

The Influence of Heat Treatment on the Properties of Shape Memory Fibers. II. Tensile Properties, Dimensional Stability, Recovery Force Relaxation, and Thermomechanical Cyclic Properties

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ABSTRACT: Shape memory fibers (SMFs) were prepared via a melt spinning process. The fibers were subject to different heat treatments to eliminate internal stress and structure deficiency caused during the melt spinning process. The influences of heat treatments on the SMF thermal properties, molecular orientation, tensile properties, dimensional stability, recovery force relaxation, and thermomechanical cyclic properties were studied. It was found that the heat treatments increased soft segment crystallinity and phase separation while decreased molecular orientation. The low-temperature heat treatment increased the breaking elongation, shape fixity ratios, and decreased boiling water shrinkage while shape recovery ratios were decreased. High-temperature treatment increased both the shape recovery ratios, fixity ratios, recovery stress stability and at the

same time decreasing the fiber mechanical strength. The results from differential scanning calorimetry, molecular orientation apparatus, and cyclic tensile testing were used to illustrate the mechanism governing the mechanical properties and shape memory effect. To obtain comprehensive outstanding properties, the SMF is expected to be treated at a high temperature because of the hard segment high glass transition temperature. Unfortunately, the heat treatment could not be conducted at a too high temperature because the SMF became too tacky and soft due to the melting of the soft segment phase. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1156–1164, 2009

Key words: fiber; polyurethanes; stimuli-sensitive polymers

INTRODUCTION

The thermally active shape memory fiber (SMF) is one smart material which can fix temporary elongation at a temperature below the switching temperature and recover the original length when heated to a temperature above the switching temperature.^{1–10} The shape memory effect of shape memory polyurethane fibers (SMFs) is due to the phase separation of the hard segments (aromatic diisocyanates and small size diols or diamines) and soft segments (aliphatic polyether or polyester) in the polyurethane molecules.^{11–17} The aggregated hard segment phase which has a higher thermal transition temperature (T_{perm}) acts as the physical crosslinking and is in charge of memorizing original shape while the soft phase which has a low transition temperature T_m or T_g (switching temperature) acts as a “switch” and is

responsible for fixing the temporary shape. If SMFs are deformed at a temperature above or below (cold draw) the switching temperature, the deformation can be fixed at the temperature below the switching temperature. Essentially, they can recover to the original shape upon being heated to be above the switching temperature.^{3,4,14,18–22} Compared with their bulk counterparts, SMFs possess higher mechanical properties, recovery stress because of the molecules orientation generated during spinning processes.^{2,5–7} SMFs may find broad applications in smart textiles and apparels, intelligent biomedical materials, high performance sensors, actuators, microgrippers, etc.

Though there has been much research on shape memory polyurethanes over the past two decades,^{3,18,20–29} the study on developing shape memory polyurethane fibers is at a preliminary state. In our group, we have developed T_g type and T_m type SMFs by wet spinning and melt spinning methods, respectively.^{2,4,6} In principle, shape memory polyurethane fibers can be prepared by using (i) dry, (ii) wet, (iii) chemical, and (iv) melt spinning technology.³⁰ Melt spinning is the most advantageous in terms of health, safety, and environmental and economy concerns, because it does not involve the use of

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DMF (dimethylformamide) or DMAc (dimethylacetamide) organic solvents.⁷

In this study, SMFs were prepared by melt spinning. To eliminate internal stress and structure deficiency caused by the spinning process, heat treatments were applied to the fibers. The influences of heat treatment on the fibers thermal properties, molecular orientation, tensile properties, dimensional stability, recovery force relaxation, and thermo-mechanical cyclic properties were studied.

EXPERIMENTAL

Materials

The shape memory polyurethane based on polyester polyol was obtained from shape memory textiles research center at the Hong Kong Polytechnic University. It is a PCL-based shape memory polyurethane^{6,8} with a soft segment glass transition at about -50°C and a melting transition at about 47°C .

Melt spinning

SMFs were spun using a laboratory spinning machine with highly pure nitrogen protection. The spinning temperature was 210°C , winding up speed 100 m/min. The prepared SMFs were 44 dtex in linear density. The fiber soft segment phase was a partially crystalline phase and the melting transition temperature was the switching temperature of the SMFs.^{21,27,31}

Heat treatment

The SMFs underwent heat treatments in a three-roller drawing unit (Alex James and Associate, Inc). The schematic representation of the heat treatment process is shown in Figure 1. The speed of the three rollers was 40 m/min. The temperature of the three rollers was same. Filaments were wound up at relaxation state without external stress. The specimens were donated as SMF- $X^{\circ}\text{C}$, i.e., SMF- 65°C , SMF- 85°C , SMF- 105°C , SMF- 125°C , where X was the heat treatment temperature. To make a comparison, the as-spun SMF is designated as SMF- 22°C (22°C ambient temperature). After heat treatments, the samples were stored at a constant temperature and humidity laboratory (temperature: 22°C , relative humidity: 61%) for 7 days before the properties were investigated.

