Melt Spun Thermoresponsive Shape Memory Fibers based on Polyurethanes: Effect of Drawing and Heat-Setting on Fiber Morphology and Properties

Jasmeet Kaursoin, Ashwini K. Agrawal

Department of Textile Technology, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

Received 11 April 2006; accepted 27 June 2006
DOI 10.1002/app.25124
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Thermoresponsive shape memory (SMP) fibers were prepared by melt spinning from a polyester polyol-based polyurethane shape memory polymer (SMP) and were subjected to different postspinning operations to modify their structure. The effect of drawing and heat-setting operations on the shape memory behavior, mechanical properties, and structure of the fibers was studied. In contrast to the as-spun fibers, which were found to show low stress built up on straining to temporary shape and incomplete recovery to the permanent shape, the drawn and heat-set fibers showed significantly higher stresses and complete recovery. The fibers drawn at a DR of 3.0 and heat-set at 100°C gave stress values that were about 10 times higher than the as-spun fibers at the same strain and showed complete recovery on repeated cycling. This improvement was likely due to the transformation brought about in the morphology of the permanent shape of the SMP fibers from randomly oriented weakly linked regions of hard and soft segments to the well-segregated, oriented and strongly H-bonded regions of hard-segments. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2172–2182, 2007

Key words: shape memory polymer; melt spinning; fibers; recovery stresses

INTRODUCTION

Polymeric materials which have the inherent ability to return to their original memorized shape after undergoing a shape deformation on exposure to a particular temperature are called thermoresponsive shape memory polymers (SMPs).[1] SMPs are linear, phase-segregated multiblock copolymers composed of two phases: a reversible phase and a frozen phase. The reversible phase is formed by the soft segments and serves as a molecular switch and enables the fixation of the temporary shape. These polymers use the glass transition temperature (T_g) or the crystalline melting temperature (T_m) of soft (switching) segment as the shape transition temperature (T_{trans}). The frozen phase is formed by the hard segments, which play the role of physical crosslinks (for example, hydrogen bonds, crystallites in a crystalline polymer, etc.) and is responsible for the permanent shape.[2]

Many polymers exhibit this effect such as *trans*-isoprene, styrene–butadiene block copolymer, copolymer of polyethylene terephthalate–polyethylene oxide, crosslinked polystyrene, and segmented polyurethanes (PU).[3] These polymers find application as temperature sensors, actuators, auto chokes, damping materials, as deployable structures, microgrippers [MEMS], and in biomedical field as catheters, stents, and drug delivery agents.[2,4–7] These polymers have an immense potential as self-tightening sutures due to their shape memory behavior.[8] These polymers have also found application in textiles and apparels as they can be used to manufacture breathable sportswear that respond to variations in temperature.[9]

Considerable work has been reported on the synthesis of segmented PU SMPs and on the testing of their shape memory property and other physical properties.[10–19] These studies dwelled on investigating the temperature of shape transition. Attempts have been made to tune the temperature of transition by changing the types or molecular weight of the soft-segment. Other than the transition temperature, the recovery behavior is also extremely important. This includes extent of recovery (%), stresses developed during recovery, and the cyclicity of the shape memory property. The content and type of the hard segments have been changed to modify these recovery properties. Also, shape memory composites have been reported where nanoparticles and glass fibers were added to SMPs to enhance the stress level during recovery and to increase their stiffness. Such attempts have successfully increased the stiffness of the SMPs and tailored the recovery parameters to optimize recovery force or displacement for specific applications.[20,21] However, there have been

Correspondence to: A. K. Agrawal (ashwini_agrawal@yahoo.com).

Journal of Applied Polymer Science, Vol. 103, 2172–2182 (2007)

some limitations to these approaches. On increasing the hard segment content, though the shape recovery improves but the shape fixity suffers. Similarly, though shape memory composites show better stresses during recovery, but their recovery is not complete. Hence, there is a necessity to investigate other approaches which may tune both the shape memory property and stress levels needed for the shape recovery.

In this study, an attempt has been made to convert a commercially available shape memory polymer into melt-spun shape memory fibers, to use postspinning operations such as drawing and heat-setting to change their morphology, and to investigate the effect of morphology on the shape memory behavior of such fibers.

EXPERIMENTAL

Materials

Shape memory polymer (SMP) chips (MM-4510) based on polyester polyol series of polyurethane were procured from DiAPLEX, Tokyo, Japan, having the glass transition temperature of 40.8°C and melting point of 159°C (as reported by the company). The monomers used in synthesizing the polymer, as informed by the manufacturer, were polyethylene adipate, methylenebis(4-phenylisocyanate), 1,4-butanediol (BDO), and bisphenol-A.

Characterization

Molecular weight

Intrinsic viscosity was measured in DMF at 30°C using Ubbelohde dilution viscometer.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed using a PerkinElmer DSC 7 calorimeter from 50°C to 220°C at a heating rate of 10°C/min under nitrogen atmosphere to detect the presence of melting point. The SMP pellet was compression molded into film, which was cut into small pieces for this study.

Melt flow index

The melt flow index (MFI) of the SMP pellets was studied using Kay Jay Indexer in a temperature range of 170°C to 220°C.

Melt spinning of SMP chips

The melt spinning of the SMP pellets was carried out in a laboratory spinning machine at 215°C at a throughput rate of 0.78 g/min, and the fiber was wound at a speed of 98.5 m/min.

Drawing

The as-spun shape memory fiber was drawn on a laboratory drawing machine at three different draw ratios, 1.5, 2.2, and 3 using a hotplate at a temperature of 55°C and at feed roller speed of 1.55 m/min. The length of the heater plate was 30 cm.

Heat-setting

The as-spun and the drawn fibers were heat-set at 100°C in a silicone oil bath under taut condition for 15 min. The heat-set fibers were washed with methanol to remove the oil and then air dried.

Testing

Cross section

Cross section of both the as-spun and drawn fiber was measured using Leica–DMLP optical polarizing microscope at 10×.

FTIR

PerkinElmer 883 FTIR was used to record infrared spectra of fiber samples. The chips were compression molded into a thin film and cut into small pieces. The as-spun, drawn, and drawn-heat-set fibers were cut into small pieces. These were mixed with KBr to form pellets. The spectra were recorded in the range of 400–4000 cm^{-1}.

X-ray spectroscopy

WAXD spectra of the procured SMP and the shape memory fibers were recorded by X′ Pert PRO machine of PANalytical between 2Θ of 10°–35° in the reflection mode. The fibers were cut into small pieces and placed on a powder sample stage for the spectroscopy.

