Polycaprolactone-Based Shape Memory Segmented Polyurethane Fiber

Qinghao Meng, Jinlian Hu, Yong Zhu, Jing Lu, Yan Liu

Shape Memory Textiles Centre, Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Kowloon, Hong Kong

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ABSTRACT: In this article, shape memory polyurethane fibers were prepared by wet spinning. The shape memory switching temperature was the melting temperature of soft segment polycaprolactone phase at 36.20°C. The fibers' mechanical properties, especially the shape memory properties, were explicitly characterized and compared with that from some commercialized polyurethane elastic fibers. The prepared 40 denier shape memory fiber (SMF) had a tenacity of about 0.93–98 cN/dtex, and the strain at break ranged from 85–115%. At ambient temperature, the modulus of SMF was in general larger than those of the Elaspan and Newstar fibers. The SMF had a shape fixity ratio of more than 80% and recovery ratio more than 95% under thermal drawing and recovery cyclic tensile testing. The results from differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to illustrate the mechanism governing the mechanical properties and shape memory effect especially. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2515–2523, 2007

Key words: polyurethanes; melting point; phase separation; stimuli-sensitive polymers

INTRODUCTION

Shape memory polymers have been widely studied and used in both academia and industries owning to its low cost, good processing ability, high shape recoverability, and large range of shape recovery temperature compared with that of shape memory alloys.[1–9] Foremost among these polymers, shape memory polyurethane draws the most attention because of the easy control of the critical recovery temperature for use in different applications.[10]

The shape memory polyurethane shape memory effect is because of the thermodynamic incompatibility between the soft segments (aliphatic polyether or polyester) and hard segments (diisocyanates and small size diols or diamines). The hard segment phase has a higher thermal transition temperature (T_{perm}), whereas the soft segment phase has a lower phase transition temperature (T_{trans}) (switching temperature), which can either be a glass transition (T_g) or a melting transition (T_m) temperature. When the shape memory polyurethane is heated to a temperature $T_{trans} < T_{high} < T_{perm}$, a deformation can be easily applied and the deformed shape can be fixed when the polyurethane is cooled at a temperature T_{low} below the T_{trans}. When the same polyurethane is reheated up to a temperature above T_{trans}, the original undeformed shape can be recovered because of the entropy elasticity.[3,4,6,7,11]

Many commercialized elastic polyurethane fibers are available now such as Fujibo, Lynel, Dorlastan, Lycra, Espa, Dorlastan, Glospan, Spancelle, Mobilon, Spantel, etc. They have been widely used in many areas such as women's undergarments, men's suits, children's wear, diapers, and footwear. All the commercialized polyurethane elastic fibers have elongations at least larger than 200% and some of them can reach above 400%. However, they do not exhibit shape memory effect. Generally, they recover quickly and almost completely to their original length when the deforming stress is released.

In this article, shape memory effect was imparted to the fiber. The shape memory fiber (SMF) has outstanding mechanical properties because of the unique molecular orientation. In addition, they may have many special applications. Till now reports on the preparation of SMFs are few, even including our pervious work.[12,13] A shape memory polyurethane fiber with soft segment poly(buthyleneadipate) or poly(ethyl acrylate) glass transition temperature as the switching temperature was developed by Hu and coworkers.[14,15] In this article, another kind of SMF was prepared by wet spinning using polycaprolactone diol as the soft segment. The switching temperature was the melting transition temperature of the soft segment phase.[3,4,16,17] The stress–strain

Correspondence to: J. Hu (tchujl@inet.polyu.edu.hk).
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behavior, shape memory effect, and thermal/mechanical properties of the fibers were investigated. We made a comparison with commercialized elastic polyurethane fibers (Elaspan fiber and Newstar fiber) afterwards. Shape memory polyurethane distinguishes itself from the common polyurethane elastic fibers by its special cyclic thermal/mechanical properties. The prepared shape memory fiber may have applications such as in textiles, actuators, medicine, etc.