Differential scanning calorimeter analyses

The thermal properties of the as-spun fiber and the SMFs after heat treatment were investigated using a differential scanning calorimeter (Perkin-Elmer Diamond) with nitrogen as the purge gas. Indium and zinc were used for calibration. First, the samples

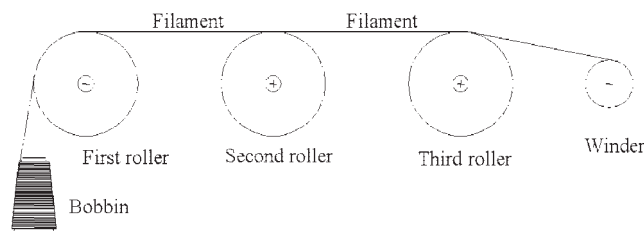


Figure 1 The schematic representation of the heat treatment process.

were cooled from ambient temperature to -70°C at a cooling rate of $20^{\circ}\text{C}/\text{min}$. Then the fibers were reheated to 250°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ to investigate the thermal properties. Fibers were washed with methanol to remove the oil, and air dried before testing.

Sonic modulus

The sonic velocities and sonic modulus of the as-spun fiber and the SMFs after heat treatment at different temperatures were measured by using the SCY-111 sonic velocity apparatus (Donghua University of China). The tests were based on the presumption that sonic waves can travel fast if the orientation of fibers increases.

Tensile properties

Tensile properties were measured with the instron 4411 (Instron Corporation of USA) according to the ASTM D2256 standard. The sample gauge length between clamps was 20 mm with a stretching speed 300 mm/min. Every experiment was conducted 10 times to produce average properties.

Boiling water shrinkage

The dimensional stability of the SMFs was evaluated by measuring the shrinkage percentage of the fibers in boiling water. First, filaments of 1 m length were immersed in boiling water for 30 min. Then they were dried at ambient temperature (temperature: 22°C , relative humidity: 61%) for 24 h. The boiling water shrinkage percentage was determined using the following equation:

$$\text{Shrinkage \%} = \frac{L - l}{L} \times 100\%$$

where L is the fiber original length; l is the final length after shrinkage in boiling water.

Stress relaxation study

In characterizing shape memory behavior, the deformation is usually conducted at a temperature above

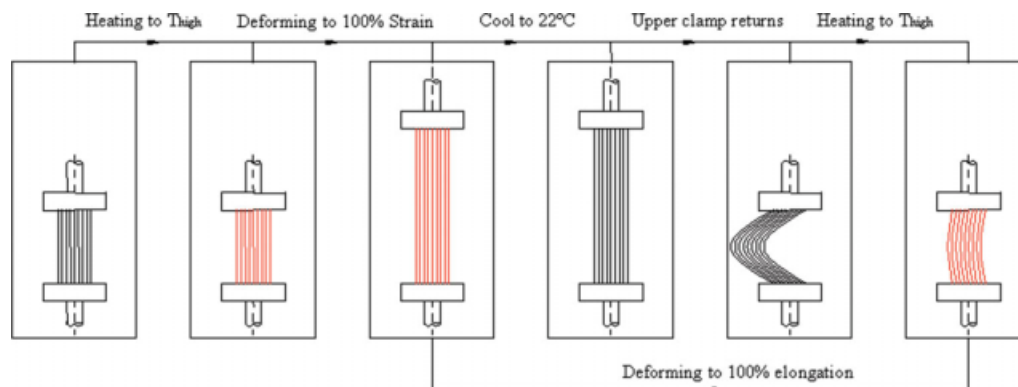


Figure 2 The thermomechanical cyclic tensile testing process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the switching transition temperature because at a high temperature, polymer shows lower elastic modulus than that at an ambient temperature. However, in practice, the elongation deformation of SMF usually happens at ambient temperatures such as the wrinkles on cloth. So it is very important to understand to what degree the stress can be stored in the fiber after deformation at the temperature below the switching transition temperature (cold drawing).³ The stress relaxation tests were carried out on the Instron 4466. First, the fibers were stretched to 100% strain at a speed of 10 mm/min at an ambient temperature,^{13,22,28,32} then the strain was kept for 15 min to record the stress relaxation for analysis. The sample gauge length was 20 mm.