Shape memory behavior

The shape memory effect was quantified by cyclic thermomechanical tests. The measurement was done on Instron (4202) using a self-fabricated thermal chamber. The stress–strain relationship during the thermomechanical cycling test is schematically shown in Figure 1. First, at the temperature T_h, the maximum strain ε_m was applied at a constant strain rate ε', and then, while maintaining ε_m, the temperature was cooled to T_L. After holding at T_l for 5 min, the

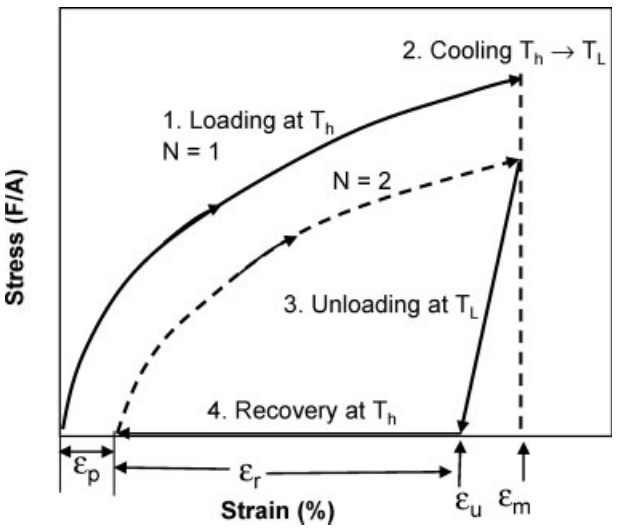

Figure 1 Stress–strain relation in a thermomechanical cycle.

fiber was unloaded. Under the no-load condition, it was heated from T_L to T_h in 5 min and held for 5 min at T_h. This thermomechanical cycle was repeated N times. In the experiment, $\varepsilon_m = 40$ and 150%, $T_h = 55^\circ$C, strain rate $\varepsilon' = 80\%$/min, and $N = 10$ were used. The two most important quantities, which describe the shape memory properties of a material at a strain, ε_m, are the shape fixity (R_f) and the strain recovery (R_r).[22]

$$\%\ \text{Shape fixity}\ (R_f) = \frac{\varepsilon_u}{\varepsilon_m} \times 100$$

$$\%\ \text{Shape recovery}\ (R_r) = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \times 100$$

where, ε_m is the maximum strain applied; ε_u is the strain at temperature $< T_{\text{trans}}$ after unloading; ε_r is the recovered strain at temperature $> T_{\text{trans}}$; ε_p is the permanent or the residual strain at the end of the cycle.

Stress hardening/softening

The physical stability of SMP fiber was studied under cycling condition. These were defined by two parameters. If the stresses at a defined strain increased with cycling it was termed as ''stress hardening'' and if they reduced with cycling it was termed as ''stress softening.'' These parameters were quantified using the following equation.

$$\text{Stress hardening/softening} = \frac{(\text{stress value of 1st cycle} - \text{stress value of } N\text{th cycle}) \times 100}{\text{stress value of 1st cycle}}$$

Tensile properties

Tensile testing of the filaments was carried out on Instron tensile testing instrument (Model No. 4301) using a gauge length of 25 mm and cross head speed of 20 mm/min. The load cell used was of 1 kg.

Shrinkage above glass transition

The stability of permanent shape was evaluated by measuring the shrinkage percentage of the as-spun, drawn, and heat-set fibers. It was determined by taking a fiber of known initial length (IL), allowing it to shrink by immersing it in water at 55°C. The final length (FL) of the fiber was determined after 10 min. The shrinkage percentage was calculated using the following relation.

$$\text{Shrinkage}\ \% = \frac{\text{IL} - \text{FL}}{\text{IL}} \times 100$$

Stress relaxation

Stress relaxation behavior of SMP fibers was studied on Instron tensile testing instrument (Model no. 4202). The filaments were drawn to a constant strain of 40% at a strain rate 80%/min above the glass transition temperature (55°C) and kept stretched for 15 min at the same temperature. The stress relaxation (%) with time (t) was calculated using the formula below:

$$\text{Stress relaxation}\ (\%) = \frac{(\text{stress at } t_0 - \text{stress at } t) \times 100}{\text{stress at } t_0}$$

where t_0 is the start of the relaxation experiment.

Birefringence

Birefringence was measured using Lieca tilting compensator and Leica–DMLP optical polarizing microscope.

Sonic modulus

Sonic modulus of the filaments was measured on Dynamic Modulus Tester PPM-5R made by H. M. Morgan Co.

RESULTS AND DISCUSSION

Characterization of shape memory polymers

The number–average molecular weight of the ester type of MM4510 shape memory polymer was found to be approximately 90,000 using K and α values of a polyester based polyurethane from the literature.[23] The DSC scans (Fig. 2) of the shape memory poly-

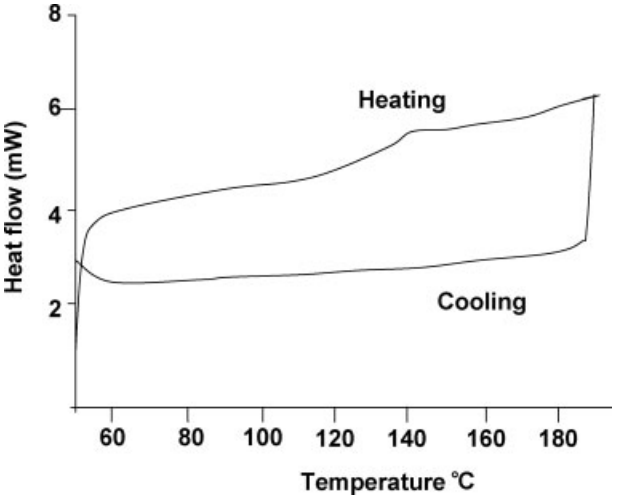

Figure 2 DSC scan of MM4510 SMP.

mer in the form of melt cast film did not show any melting peak. The cooling curve also did not show any crystallization. This indicated that the hard segments in the copolymer were not crystallizable. A weak thermal transition was observed at about 140°C, which may be due to the increased mobility of the hard segments which are strongly bonded with the hydrogen bonds. Melt flow behavior of the SMP was similar to that of a thermoplastic polymer. MFI was found to rise exponentially with increasing temperature. From Figure 3, it can be observed that the appropriate value of MFI for fiber spinning is at a temperature of around 215°C.

X-ray of both chips and as-spun material showed a broad peak at $2\theta = 19.5^{\circ}$, which was indicative of noncrystalline or poorly crystalline structure (Fig. 4).[17] This observation was supported by DSC scan, which only showed a weak thermal transition corresponding to movement in hard segments.