EXPERIMENTAL

Materials

Shape memory polymer was synthesized using polycaprolactone diol (PCL)-4000 (Daicel Chemical Industrial) as the soft segment, 4,4′-diphenylmethane disocyanate (MDI)(Aldrich Chemical Company) and 1,4-butanediol (BDO)(Acros Organics) as the hard segment by solution polymerization. All the glass apparatus were cleaned and heated in an oven at 400°C for 8 h prior to use. The PCL-4000 was demoisturized under vacuum at 70°C for 12 h. MDI was taken out from a refrigerator and put in fume hood for about 20 min before use. It was then further demoisturized at 70°C for 1 h in a vacuum oven. The MDI dimer at its melt state was filtered to remove its precipitate and any impurities before use. Molecular extender BDO was demoisturized in a vacuum oven at 100°C for an hour prior to use. The shape memory polyurethanes used in this study were synthesized by a prepolymerization method in HPLC *N*,*N*-dimethyllformamide (DMF) (International Laboratory) with highly pure nitrogen protection.[3,14,15]The prepolymerization was conducted by terminating PCL-4000 with excess diisocyanate MDI in DMF at 90°C for 2 h, after that it was chain-extended with BDO for about 2 h at 85°C. At the last step of the reaction the solid concentration was adjusted to 25 wt %. The number average molecular weight of the PU was of $\sim 2.13 \times 10^5$, measured by a high performance liquid chromatography equipped with an Optilab® rEX refractive index detector. The solvent for measuring the average molecular was HPLC graded DMF, used as it was bought from International Laboratory. The shape memory fiber was prepared by wet spinning. The SMF was coagulated in a water bath after being ejected from a 36 holes spinneret. The spinning solution was of 60°C and the water bath was of room temperature. The fibers were then passed through two pairs of rinsing rollers and two pairs of hot rollers before being winded on a friction winding up head. The roles of the four pairs of roller were to remove any residual solvent with the required drawing ratio and to release internal stress. The hot rollers temperature was held at 110°C. The total drawing ratio from the spinneret to the last roller is 3.6. Winding up speed was equal to the last roller's speed $\sim$ 20 m/min. The obtained fiber was of 40 denier in linear density. Commercialized elastic polyurethane fiber Elaspan fiber having a linear density of 40 denier was bought from Invista Shanghai of China (Dupont technology), and Newstar fiber having the same density was bought from Yaitai Spandex Co. Ltd. of China (Toyobo Technology).

Testing

Mechanical property

Mechanical properties were investigated with an instron 4411 according to the ASTM D2256 standard. The sample length was 20 mm and the tensile speed was 300 mm/min. On every sample the test was conducted 10 times to get the average values.

Cyclic tensile investigations

Cyclic tensile testing was carried out using a tensile tester (Instron 4466) equipped with a temperature controlled chamber. A typical shape memory test on the shape memory polyurethane can be summarized by four steps as follows: first, the sample is heated up to a temperature T_{high} above the switching temperature T_{trans} (but lower than the highest thermal transition temperature T_{perm}, which is the melting temperature of the hard segment, lying in the range between 200 and 240°C) and stretched to a specific strain ε_m. To fix the temporary shape, the sample is then cooled down to a temperature T_{low} below the T_{trans} under the same strain ε_m. While holding the same sample, the clamps are allowed to recover to their original position. Lastly, the sample is heated to T_{high}, and ready for repeating the second cycle.

In the article, three testing methodologies were developed to test the shape memory effect of our SMF and to compare it with commercialized polyurethane elastic fibers. The T_{high} value was set at 70°C and T_{low} at ambient temperature (22°C).[10] Sample length was of 20 mm in length, and linear density was 40 denier.

Thermal drawing and recovery. (1) The fibers were heated to 70°C and then stretched to 100% strain at a speed of 10 mm/min; (2) the fibers were cooled to ambient temperature while the same 100% strain were kept for 15 min; (3) the clamps were unloaded so that they returned to their original position at a speed of 40 mm/min; (4) the fibers were heated again to 70°C; (5) and the second cycle began. The cyclic tensile testing path is shown in Figure 1.[6]

Cold drawing. Foremost among the advantages of commercialized elastic fibers, the repeated stretching

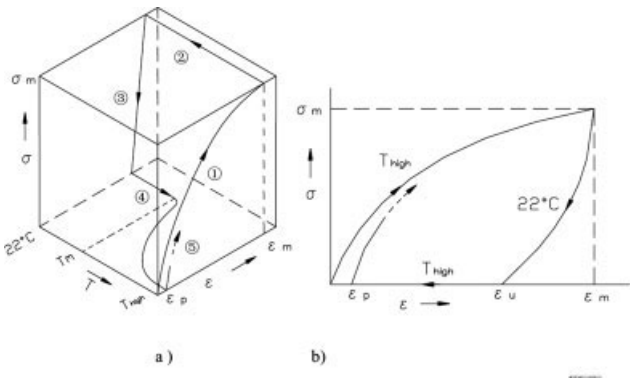

Figure 1 (a) Cyclic tensile testing path under thermal drawing and recovery; (b) schematic stress–strain curve by thermal drawing and recovery cyclic tensile testing (T_{high} was set at 70°C).

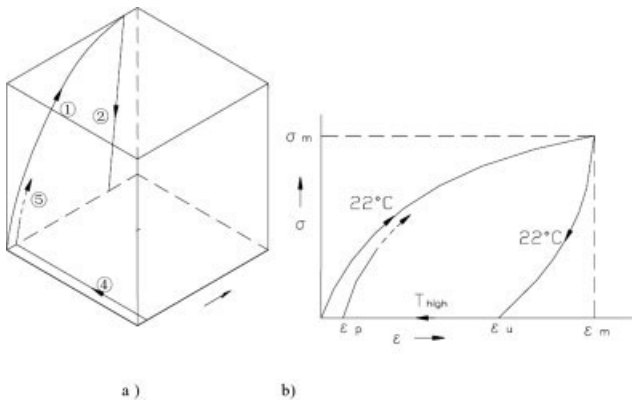

Figure 3 (a) Cyclic tensile testing path under cold drawing and thermal recovery; (b) schematic stress–strain curve by cold drawing and thermal recovery cyclic tensile testing (T_{high} was set at 70°C).