Thermomechanical cyclic tensile investigations

Thermomechanical cyclic tensile tests were carried out by using the Instron 4466 equipped with a temperature controlled chamber. In the measurement, the fiber has a gauge length of ~ 20 mm. The programmed thermomechanical cyclic tensile testing progress and testing path are shown in Figures 2 and 3.³ In Figure 3, ϵ_m is the defined maximum deformation in the cyclic tensile testing. It is 100% strain for this study. ϵ_u is the strain after unloading at T_{low} , and $\epsilon_p(N)$ is the residual strain after recovering in the N th cycle. The thermomechanical cyclic tensile test consists of five steps: (1) The fiber was first stretched to 100% elongation ratio at 70°C (T_{high}) which is above the switch transition temperature at a drawing speed of 10 mm/min.^{13,28} (2) Subsequently, cool air was vented passively into the chamber to cool down the sample to 22°C and the temperature was kept for 15 min to fix the temporary elongation. (3) Then upper clamp returned to the original position at a speed of 40 mm/min and the fiber shrank from ϵ_m to ϵ_u due to instant elastic recovery. (4) Finally, the fiber was heated to 70°C to allow the shape memory recovery with the result

that the elongation returned to ϵ_p . (5) After completing 1–4 above all four steps, the second cycle began. The fixity ratio (R_f) and recovery ratio R_r after the N th cycle are calculated according to following equations^{7,10}:

$$R_f(N) = \epsilon_u(N)/\epsilon_m \times 100\%$$

$$R_r = [\epsilon_m - \epsilon_p(N)]/\epsilon_m \times 100\%$$

RESULTS AND DISCUSSION

Thermal properties of SMFs

The DSC thermograms of the SMFs are presented in Figure 4. The thermal transition temperature, heat of

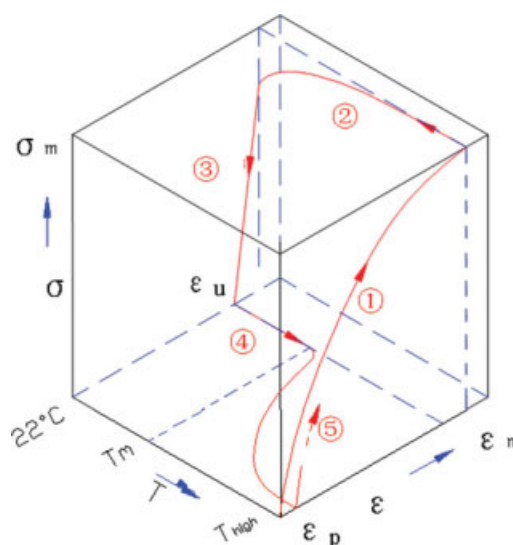


Figure 3 The schematic representation of the cyclic tensile testing path. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

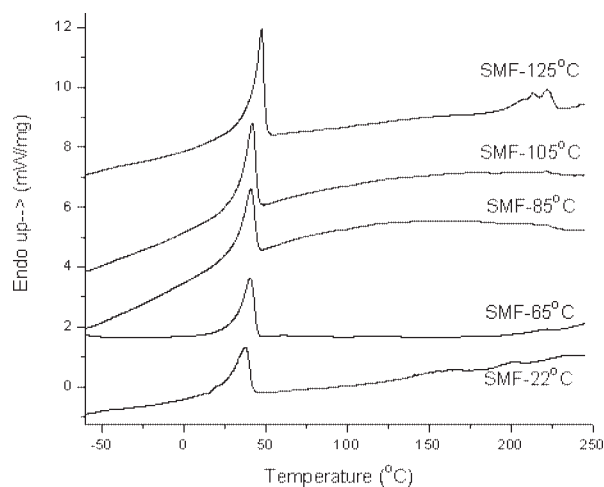


Figure 4 DSC thermograms of the as-spun SMF and SMFs after heat treatment.

fusion, and crystallinity of the as-spun fiber and SMFs after heat treatment are tabulated in Table I. The melting transition peak at around 41.2–48.6°C is ascribed to the melting transition of the soft segment phase.^{20,21} It can be seen that the heat treatment has remarkable influences on the SMFs soft segment phase. With the increasing heat treatment temperature, the soft segment crystallinity increases from 18.8% of as-spun SMF to SMF-125°C 28.4%. The melting transition temperature increases from 41.20 to 48.58°C. According to Figure 4, after 125°C heat treatment, the SMF shows an obvious hard segment endothermic peak which is supposed to be the endothermic peak because of relatively short-range ordered hard segments, which suggests that the high temperature heat treatment at 125°C has remarkable influence on the SMFs hard segment phase. According to previous studies,^{34,35} the glass transition temperature of the hard segment phase in polyurethane is located round 125°C and the melting point of