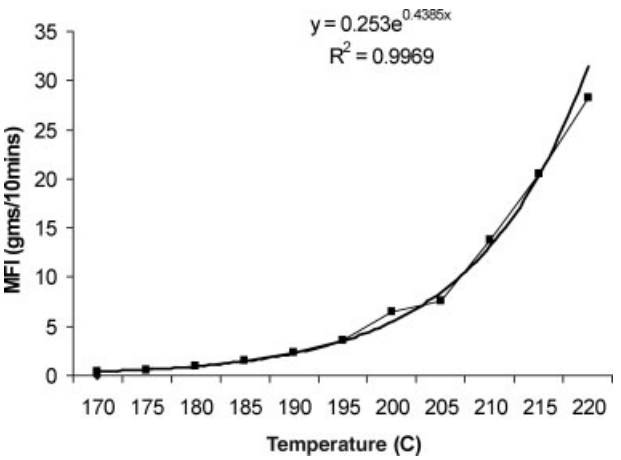

Figure 3 Melt flow index with temperature of MM4510 SMP.

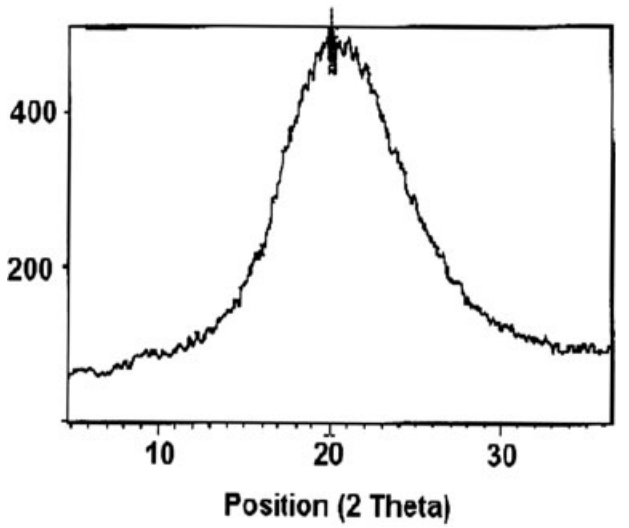

Figure 4 WAXD scan of the MM4510 SMP.

Melt spinning and postspinning operations

The SMP could be readily melt spun at 215°C. The as-spun fiber was drawn to different draw ratios and subsequently heat-set. The selection of heat-setting temperature of 100°C was arbitrary; it was taken to be close to the expected melting point of 140°C and much above the T_g, so that heat-setting may be effective. Table I shows the machine draw ratio and actual draw ratio along with the denier of the fibers drawn at different draw ratios. The cross section of the melt-spun thermoresponsive shape memory fiber is shown in Figure 5. From the figure, it may be seen that the cross section of the fibers is round and uniform.

Structure and properties of melt-spun SMP fibers

FTIR

The FTIR spectra of the chips, as-spun, drawn, and drawn and heat-set fibers (3.0) are shown in Figure 6. The spectra show a shift in the peak values of N—H stretching of the urethane linkage from 3392 cm^{-1} in the chips to 3370 cm^{-1} in drawn and heat-set fibers. This indicates that the hydrogen bonding between urethane linkages was getting stronger as the chips

TABLE I
Sample Codes, Denier, and Draw Ratios of Shape Memory Fibers

Sample code	Machine draw ratio	Denier	Actual draw ratio
As-spun	0	100	0
D1.5	1.5	63.9	1.56
D2.2	2.2	49	2.04
D3.0	3.0	36	2.8

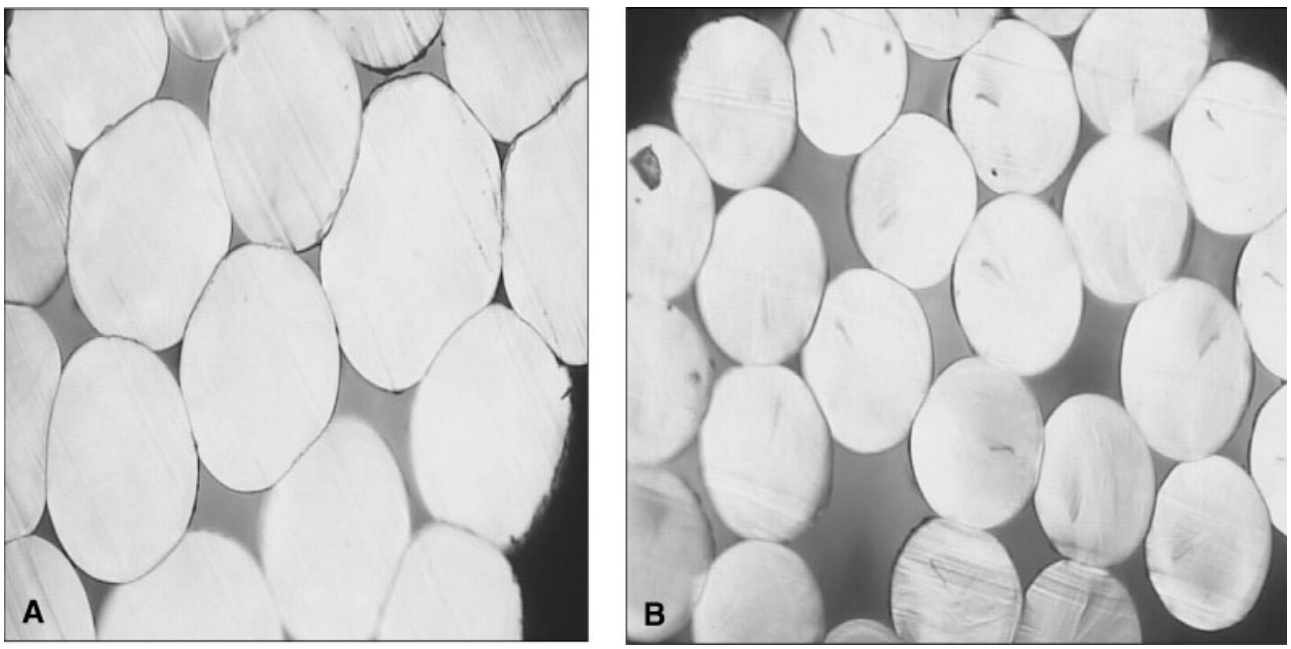

Figure 5 Cross sections of (a) as-spun fiber and (b) drawn fiber (D1.5).

were processed to the fiber, drawn, and subsequently heat-set. This shift[24–26] was indicative of formation of hard segment domains in the fiber structure with drawing and heat-setting.