recovery at ambient temperature is critical. To make a comparison between our SMF and commercialized elastic fibers, the cold drawing (ambient temperature) cyclic tensile testing (usually used for testing elastic fibers' properties) was employed. The cyclic tensile testing path is shown in Figure 2. (1) The fibers were stretched to 100% strain at a speed of 10 mm min^{-1} at ambient temperature and kept at 100% strain the temperature for 15 min; (2) the clamps were unloaded and allowed them to return to their original position; (3) the above cycle was repeated.

Cold drawing and thermal recovery. Because in practice, the deformation of SMF usually occurred at ambient temperature, the cold drawing (at ambient temperature) and thermal recovery testing was used to test the shape memory effect. The cyclic tensile testing path is shown in Figure 3. (1) The fibers were stretched to 100% strain at a speed of 10 mm/min at ambient temperature kept at 100% strain the temperature for 15 min; (2) the clamps were unloaded and let them return to the original position at a speed of 40 mm/min; (3) the fibers were heated to 70°C and kept for 5 min; (4) the fibers were cooled to ambient temperature and left for 5 min; (5) the second cycle started.

All of the above cycles were repeated four times and the stress–strain behaviors were recorded for further analysis. Schematic representation of a typical stress–strain behavior is shown in Figures 1(b), 2(b), and 3(b). ε_m is the maximum strain in the cyclic tensile tests, ε_u is the strain after unloading at T_{low}, and $\varepsilon_p(N)$ is the residual strain after recovering in the Nth cycle. The ε_m value is set at 100% strain for the study. The fixity ratio (R_f (N)) and recovery ratio ($R_r(N)$) at the Nth cycle and total recovery ratio after Nth cycle $R_{r,tot}$ are calculated according to following equations:[6]

$$R_f(N) = \varepsilon_u(N)$$

$$R_r(N) = \lfloor 1 - \varepsilon_p(N-1) \rfloor \times 100\%$$

$$R_{r,\mathrm{tot}} = \lfloor 1 - \varepsilon_p(N) \rfloor \times 100\%$$

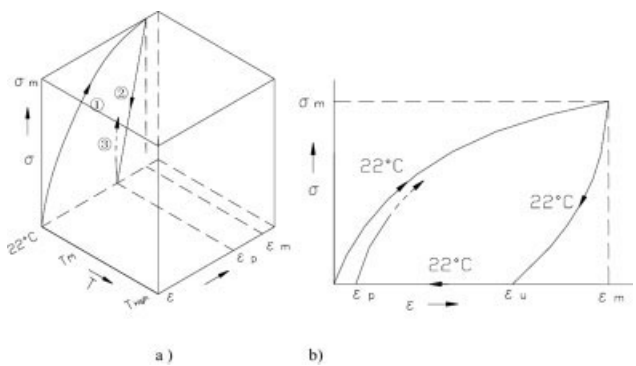

Figure 2 (a) Cyclic tensile testing path under cold drawing; (b) schematic stress–strain curve by cold drawing cyclic tensile testing (T_{high} was set at 70°C).

Thermal properties investigation

The thermal properties of the prepared SMF, and that of Elaspan and Newstar fibers were investigated through DSC (Perkin-Elmer Diamond Differential Scanning Calorimeter) with nitrogen as the purged gas. Indium and zinc were used for calibration. Spinning oil on the filament was removed before testing. The samples were heated from −70 to 230°C at a heating rate of 10°C/min.

Dynamic mechanical analyses

DMA tests were performed on a Perkin-Elmer Diamond Dynamic Mechanical Analyzer operated in a tensile mode. The heating rate was 2°C min^{-1}, the frequency was 2 Hz, and the oscillation amplitude was 5.0 μm. Tests were conducted over the tempera-

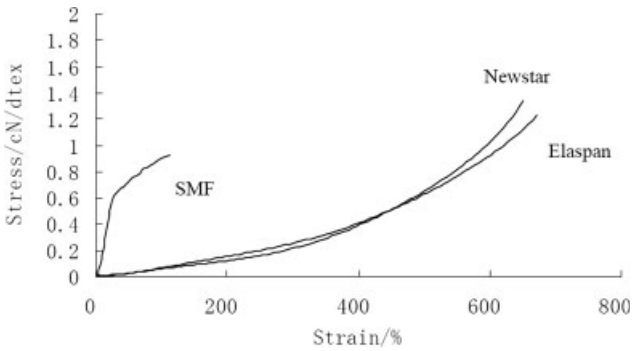

Figure 4 Stress–strain curves of the Elaspan and Newstar fibers, and our SMF.

ture range from −120 to 250°C. The gauge length between the clamps was 15 mm.