TABLE I
Thermal Properties of the PCL, as-spun SMF, and SMFs after Heat Treatment

	Soft segment		
	T_m (°C)	ΔH (J/g)	Crystallinity (%)
PCL-4000	59.0	53.7	39.8
SMF-125°C	48.6	38.4	28.4
SMF-105°C	46.5	36.9	27.3
SMF-85°C	45.4	34.9	25.9
SMF-65°C	43.6	31.7	23.5
As-spun SMF	41.2	25.3	18.8

T_m is crystal melting temperature, ΔH the heat of fusion. The soft segment crystallinity was calculated from the enthalpy data ΔH of the crystallization by using the 140 J/g enthalpy value for fusion of 100% crystalline PCL given by Crescenzi et al.^{32,33}

hard segment phase crystals is in the range of 200–240°C.³⁶ The above results suggest that heat treatment can increase the soft segment crystallinity and the high temperature heat treatment benefits the formation of a more stable hard segment phase.

In polymers, the chain rotation and flexibility are required to enable packing of molecules and the formation of an order structure. In the polyurethane, firstly, high temperature heat treatment may decrease chain entanglement and improved the ability of the polyurethane to crystallize. Secondly, the heat treatment especially the high temperature heat treatment promotes the aggregation of hard segments as has been demonstrated above. As a result, the soft segment phase became more “pure” after high temperature heat treatment. Consequently, crystallinity and melting transition temperature of soft segment phase increase. Thirdly, the heat treatment may have the ability to repair polyurethane crystals that are destroyed during the spinning process because of drawing. Therefore, the crystallinity and melting transition temperature of SMFs soft segment phase increased with the increasing heat treatment temperature.

Sonic modulus

The sonic velocities C and sonic modulus E of the SMFs, before and after heat treatments are shown in Figure 5. For the SMFs under study, the sonic modulus decreases significantly after low temperature heat treatment, which suggests the molecular orientation in the SMF decreases. This is because the SMF has a melting transition at a low temperature. During the low temperature heat treatment, the internal stress stored among the hard segment phase during the melt spinning process releases accompanied with the soft segment disorientation. With the increasing heat treatment temperature, the influence

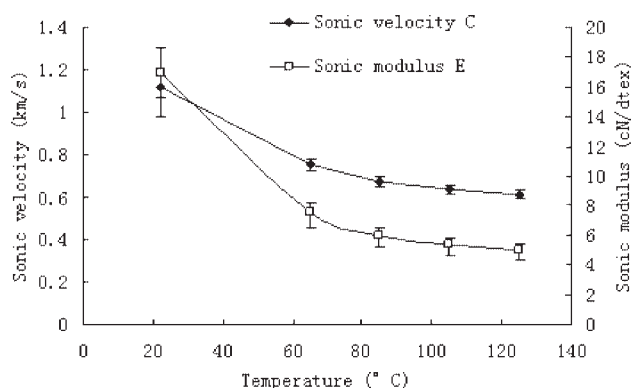


Figure 5 The sonic velocity C and sonic modulus E of the as-spun fiber and SMFs after different temperature heat treatments.

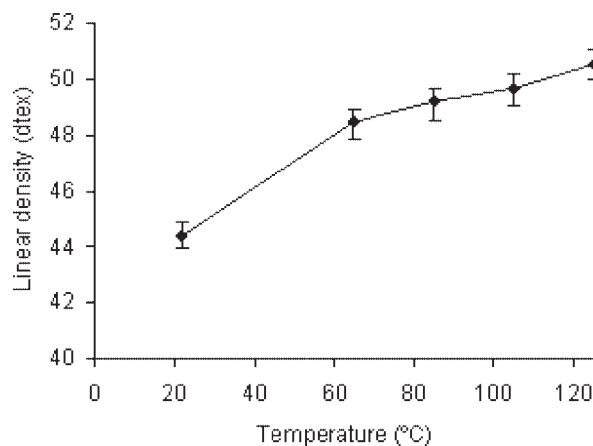


Figure 6 Influence of heat treatments on SMF linear density.

of the heat treatment on the sonic modulus of the SMF decreases prominently.