Sonic modulus

The sonic modulus measures the ability of the sound waves to travel through the fiber. Sonic waves can travel faster if the fiber consists of polymer chains, which are well connected and are rigid to allow proper transmission of waves. This implies that the sonic modulus increases for a fiber when orientation of the polymer chains increases as well as when the connectivity improves due to crystallization of the oriented structure. For the fibers under study, the sonic modulus increased significantly with the increase in draw ratio (Fig. 7). This was expected because drawing imparts orientation to the polymer chains and hence would increase the sonic modulus.

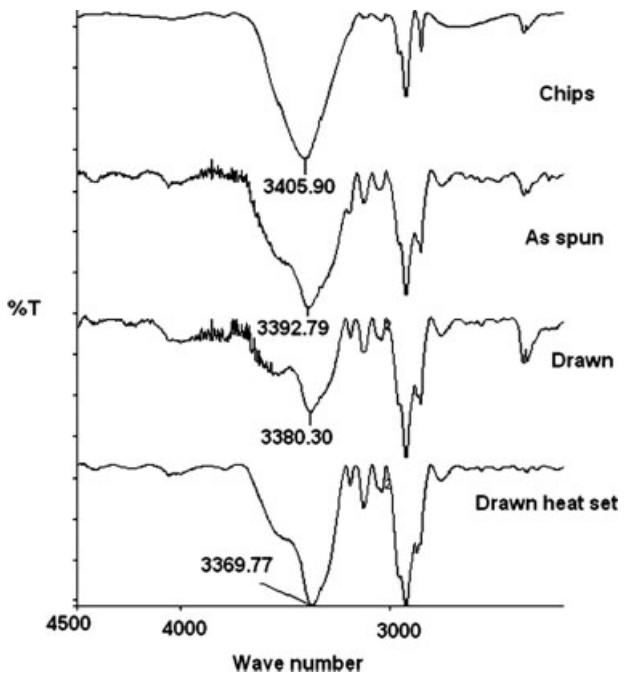

Figure 6 FTIR spectra of SMP/fiber at different stages.

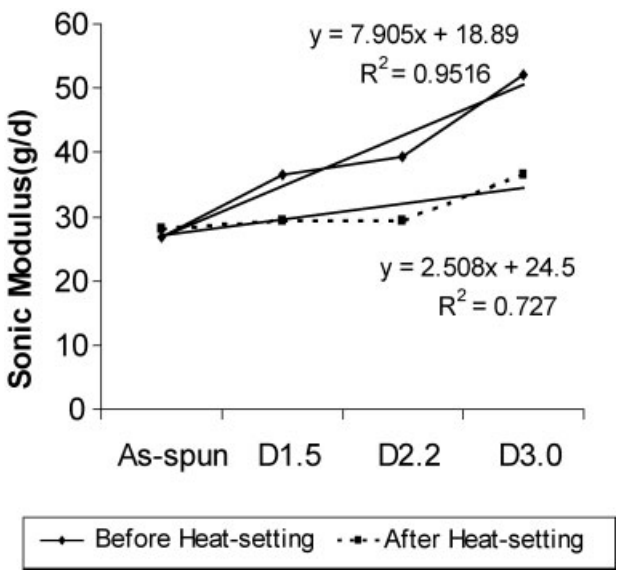

Figure 7 Effect of postspinning operations on sonic modulus of shape memory fiber.

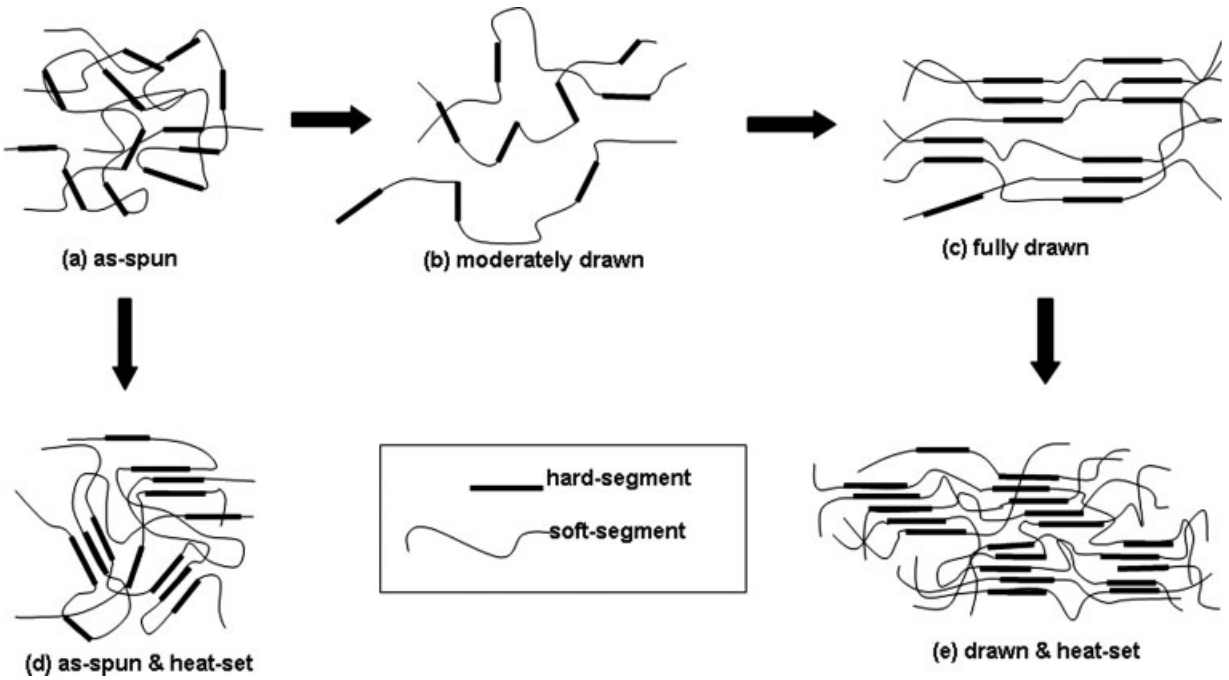

Figure 8 Schematic representation of the fiber morphology with processing.

The sonic modulus was very high in the fibers drawn at DR-3.0 (D3.0) possibly because of the combined orientation of both the soft and the hard segments in this case. However, on heat-setting under taut condition, the sonic modulus decreased for all fibers. This was contrary to other thermoplastic fibers where sonic modulus tends to increase due to the increase in number of tie points (crystallites) with heat-setting under taut condition. In the present case, though the number of tie points might have increased due to better association of chains in the hard-segment domains, the soft-segment domains might get mostly disoriented to dampen the sound waves traveling along the fiber axis. Further, the hard- and soft-segment regions might get connected in series [as schematically shown in Figs. 8(a–e)] to each other upon drawing and heat-setting because only this arrangement would significantly affect the travel path of the sonic waves.