RESULTS AND DISCUSSION

Mechanical properties

The typical stress-strain curves of the Newstar and Elaspan fibers, and our SMF are shown in Figure 4 and the mechanical results were summarized in Table I. The prepared 40 denier SMF has a tenacity of about 0.93–0.98 cN/dtex, and the strain at break ranged from 85 to 115%. The tenacity of the SMF is a little lower than that of Elaspan and Newstar fibers. The elongation at break of the SMF is much lower than that of Elaspan and Newstar fibers. The difference in mechanical properties between the commercialized elastic fibers and the SMF has many proposed reasons; Elaspan and Newstar fibers are prepared by dry spinning and using diamines as the molecular extenders.[18] The formed urea group has a high cohesion energy that gives rise to both high phase separation and hard segment stability. Thus, the SMF using diol as the molecular chain extender has poor mechanical properties compared with that of fibers prepared by dry spinning. The high elongation ratio of polyurethane fibers at break is ascribed to the high molecular weight polyether or polyester diol forming soft segment phase. The soft segments of the fibers from Elaspan and Newstar are highly flexible and more easily to be extended to their full elongations, whereas the soft segment PCL phase in the SMF is partially crystallized and more difficult to be stretched to their full lengths. Meanwhile, the elongation of the noncrystallized soft segment phase is restricted by the crystallized soft segment phase. As a result, our SMF has lower elongation ratio at break even though a higher molecular weight soft segment PCL is used. Besides, many other important factors may give rise to the observed difference in mechanical properties between different fibers from different sources. We list some of the most important factors here to complete this section: Soft segment, hard segment contents, spinning techniques, thermal treatment.

TABLE I
Mechanical Properties of the Different Filaments

Sample	Tenacity (cN/dtex)	Strain at break (%)
Newstar fiber	1.22–1.31	650–670
Elaspan fiber	1.13–1.23	668–730
SMF	0.93–0.98	85–115

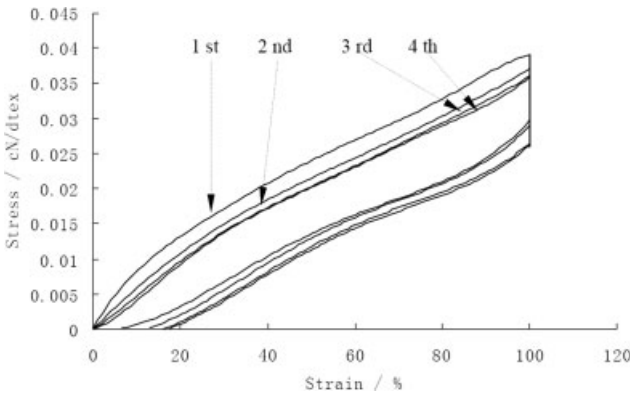

Figure 5 Cyclic tensile testing curves of the Elaspan fiber under thermal drawing and recovery.

Cyclic tensile investigation

Cyclic tensile properties under thermal drawing and recovery

The stress–strain curves of commercialized elastic fibers and our SMF under thermal drawing and recovery cyclic tensile testing method are shown in Figures 5–7, respectively. There is much difference in feature between the cycles and the most different one is the first cycle. This is partially because during elongation, the fiber molecules reorganize themselves involving molecular orientation, crystalliza-

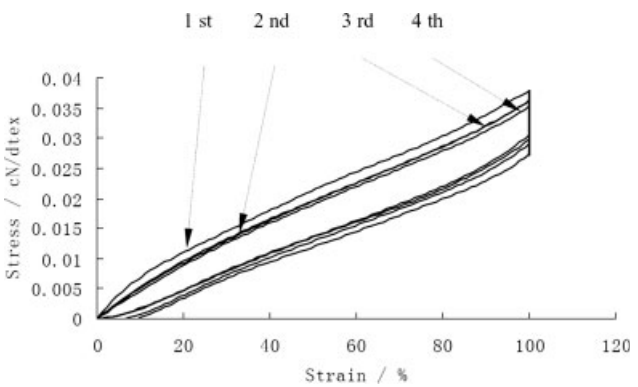

Figure 6 Cyclic tensile testing curves of the Newstar fiber under thermal drawing and recovery.

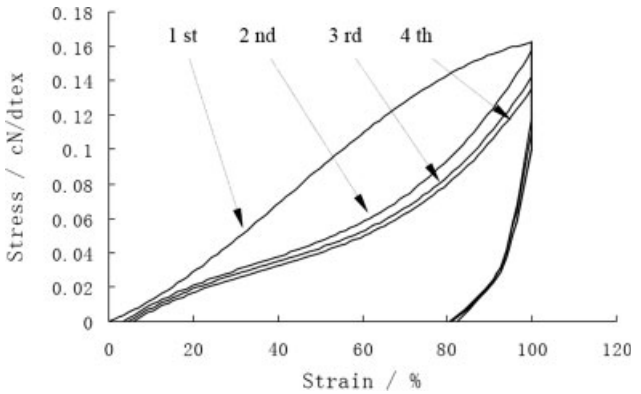

Figure 7 Cyclic tensile testing curves of the SMF under thermal drawing and recovery.

tion, and weak point break. The curves become highly reproducible after two cycles. As can be seen from the Figures 5 and 6, commercialized elastic polyurethane fibers have higher repeated stretching recovery ratios but low fixity ratios. They recover to their original length completely once the external force is released. This suggests that the Elaspan and Newstar fibers have a tendency to recover to their original length and cannot hold the temporary deformation when cooled from a high temperature to ambient temperature. In contrast, the SMF has a fixity ratio of more than 80.0% in every cycle. The recovery ratio is also very high, approaching 100% in every cycle.