Linear density

From Figure 6 it can be seen that the linear density of the SMF has a prominent increase after the heat treatment at 65°C. With increasing heat treatment temperature, the influence of heat treatment on the linear density becomes not so remarkable. This is also because the prepared SMFs have a soft segment phase melting transition at about 41°C. When the SMF is heated to 65°C, because the soft segments have enough mobility to rearrange and disorientate themselves, the stress residual between the soft segment and that of between soft and hard segments releases. Simultaneously, the polyurethane molecules disorientates partially as established above. As a result, the fiber linear density increases noticeably after the low temperature heat treatment. However, continuously increasing heat treatment temperature does not have such obvious influence on the linear density. This may be because after 65°C heat treat-

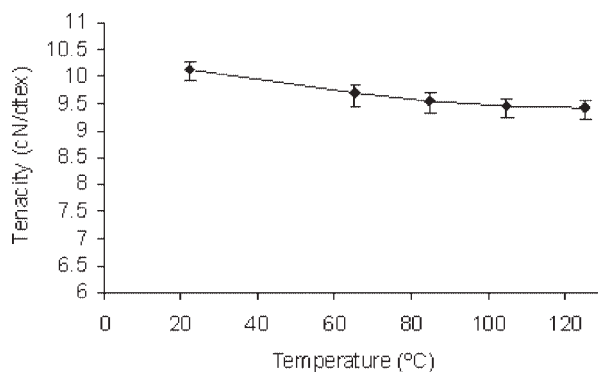


Figure 7 Influence of heat treatments on SMF tenacity.

ment most of residual stress between the soft segments and that between soft segment phase and hard segment phase has been released.

Tenacity

The tenacity of SMFs as a function of heat treatment temperature is shown in Figure 7. Heat treatment especially low-temperature heat treatment decreases the SMF tenacity. Further increasing heat treatment temperature, the tenacity has little change. These results may be attributed to two factors: molecule disorientation and phase separation during the heat treatment. Low-temperature heat treatment at above the soft segment phase melting transition temperature decreases the molecular orientation, while at the same time the heat treatment increases the phase separation of soft segment phase and hard segment phase. Especially, it has been demonstrated above that the high-temperature heat treatment increases the hard segment phase stability. At a low-temperature heat treatment, the soft segment molecule disorientation is dominant, so the fiber tenacity decreases. While with increasing heat treatment temperature at about the hard segment glass transition temperature, most of the soft segment molecules disorientation has finished. At this temperature, the hard segments have slight mobility to reorganize to form more stable hard segment domains, so the tenacity of the SMF does not decrease so markedly.

Breaking elongation

The breaking elongation of the SMFs as a function of heat treatment temperature is given in Figure 8. It can be seen that the breaking elongation increases after heat treatment especially at below 85°C heat treatment temperature. Continuously increasing heat treatment temperature has little influence on the breaking elongation. During the heat treatment, the

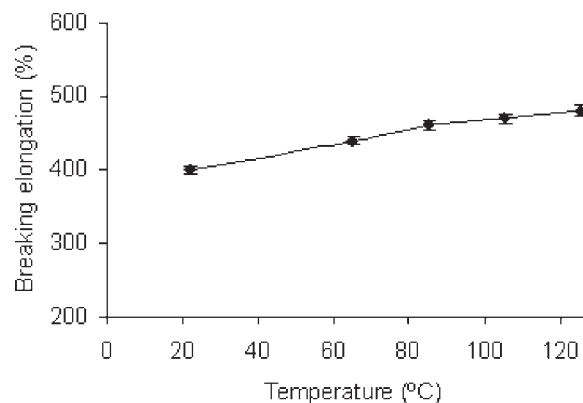


Figure 8 Influence of heat treatments on SMF breaking elongation.

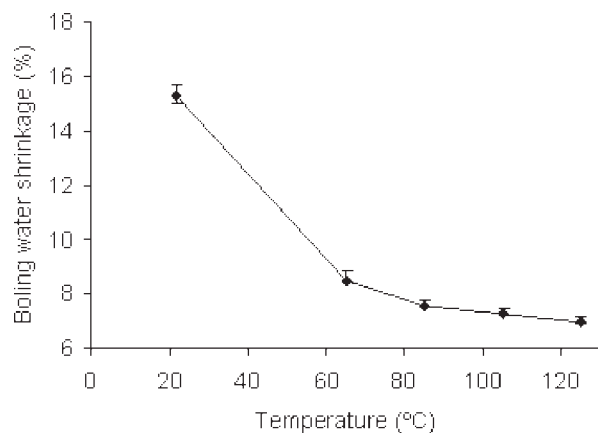


Figure 9 Influence of heat treatments on SMF boiling water shrinkage.

molecules disorientate and internal stress releases, so the breaking elongation of the SMF after heat treatment increases. The breaking elongation after high-temperature heat treatment has limited changes as most of the internal stress has been released and most of the molecules disorientation has finished at the low temperature.