Birefringence

Birefringence is a measure of overall orientation of the molecular chains in a fiber, where the oriented crystalline or compact regions contribute more significantly to birefringence values than amorphous regions. Figure 9 shows the birefringence of the various samples. Birefringence of the fibers increased with the increase in draw ratio and was the highest for the fiber drawn at DR-3.0 (D3.0). This may be because of the combined orientation of the soft- and the hard-segments as mentioned earlier. The as-spun fiber was also observed to have a small birefringence value, which may be due to some orientation developed during the melt spinning of the fiber. The birefringence decreased to some extent after heat-setting in the case of drawn fiber, whereas it was negligible for the as-spun fiber after heat-setting. This was mainly because oriented molecular chains undergo some degree of randomization during heat-setting. However, the effect of drawing was not completely lost and the birefringence values were still significantly higher for the drawn and heat-set fibers when compared with those of the as-spun fibers. This

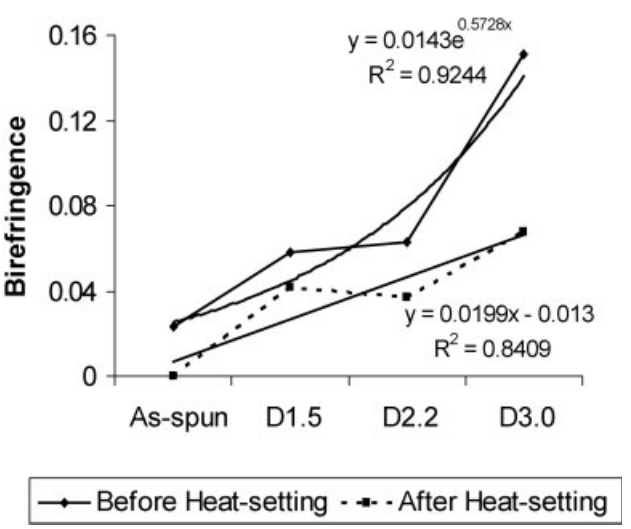

Figure 9 Effect of postspinning operations on birefringence of shape memory fiber.

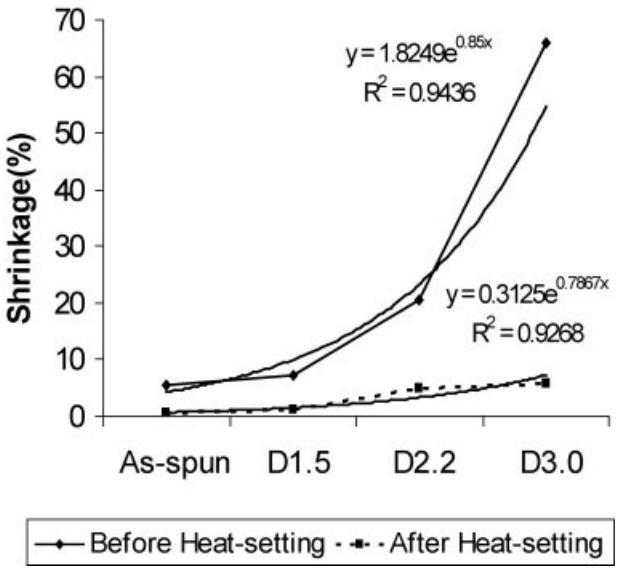

Figure 10 Effect of postspinning operations on heat-shrinkage of shape memory fiber.

result together with the observation of sonic modulus suggested that the loss of orientation might be occurring mostly in the soft-segment domains, and the orientation achieved in hard-segment regions were retained to a large extent even after heat-setting [Fig. 8(e)].

Thermal shrinkage

Thermal shrinkage in a fiber is indicative of the degree of stability of the morphological structure. In SMPs, if the deformation is carried out to make a temporary shape, such as extension of the fiber, the deformation should completely reverse to give the original spun fiber on heating above the transition temperature. The recovery of deformed structure to exact permanent shape is possible only if the permanent shape is stable (does not shrink) above the transition temperature. In this study, the as-spun fiber were subjected to drawing and heat-setting in an attempt to give the fiber a new morphology and a new permanent shape with improved mechanical and shape memory properties. This was possible only if the changes brought in by the above-mentioned postspinning operations were permanent.

Figure 10 shows the shrinkage behavior of all fibers at above the transition temperature. The as-spun fiber showed some degree of instability as it exhibited shrinkage at 55°C due to coiling of molecular chains above the transition temperature, a behavior similar to the other man-made fibers. When the as-spun fiber was drawn, as expected, the shrinkage percentage was found to increase with the increase in draw ratio. However, there was a significant decrease in shrinkage percentage after the fibers were subjected to heat-setting. The shrinkage also reduced in the case of as-spun-heat-set fiber and was found to be the least among all the samples. This may be explained on the fact that residual stresses of spinning in as-spun fiber got released on heat-setting and the fiber attained the thermodynamic equilibrium. The shrinkage also reduced significantly for all drawn and heat-set fibers because heat-setting could release the elastic stresses developed during the drawing process and form a stable permanent morphology due to molecular rearrangement. Clearly, the drawn and heat-set fibers have a stable transformed structure with hard-segment domains strongly bonded with hydrogen-bonds [Fig. 8(e)].

Tensile properties

The stress–strain curves of the various fibers are shown in Figure 11. The as-spun SMP fiber showed the presence of a neck-type deformation and a very long plastic region. This region disappeared after drawing operation and the stress values increased significantly for all strains. The tenacity of the SMP fiber increased significantly with the increase in draw ratio and was almost 300% higher in case of fiber drawn at draw ratio 3.0 (DR 3.0), compared with that of the as-spun fiber. It was also observed that elongation decreased with the increase in draw ratio. This may be due to the fact that below a draw ratio of 2 (i.e., moderate draw ratio) only soft segments tend to orient in the direction of stretch, whereas the aromatic urethane segments or the hard segments remain perpendicular to the stretch direction [Fig. 8(b)]. This may be responsible for the lower tenacity and higher elongation for draw ratios of up to 2. However, stretching the fibers above DR-2 may result in orientation of even the hard segments in the direction of stretch [Fig. 8(c)]. Similar morphological changes have been reported when elastomer