Commercialized elastic polyurethane fibers exhibit no shape memory effect. They have elongations larger than 600%. They recover quickly and almost completely to their original length when the deforming stress is released.[19–23] The SMF has shape memory effect because it can not only recover to the original length but also can fix the temporary deformation at temperature below T_{trans}. The SMF shape memory effect is illustrated in Figure 8. During wet spinning (after spun from solution), the fiber is drawn and winded up and the permanent fiber shape is then cast. In the unstretched state, the fibers have their molecules slightly oriented, resulting from the spinning process. In Figure 8, the soft segments of polyester are shown as being coiled or folded on themselves. The schematic section length of the zig-gag line corresponds to one repeating unit within the polyol. The isocyanate is shown as rigid circle. The hard segments are set in space but have a tendency to adhere each other through strong hydrogen bonding. When the fiber is heated above $T_{trans,}$ the soft segment phases are melted. If they are stretched, the soft segment phases are extended. When the temperature is cooled below T_{trans} and the fiber is kept at constant strain, the soft segment phases crystallize. As a result, the internal stress is stored in the fiber and the associated deformation is fixed temporally. When it is reheated to above T_{trans}, its soft segment phase becomes flexible. It resumes to the folded configuration because of the internal stress stored between hard segments. As a result, the fiber recovers to its original length.

The SMF cannot fix the deformation completely when cooled from 70°C to ambient temperature, as can be seen in Figure 7. This is because the deformation of the uncrystallized areas at 70°C includes elastic deformation, which will recover once the external force is released. It can be deduced that the fixity ratio can be strengthened by improving the crystallizability of the soft segment phases.

Cyclic tensile properties under cold drawing

The commercialized polyurethane elastic fibers prominent property is its repeat stretching recovery at ambient temperature. To make a comparison between elastic fibers and SMF, the cold drawing (at ambient temperature) cyclic tensile testing was employed. The cyclic tensile curves of the Elaspan and Newstar fibers and our SMF are shown in Figures 9–11 respectively. During cold drawing cyclic tensile testing, Elaspan and Newstar fibers have very high recovery ratios of 100% and negligible fixity ratios. The curves are highly reproducible. As can be seen from Figure 12, the first stress–strain curve cycle of the SMF is much different from the other cycles. This is because the SMF soft segment phases have more crystalline areas. During elongation, not only weak net-points are destroyed but also the crystalline areas develop more yielding followed by an increasing formation of an ideal elastic network and high orientations of the SMF. After one cycle, the stress–strain curves of the SMF are more like those

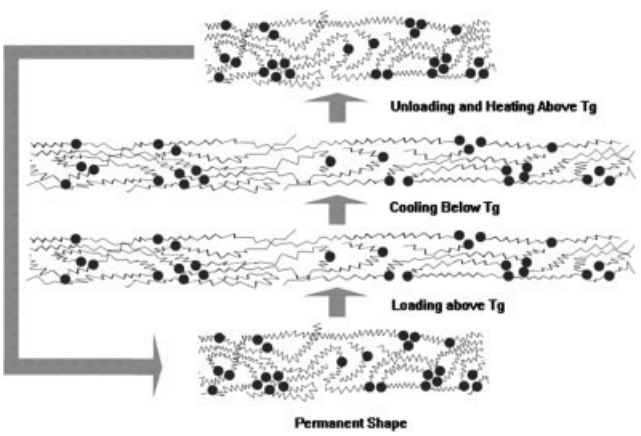

Figure 8 Schematic representation of the molecular mechanism of the shape memory effect of the SMF, zig-zag represents coiled or folder chains of polyols, circles represent isocyanate groups.

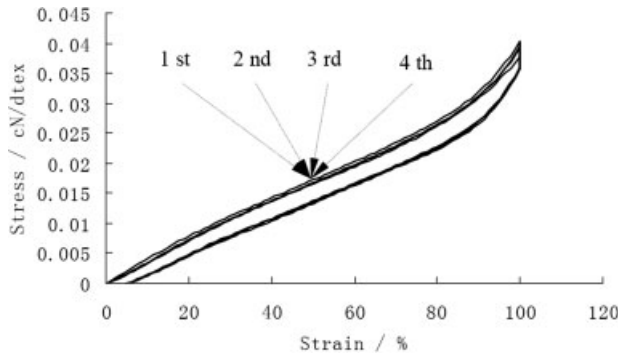

Figure 9 Cyclic tensile testing curves of the Elaspan fiber under cold drawing.