Boiling water shrinkage

The results of heat treatment on the SMF boiling water shrinkage are shown in Figure 9. It can be seen that with increasing heat treatment temperature, the fiber dimensional stability increases because of molecules disorientation and rearrangement. At 65 and 85°C which are above the soft segment melting transition temperature, the soft segments have enough mobility to rearrange themselves. Continuously increasing heat treatment temperature had hardly any influence on the boiling water shrinkage. However, it can be seen that after 125°C heat treatment, the SMFs still have high boiling water shrinkage. This may be because that at the experiment temperature 125°C, the hard segment mobility is not active enough. Even though the heat treatment improves the soft segment dimensional stability and has some influence on the hard segment crystallinity, the hard segment phase does not obtain enough energy to release the residual stress stored in the hard segment phase. According to previous studies,^{34,35} the glass transition temperature of the hard segment phase in polyurethane is located at around 125°C and the melting point of hard segment phase crystals is in the range of 200–240°C.³⁶ From this point of view, the SMF should be heat treated at a much higher temperature above the hard segment glass transition temperature. Unfortunately, when the temperature is higher than 125°C, the SMFs become too soft and tacky because of the melting of the soft

segment phase so that the heat treatment cannot be conducted. At this temperature, the hydrogen bonding as physical crosslink which restricts the free movement of the soft segments above its melting temperature may begin to be destroyed. So, the SMF becomes too soft and tacky.

Stress relaxation

It is very important to investigate the influence of heat treatment on the stress decay of SMFs during deformation because actually the shape recovery driving force of SMFs is the stress stored in the hard segment phase during deformation. This property is especially important if the SMF is used for a long term. The results of stress relaxation process of various SMFs after stretching to 100% are presented in Figure 10. The stresses reach the maximum values after 2 min. It can be seen that with increasing heat treatment temperature, the maximum stress and plateau stress decrease greatly. This is mainly due to the disorientation of the SMFs with increasing heat treatment temperature. However, Figure 10 shows that the stress decay speed of SMFs decreases with increasing heat treatment temperature. The stress of SMF-125°C at plateau area nearly has no obvious change in the testing range. These may be due to two reasons: First, the heat treatment increases the phase separation as has been established by DSC. Second, hard segments transferred to well-ordered structures with strongly H-bonding after the high-temperature heat treatment. As a result, the stress of the SMF after high-temperature heat treatment is more stable at the plateaus area.

Shape memory effect

The thermomechanical cyclic stress–strain curves of the as-spun SMF and SMFs after heat treatment are shown in Figure 11. The detailed data of fixity ratios,

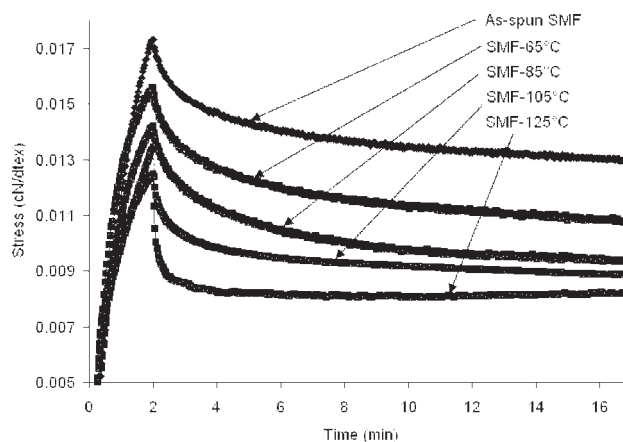


Figure 10 Stress relaxation of SMFs.