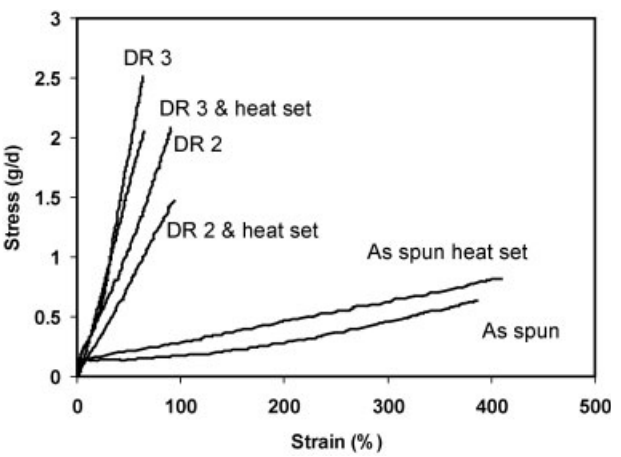

Figure 11 Stress–strain plot of shape memory fibers.

fibers are stretched at high extensions.[27] The high degree of orientation is evident from the high values of sonic modulus and birefringence for the drawn fibers at DR of 3. Better hydrogen-bonding may take place at such high draw ratios as the free space around chain may reduce. This combined effect of orientation of soft- and hard-segments and the formation of hydrogen-bonds among hard-segments resulted in better mechanical properties of the drawn SMP fibers.

It was observed that both the tensile strength and elongation increased with the heat-setting in the case of as-spun fiber [Fig. 8(d)]. This small increase in tensile strength might be because of the better hydrogen bond formation at the heat-setting temperature among the urethane bonds in the hard-segment regions, which allowed easy transfer of applied stresses through the fiber. The increase in elongation upon heat-setting may be due to the fact that the structure after heat-setting has relaxed into disoriented domains of hard and soft segments, which can be extended upon application of tensile force.

The improvement in tenacity achieved due to drawing was retained to a large degree upon heat-setting of the drawn SMP fibers. There was only a decrease of 20–25% in tenacity while elongation improved marginally or remained nearly same upon heat-setting of the drawn fibers. This may be due to the overall decrease in orientation of the fiber on molecular rearrangement of polymer chains into a more stable structure. The important achievement was that the drawing and heat-setting operations were able to impart significantly higher mechanical properties to SMP fibers compared to their as-spun state.

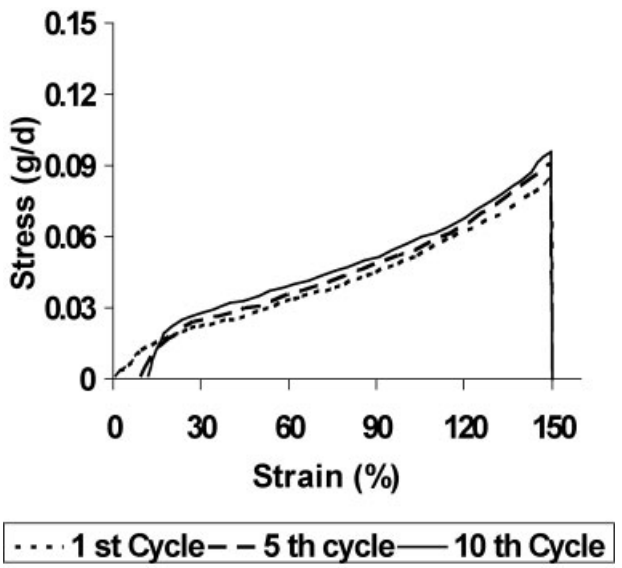

Figure 12 Shape memory behavior of as-spun fiber at $\varepsilon_m = 150\%$.

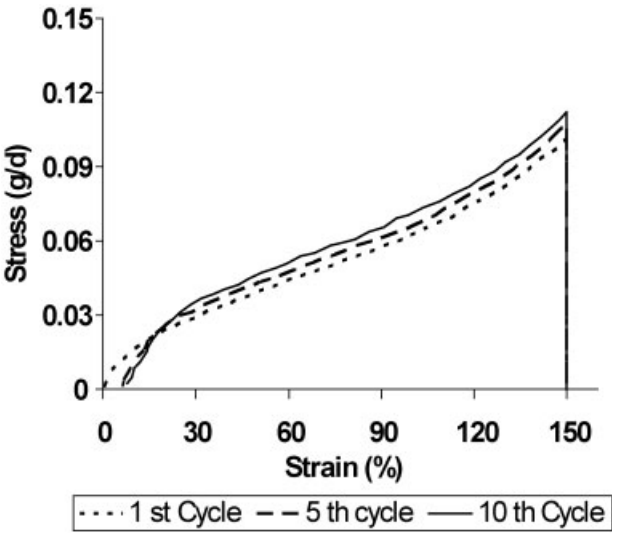

Figure 13 Shape memory behavior of as-spun and heat-set fiber at $\varepsilon_m = 150\%$.

Shape memory behavior of SMP fibers

The stress–strain curve of the as-spun fiber obtained in the thermomechanical cycling test are shown for the case of maximum strain $\varepsilon_m = 150\%$ in Figure 12. It may be noted that ε_u is nearly equal to ε_m and does not vary with cycling and takes a constant value. This verifies the shape fixity of the temporary shape, which is the function of soft segments in the polymer. The fiber was found to be very stable against thermomechanical cycling. The shape memory property was also studied at $\varepsilon_m = 40\%$ and shape fixicity was found to be similar at this strain level as well. On the other hand, the shape recovery at temperature $> T_c$ was nearly complete only at low strains of 40% for all the 10 cycles; however, the residual strain increased from 9 to 12% from 5th to 10th cycle at higher strain of 150%. Stress hardening was observed with cycling in case of the as-spun fiber and stress values increased by 6% from 5th to 10th cycle. The residual strain increased with cycling possibly because initially the chains were not oriented in case of the as-spun fiber, but as the number of cycles increased, the segments started to orient to a higher extent with each cycle, and the original polymer chain network was no longer present for complete recovery. This supports the earlier result that there was poor packing and hydrogen bond interaction among hard segments in the as-spun fiber [Fig. 8(a)].