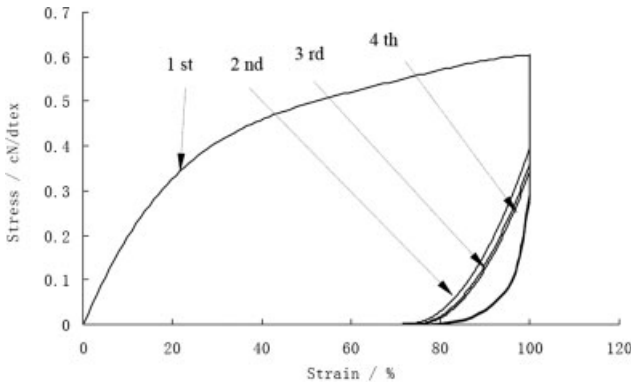

Figure 11 Cyclic tensile testing curves of the SMF under cold drawing.

of the Elaspan and Newstar fibers except that they have higher slopes, suggesting that the SMF have higher modulus.

In Figures 5 and 9, the stresses at 100% strain of the Elaspan fiber under cold drawing cyclic tensile testing are not much higher than those of the Elaspan fiber under thermal drawing and recovery cyclic tensile testing. This is also the case for the Newstar fiber. This suggests that the moduli of Elapan and Newstar fibers do not change much after heating from ambient temperature to 70°C. However, according to Figures 6 and 10, the stress of the SMF at 100% strain by cold drawing cyclic tensile testing are much higher than those of the SMF by thermal drawing and recovery cyclic tensile testing. This suggests that the SMF has a larger modulus change in the temperature range. This is because at cold drawing cyclic tensile testing, the SMF is stretched at an ambient temperature, which is below $T_{trans} \sim 47.02$°C, as can be seen from the DSC curve in Table II. At this temperature, the crystallized soft segment phases are in their rigid state. During stretching, the soft segment extension is restricted by the crystallized soft segment phases.[8] In thermal drawing and recovery cyclic tensile testing, the SMF is heated to 70°C, which is above the T_{trans}; the crystallized soft segment phase is flexible, resulting in easy extension of the SMF.

Cyclic tensile properties under cold drawing and thermal recovery

In polymer shape memory effect characterization, the deformation is usually conducted at a temperature higher than the transition temperature because polymer has a lower elastic modulus and thus the deformation is easy to be developed.

However, in practice, the deformation in the SMF, such as the creation of crease on fabric, usually occurs at ambient temperature. So the cold tensile (at ambient temperature) and thermal recovery testing has been used to study the shape memory effect of fibers. The cyclic tensile testing path is shown in Figure 3. Hu and Hashimoto[2,8]have reported the influence of loading temperature on the shape memory effect in films.

The cold drawing and thermal recovery cyclic tensile curves of the SMF are shown in Figure 12. The SMF under cold drawing and thermal recovery

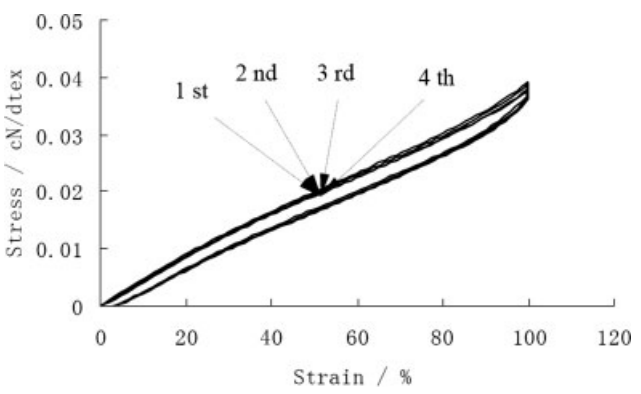

Figure 10 Cyclic tensile testing curves of the Newstar fiber under cold drawing.

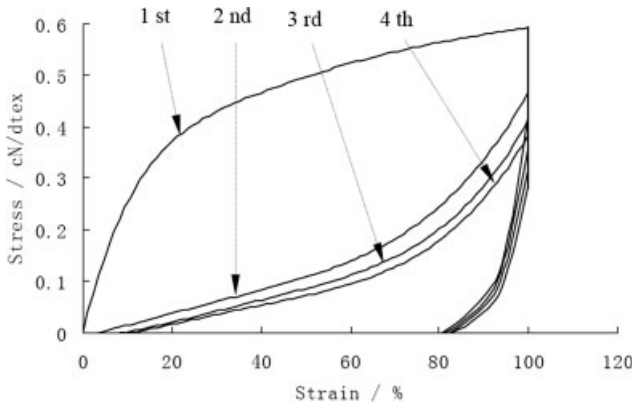

Figure 12 Cyclic tensile curves of the SMF under cold drawing and thermal recovery.