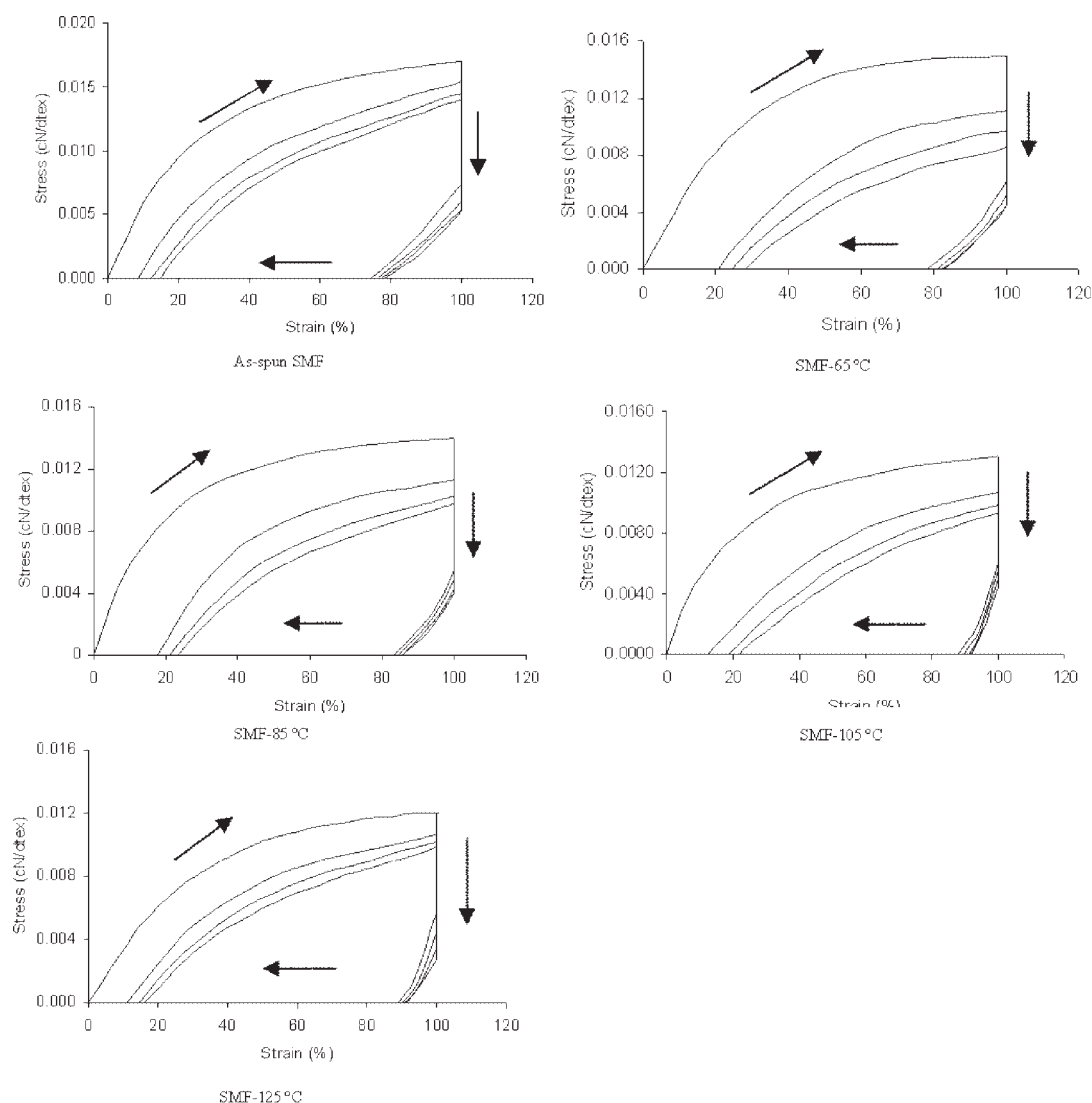


Figure 11 Thermomechanical cyclic tensile testing strain–stress curves of the SMFs.

recovery ratios, and maximum stress at 100% strain are tabulated in Table II. After 65°C heat treatment the recovery ratios of the SMF decrease greatly, while the fixity ratios increase. With increasing heat treatment temperature, both the shape recovery ratios and fixity ratios increase.

Generally, it has been widely accepted that in the polyurethane system, the soft segment phase is in charge of shape fixity by freezing the polyurethane molecules after being cooled to below the switching transition temperature, and the hard segment phase acting as physical crosslinking is responsible for shape recovery by releasing the stress stored during deformation.^{3,6,7,20,22,27,37} However, for the SMFs which have molecular orientation and internal stress caused by melt spinning, they will shrink because of the stress releasing and molecules disorientation during heat treatment. During 65°C heat treatment, the internal stress releases and molecules partially disorientate because of the melting of soft segment

phase. Therefore, the recovery ratios decrease and fixity ratios increase after 65°C heat treatment. With increasing heat treatment temperature, as has been established above, the soft segment phase crystallinity and phase separation increase and the hard segment phase stability especially after 125°C is also improved. So the soft segment has more ability to freeze the polyurethane molecules when cooled from temperature above the switching transition temperature to ambient temperature. And the hydrogen bonded hard segment phase has more power to recover to the original position. As a result, the SMF shows higher shape recovery ratios. So, the shape fixity ratios and recovery ratios increase with increasing heat treatment temperature.

