figure 11 Cyclic dependence of various strains for the PU film prepared from HTP with 30% soft segment. $\epsilon_m = 50\%$. M_n of HTP was 3.2×10^4 .

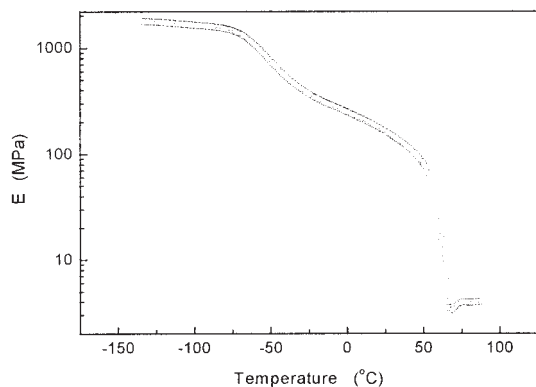


Figure 12 DMA plot of TPI-urethane copolymer.

Thus, this sample after cooling may possess a uniform structure, probably with the hard domains being well dispersed. Moreover, the film is expected to have satisfactory shape memory effects as result of its uniform structure. It is noteworthy that the other films tested here show inelastic deformations at the loading temperature, similar to the shape memory polymers in literatures.

Internal dissipation energy is one of the important parameters defining the shape memory qualities of materials. Its value can be estimated from the area enveloped by the loading and unloading plots.^{7,15} One can see that for each sample of this work, the loading plots are separated far from each other during the first two cycles ($N = 1, 2$). It indicates that a considerable reduction in the dissipation energy takes place due to the stress applied. For the film of 30% soft segment, the dissipation energy of the second cycle is one-fourth that of the first cycle. On comparisons, the reduction in dissipation energy is found to significantly depend on the compositions of the films.

It was claimed that the energy changes that occurred in the first few cycles are associated with thermal history of the sample and partial debonding of covalent bonds by the stress.¹ In our experiments, for each film, either the processing or the storage is conducted under similar conditions, such that the history effects may be negligible. It appears that the observed change in the energy is ascribed to the debonding at the interfaces. As seen in all the loading plots obtained, the plots almost overlap after the first loading cycle. The reason accountable for this phenomenon may be that the debonding that occurred at first cycle cannot reestablish immediately.

Figure 12 shows the storage modulus E' of the copolymer film plotted as a function of temperature. A short rubbery plateau appears at the temperature ranging from 65 to 90°C. During the plateau where TPI crystallites are melted, the urethane domains are totally responsible for carrying the external loading. According to viscoelastic theories of polymers,^{18,19} the

rubbery plateau is a reversible process associated with short-range motions of polymer chains, including entanglements and disentanglements. The long-range motions of the polymer chains are limited by the cross-links, here the physical cross-links of the urethane domains. Once the temperature is enhanced up to the degree such that the cross-links are not strong enough to prevent the chains from sliding, the polymer will turn into a viscous fluid, leading to the end of the rubbery plateau.^{15,19} Therefore, the end temperature of the rubbery plateau in Figure 12 is actually determined by the nature of the cross-links in the film. If the temperature is enhanced over the end temperature, a deformation with the viscoelastic fluid would take place, and it cannot be well recovered. From the aforementioned discussions, it can be deduced that the loading temperature of shape memory should be set below 90°C for the copolymer films.

The results obtained in this work show that the TPI-urethane copolymers developed in our laboratory are able to show high recovery rates depending on their composition, and consistently show excellent shape fixities. This material can easily be processed into various desired shapes by means of the reaction inject molding like the conventional polyurethanes, though this work uses the solution casting for samples preparation. From its switching temperature of about 65°C, this copolymer is expected to be a promising candidate of surgery fixation materials and can find other suitable applications.²⁰ It is known that TPI is one of the naturally occurring polymers and can be obtained from guttiferous trees throughout the pacific rim. At present, this polymer cannot have applications other than in golf materials. This work dealing with preparations of shape memory materials from TPI will probably make this polymer acquire broader applications.

CONCLUSIONS

The films of TPI-urethane copolymer can show good shape recovery depending on their compositions, while each film with different compositions consistently shows excellent shape fixity. For the film with 70% TPI segments, the recovery rate reaches to 85% and the shape fixity is close to 100%, at the maximum strain (ϵ_m) of 100%. The shape memory properties of this film can be well retained after several loading cycles. The copolymer films show a distinct microphase separation with urethane segments being arranged into spherical domains. The hard domains serve as physical cross-links responsible for fixation of the original shape. The driving force for the phase separation is the incompatibility of TPI and urethane segments. The tensile behaviors of the copolymer films are associated with their morphological structures that can readily evolve with their compositions.

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