The stress–strain curve of as-spun and heat-set fiber obtained in the thermomechanical cycling test is shown for the case of maximum strain $\varepsilon_m = 150\%$ in Figure 13. It was observed that, although the recovery was not complete for this strain value, the residual strain decreased after heat-setting when

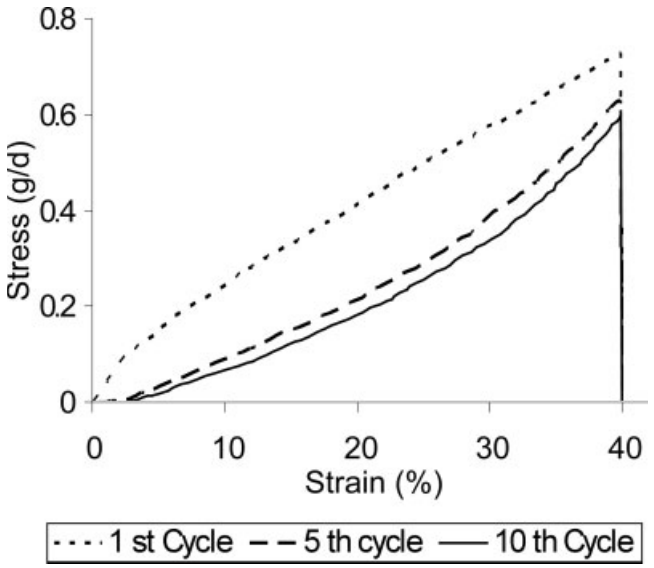

Figure 14 Shape memory behavior of drawn fiber (DR = 3.0) at $\varepsilon_m = 40\%$.

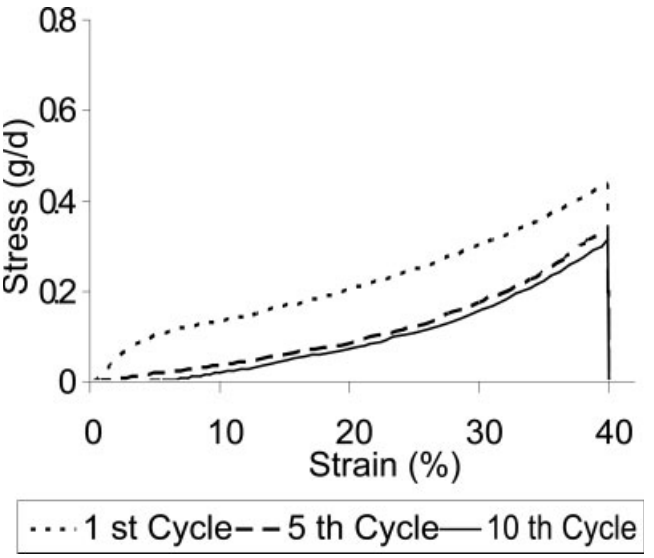

Figure 15 Shape memory behavior of drawn (DR = 3.0) and heat-set fiber at $\varepsilon_m = 40\%$.

compared with the as-spun sample. The recovery was complete for the first cycle, but the residual strain increased only from 6 to 8% from 5th to 10th cycle. However, the stress hardening values increased by a similar value of 6% from 5th to 10th cycle. The residual strain was less after heat-setting possibly because the molecular rearrangement during heat-setting could create an elastic network with higher stability [Fig. 8(d)]. This elasticity was also indicated by the fact that slightly higher recovery forces were seen in the case of the as-spun-heat-set fibers.

In case of the drawn fiber (DR-3.0), the recovery was complete in all cycles as shown in Figure 14. The stresses were much higher by about six times in the drawn fiber compared to the as-spun fiber. Also, instead of stress-hardening observed in as-spun fibers, a stress softening phenomena was observed, i.e., stresses were higher for the first cycle and decreased with the increase in number of cycles for all cases of drawn fiber. There was a decrease in stress values by 13% in the fifth cycle and by 17% in the 10th cycle, compared with the stress values in the 1st cycle. The increase in recovery in the drawn fiber may be explained on the fact that in drawn condition, the soft and hard segments are oriented and under stress. During drawing, the alignment of chains along the direction of stretch may allow the chains to come close and the hard segments to H-bond with each other. This bonding may improve with the pass of each cycle as hard segment of one chain may get better chance to come opposite to that of other chain on repeated deformation and recovery. This may explain the stress-softening phenomenon observed in these fibers. The important observation from these experiments is that the stress values for recovery in SMP fibers can be simply controlled by altering the drawing parameters. However, just the drawn SMP fibers are not good candidates for the shape memory applications. This is because they have excessive internal stresses even at the recovered positions. This was supported by the fact that shrinkage was high in the drawn fibers. Because of the high shrinkage, the permanent shape in the drawn fibers was not fixed. Therefore, it was important to stabilize the permanent shape and achieve complete recovery as well.

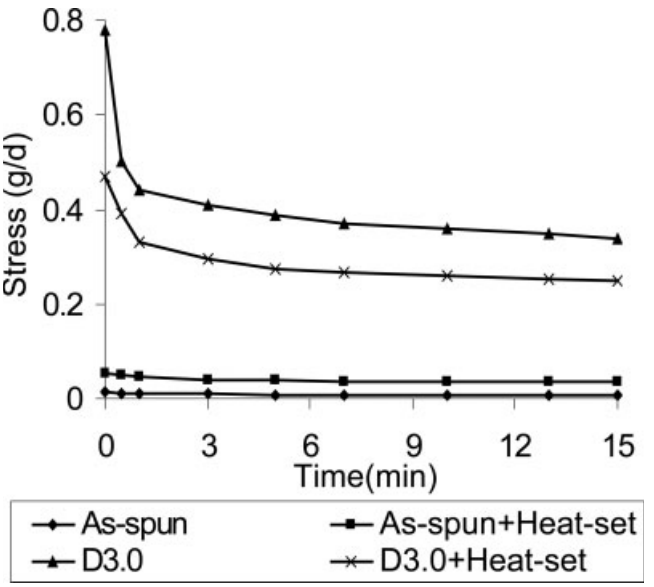

Figure 16 Effect of postspinning operations on stress–relaxation of shape memory fiber.

TABLE II
Stress–Relaxation of Different Shape Memory Fibers

	Immediate stress–relaxation (%)		Final stress–relaxation (%)	
Sample	Before heat-setting	After heat-setting	Before heat-setting	After heat-setting
As-spun	12	5.2	44	33.3
D1.5	15.5	11.8	43.7	34.7
D2.2	32.4	14.4	58.8	40.3
D3.0	35.9	16.8	56.5	47.1

Figure 15 shows the recovery behavior of the drawn and heat-set fiber (DR-3.0). The recovery was complete in this case, and this behavior was found to be same for the heat-set fibers drawn at different draw ratios. However, the recovery stresses of drawn and heat-set fibers, although significantly lower compared with those of drawn fibers, were still higher by about 1000%, compared with those of as-spun fibers. This is a significant achievement in developing shape memory structures with high recovery stresses by simply playing with the morphology of the permanent shape.