Heat treatment

A model shown in Figure 12 can be employed to explain the molecule disorientation and phase

TABLE II
Thermomechanical Cyclic Tensile Testing
Result of SMFs

Circle no.	ε_p (N)	ε_u [R_f (N)]	Stress at 100% strain (cN/dtex)	R_r (N)
As-spun SMF				
1	0.0%	74.2%	0.0170	100.0%
2	8.5%	76.5%	0.0155	91.5%
3	12.4%	77.3%	0.0145	87.6%
4	15.0%	78.1%	0.0140	85.0%
SMF-65°C				
1	0.0%	78.0%	0.0158	100.0%
2	20.8%	81.0%	0.0111	79.2%
3	24.6%	82.4%	0.0097	75.4%
4	28.0%	83.0%	0.0086	72.0%
SMF-85°C				
1	0.0%	83.0%	0.0140	100.0%
2	17.8%	84.5%	0.0120	82.2%
3	21.1%	85.5%	0.0102	78.9%
4	23.6%	85.7%	0.0098	76.4%
SMF-105°C				
1	0.0%	87.8%	0.0120	100.0%
2	12.6%	88.9%	0.0107	87.4%
3	19.0%	90.0%	0.0098	81.0%
4	22.1%	90.4%	0.0093	77.9%
SMF-125°C				
1	0.0%	89.0%	0.0120	100.0%
2	11.0%	90.0%	0.0107	89.0%
3	14.5%	90.5%	0.0102	85.5%
4	16.2%	91.0%	0.0098	83.8%

changes process of the SMFs during heat treatment. In Figure 12, the soft segments are shown as thin lines. The hard segments having a tendency to adhere to one another through strong hydrogen bonding form hard segment domains. They are shown as island phase. During melt spinning, at the spinning temperature which is higher than the hard segment melting transition temperature, the fiber is extruded from a spinneret. Upon being cooled to an ambient temperature which is below the soft segment melting transition temperature, the fiber is wound up and the fiber shape is cast. The soft segment phase is partially crystallized and orientated at an ambient temperature and the hard segment phase is also stretched in the fiber axial direction after the spinning process.^{6,7} During the heat treatment above the soft segment melting transition temperature, the soft segments disorientate and reorganize following the release of the internal stress caused during the spinning process.

However, at the low temperature which is below the hard segment phase glass transition temperature, the orientated hard segments are intact. Because of the fact that at a low temperature the hard segments do not have enough mobility to rearrange and release the internal stress, the low temperature heat treatment is not completely effective for the SMF comprehensive properties improvement. Unfortu-

nately, if the heat treatment temperature is continuously increased, the heat treatment cannot be conducted because the SMFs become too soft and tacky because of the melting transition of the soft segment phase.

CONCLUSIONS

SMFs were prepared via a melt spinning process. The fibers underwent different heat treatments to eliminate internal stress and structure deficiency generated during the melt spinning. The influences of heat treatments on the SMF thermal properties, tensile properties, molecular orientation, dimensional stability, recovery force relaxation, and thermomechanical cyclic properties were studied. Several main physical property changes of SMFs after heat treatment were observed.

1. Heat treatments increased soft segment crystallinity and phase separation.
2. Low-temperature heat treatment increased breaking elongation and shape fixity ratios, decreased boiling water shrinkage, tenacity, and shape recovery ratios.
3. High-temperature heat treatment benefited the improvement of hard segment phase stability. The boiling water shrinkage was still very high even after 125°C heat treatment because it had little influence on the release of the residual stress in the hard segment phase.
4. Increasing the heat treatment temperature increased both the shape recovery ratios and fixity ratios.

The SMF is expected to be treated at a high temperature considering the high glass transition temperature of the hard segment. Unfortunately, the heat treatment could not be conducted at 125°C because the SMF became too tacky and soft due to the melting of the soft segment phase.

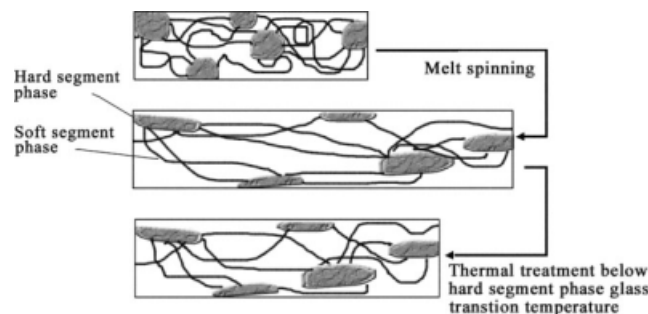


Figure 12 Schematic representation of molecular disorientation and phase changes of SMFs induced by heat treatment.

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