TABLE II
Results of Differential Scanning Calorimetric Analysis of the Elaspan Fiber, Newstar Fiber, and SMF

	Elaspan fiber	Newstar fiber	SMF
T_m (°C)	−1.55	−1.24	36.20
ΔH (J/g)	14.296	12.207	22.783

tensile testing has recovery ratios of more than 95% and fixity ratios of more than 80% in every cycle. This suggests that, different from commercialized elastic fiber, which can recover simultaneously and completely to the original length, the SMF can fix the deformation at ambient temperature and the original length can be recovered when it is reheated above T_{trans}.

Comparison of differential scanning calorimeter analyses

The DSC scans of the fibers from Elaspan and Newstar and our SMF are shown in Figure 13. The melting temperature and crystalline enthalpy are summarized in Table II. The soft segment phases of the Elaspan and Newstar fibers have T_ms lower than 0°C, which are below the ambient temperature. It can be seen from the DSC curve of the SMF that the soft segment phases display a melting transition at 36.20°C. The SMF has a narrow transition temperature. The crystallinity of the SMF is calculated to be 16.27% from the enthalpy data ΔH of the crystallization peak using the 140 J/g enthalpy value for fusion of 100% crystalline PCL.[24,25] At ambient temperature during elongation, the Elaspan and Newstar fibers are nearly completely elastic whereas our SMF is partially elastic because not only the hard segment

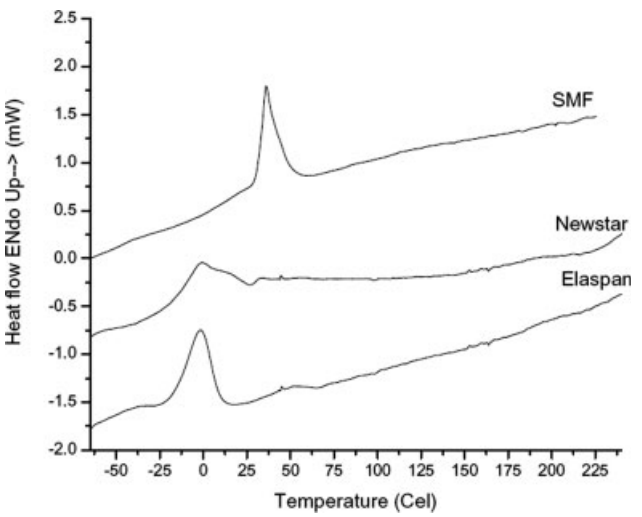

Figure 13 Differential scanning calorimetric analysis of the Elaspan fiber, Newstar fiber, and the SMF.

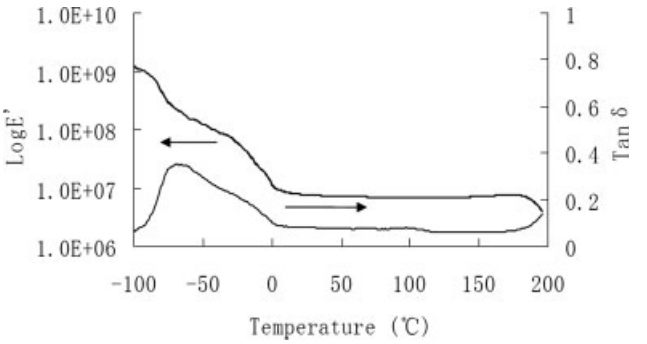

Figure 14 log E', temperature curve, and tan δ, temperature curve, of the Elaspan fiber, E' (Pa).

phases but also the neighboring crystals of the soft segment of the SMF restrict the extension of soft segments. When the SMF is heated to 70°C, which is above the T_m value, the modulus of the SMF fiber decreases because the soft segment phases melt. Without impedance in the crystalline region, the fiber can be readily stretched. When the SMF is cooled to ambient temperature, the elongation and internal stress are fixed because of the crystallization of soft segment. When the sample is reheated to a temperature above T_m, soft segment phases melt and the internal stresses stored between hard segments phases relax. As a result, the SMF returns to it original length. It can be deduced that the shape memory effect of the SMF can be improved by increasing the soft segment phase crystallinity at the expense of the SMF elasticity.

Comparison of dynamic mechanical analysis

The elastic modulus (E') and loss tangent (tan δ) of the fibers from Elaspan, Newstar, and the prepared SMF over the temperature range from −100 to 230°C are presented in Figures 14–16. The tan δ peak of Elaspan fiber shows feature in the vicinity of −68.99°C that can be ascribed to the glass transition

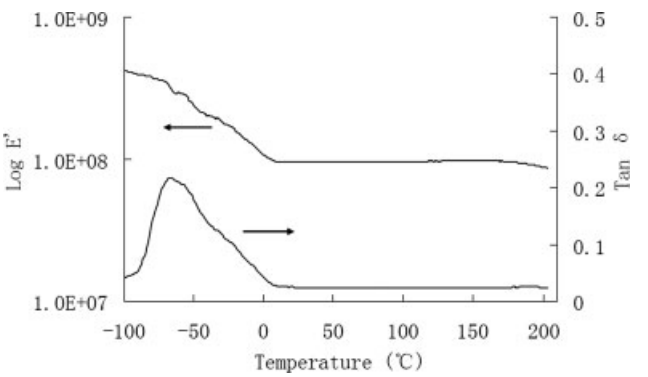

Figure 15 log E', temperature curve, and tan δ, temperature curve, of the Newstar fiber, E' (Pa).