Stress-softening phenomena was also observed in the drawn and heat-set fibers. There was a decrease in stress values by 24% in 5 cycles and by a total of 28% in 10 cycles compared to the stress values of the 1st cycle. The complete recovery of the drawn and heat-set fibers was indicative of the formation of stronger hydrogen bonds in hard segment regions, which act as physical crosslinks and help in better stability of the permanent shape. The low shrinkage of the heat-set fibers also supports the formation of the stable structure. However, stress-softening was still present probably because the hard-segments to do not lock themselves in a crystalline phase.

Stress relaxation studies of SMP fibers

It was shown in the earlier section that drawing and heat-setting of SMP fibers resulted in a significant increase in their recovery stresses when deformed to a temporary shape above the transition temperature. However, it is also important to understand how these stresses decay with time when the structure is held in a temporary shape at above the transition temperature during deformation or recovery. Figure 16 and Table II give the stress–relaxation behavior of different SMP fibers. The stress–relaxation was higher in the case of drawn fibers. There was an instantaneous relaxation followed by a slow and steady decrease in stresses with time. However, on heat-setting, the same fibers were able to retain the developed stresses to a better extent. This was because in the drawn fibers both the soft and hard segments were oriented and under high level of stress, which tend to rearrange the molecular chains at a high rate. However, the extent of both the instantaneous stress–relaxation and that with time became less after heat-setting for both the as-spun and drawn fibers. This was because the heat-set fibers had more stable physical-crosslinks (strongly bonded hard segment regions) that do not adjust easily with time unlike the loosely held secondary bonds in the as-spun or drawn fibers.

CONCLUSIONS

Thermoresponsive shape memory (SMP) fibers could be successfully produced through the melt spinning technique. A spinning temperature of 215°C was found to be appropriate melt spinning temperature for effective fiber formation.

The shape recovery of the thermoresponsive shape memory (SMP) fiber improved with the postspinning operations. The drawn fiber gave complete recovery, whereas the as-spun fiber gave residual strain, as the number of cycles were increased in thermomechanical cyclic test. The as-spun fiber underwent stress-hardening, whereas the drawn fiber showed stress-softening with cycling.

The recovery percentage increased after the heat-setting operation both in the case of as-spun and the drawn fiber. The stability of the fiber increased after heat-setting, which was evident by decrease of the difference in stress values between 5th and the 10th cycles. The improved stability of the transformed permanent shape was also indicated by the changes in the thermal shrinkage, which increased from 5% for the as-spun to 66% for the drawn fiber and got reduced again to 5% after the heat-setting operation.

The tensile strength of the thermoresponsive shape memory fiber increased by almost 300% from as-spun to the fiber drawn at DR-3.0. The tensile strength decreased by only about 20–25% after heat-setting of the drawn fiber. The as-spun-heat-set fiber showed an improvement in strength by $\sim$ 30% after heat-setting. The recovery stresses of SMP fibers improved by about 1000% after drawing and heat-setting when compared with those of as-spun fibers.

This improvement in the shape memory behavior and mechanical properties of SMP fibers was possible due to the permanent changes brought about in the morphology of the fibers upon drawing and heat-

treatment. The structural characterization suggested that the permanent structure was formed due to the formation of oriented hard-segment regions that are strongly bonded with hydrogen bonds with each other.

References

1. Lendlein, A.; Kelch, S. Angew Chem Int 2002, 41, 2034.
2. Langer, R. S.; Lendlein, A. U.S. Pat. 6,388,043 B1 (2002).
3. Park, H. S.; Kim, J. W.; Lee, S. H.; Kim, B. K. J Macromol Sci Phys 2004, 43, 447.
4. Sokolowski, W. M.; Chmielewski, A. B.; Hayashi, S.; Yamada, T. Proceedings of SPIE—The International Society for Optical Engineering; Electroactive Polym Actuators Devices 1999; pp 179–185.
5. Monkman, G. J. Mechatronics 2000, 10, 489.
6. Kondo, S.; Hayashi, S. Jpn. Kokai Tokkyo Koho 03,183,920 (1991).
7. Ken, G.; Paul, K.; David, T.; Michael, H. J Microelectromech Syst 2004, 13, 472.
8. Lendlein, A.; Langer, R. Science 2002, 296, 1673.
9. Jinlian, H.; Ding, X.; Tao, X.; Yu, J. Text Asia 2001, 42.
10. Hayashi, S. Properties and Application of Polyurethane Based Shape Memory Polymer; Inoue, K.; Shen, S.; Taya, M., Eds.; Proceedings of the U.S.—Japan Workshop on Smart Materials and Structures; Mitsubishi Heavy Industries, Seattle, 1996.
11. Fengkui, L.; Hou, J.; Wei, Z.; Zhang, X.; Mao, X.; Kim, B. K. J Appl Polym Sci 1996, 62, 631.
12. Fengkui, L.; Hou, J.; Wei, Z.; Zhang, X.; Mao, X.; Kim, B. K. J Appl Polym Sci 1997, 64, 1511.
13. Kim, B. K.; Lee, S. Y.; Xu, M. Polymer 1996, 37, 5781.
14. Peng, P.; Wang, W.; Chen, X.; Jing, X. Biomacromolecules 2005, 6, 587.
15. Kim, B. K.; Lee, S. Y.; Lee, J. S.; Baek, S. H.; Choi, Y. J.; Lee, J. O.; Xu, M. Polymer 1998, 39, 2803.
16. Lin, J. R.; Chen, L. W. J Appl Polym Sci 1998, 69, 1563.
17. Jae, Y. H.; Byong, C. C.; Yong-Chan, C.; Jae, C. H. Polymer 2003, 44, 3251.
18. Lin, J. R.; Chen, L. W. J Appl Polym Sci 1998, 69, 1575.
19. Takahashi, T.; Hayashi, N.; Hayashi, S. J Appl Polym Sci 1996, 60, 1061.
20. Ohki, T.; Ni, Q.; Ohsako, N.; Iwamoto, M. Compos A 2004, 35, 1065.
21. Gau, K.; Dunn, M. L.; Liu, Y.; Finch, D.; Munshi, N. A. Acta Materialia 2002, 50, 5115.
22. Hisaaki, T.; Shunichi, H.; Shinichi, K. JSME Int J Ser 1992, 35, 296.
23. Seefried, C. G., Jr.; Koleske, J. V.; Critchfield, F. E.; Pfaffenberger, C. R. J Polym Sci Polym Phys Ed 1980, 18, 817.
24. Kendagannaswamy, B. K.; Siddaramaiah. J Appl Polym Sci 2002, 84, 359.
25. Gogolewski, S. Colloid Polym Sci 1978, 256, 323.
26. Skarja, G. A.; Woodhouse, K. A. J Appl Polym Sci 2000, 75, 1522.
27. Bonart, R. J Macromol Sci Phys 1968, 2, 115.