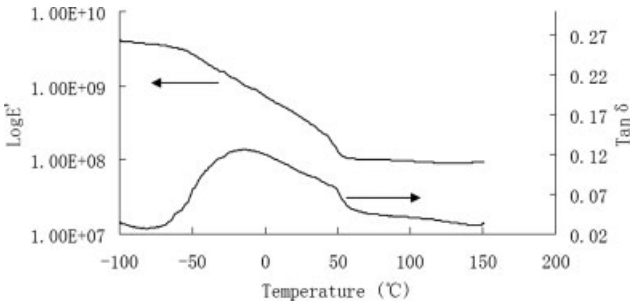

Figure 16 log E', temperature curve, and tan δ, temperature curve, of the SMF, E' (Pa).

of the soft segment phase. The E' has a sharp decrease at −68.99°C accordingly. At about −1.55°C, E' has another abrupt decrease because of the melting of the soft segment phases. At temperature above 0°C, the elasticities of the Elaspan and Newstar fibers are mostly contributed by the hard segment phases,[26] as can be seen by the plateau region of E'. Upon heating above 180°C another sharp decrease in E' is observed, indicating that the physical and chemical crosslinking sites between hard segments are totally destroyed. Same case is also applied to the Newstar fiber. Its DSC result shows a glass transition at −66.67°C and a melting transition at −1.24°C. All these are in correspondence with the mechanical properties of the Elaspan and Newstar fibers. As can be seen from the tan δ curve of the SMF, there is a broader peak ranging from −70 to 50°C compared with those of the fibers from Elaspan and Newstar which is about −80 to 0°C. The E' of the SMF has two abrupt decreases at −50°C and 36.20°C, respectively. They are attributed to the SMF soft segment phase having a glass transition temperature at −50°C and melting transition at 36.20°C.

As can be seen from Figures 14–16, when temperature is below 99.15°C, the E' of the SMF is higher than those of Elaspan and Newstar fibers. This is because the SMF soft segment phases are partially crystallized. During elongation, the neighboring crystallites restrict the extension of the amorphous chains. As a result not only the hard segment phases but also soft segment phases contribute to E'. At a temperature of about 36.20°C, the E' of the SMF has a sharp decrease because melting transition occurs in the soft segment phase. At a temperature above 99.15°C to the maximum heat resistance temperature of the SMF ∼ 170°C, the E′ is more like that of the Newstar fiber. At the plateau region, the E' of the SMF slightly decreases compared with those of the fibers from Elaspan and Newstar, which show no significant change. The maximum heat resistance temperature of the SMF is 170°C, whereas that from the Elapan and Newstar fibers have higher heat resistance temperature of 180°C. This is because the fibers from Elapsan and Newstar are extended by diamine, forming urea group (not urethane) as the SMF extended by diol. Urea groups have higher cohesion density and the groups give rise to much hydrogen link between both hard and soft segments. In future work, the mechanical properties and maximum heat resistance temperature of the SMF can be improved by employing some prepolymer crosslink method or end capping method, which have been applied by melt spinning of commercialized polyurethane elastic fibers.[21,27]

CONCLUSION

In this article, shape memory polyurethane was synthesized by prepolymerization method, and the SMF were prepared by wet spinning using PCL as the soft segment whereas diisocyanate and small size molecular diol extender as the hard segment. The mechanical properties, shape memory effect, thermal and dynamic properties of the SMF were studied and compared with that from the commercialized polyurethane fibers. It was found that the 40 denier SMF had a tenacity of about 0.93–0.98 cN/dtex and strain at break was of 85–115%. At ambient temperature, the modulus of the SMF was higher than those of the commercialized polyurethane fibers. At temperature above 99.15°C, the modulus of the SMF was similar to those of commercialized fibers. The SMF had a fixity ratio of more than 80% and recovery ratio more than 95% under thermal drawing and recovery cyclic tensile testing. The SMF had shape memory effect because it could fix the temporary length after stretching. The shape memory mechanism of the SMF was illustrated using differential scanning calorimetric and dynamic mechanical analysis. Our SMF, different from commercialized polyurethane fibers, has a melting transition at 36.20°C and crystallinity of 16.27%, which helps the SMF to fix the temporary shape once the fiber was cooled to ambient temperature from 70°C. It could recover to its original length by reheating the fiber above 36.20°C at which the crystallized soft segment phases melt.

References

1. Hyashi, S. Int Prog Urethanes 1993, 6, 90.
2. Tobushi, H.; Hashimoto, T.; Ito, N.; Hayashi, S.; Yamada, E. J Intell Mater Syst Struct 1998, 9, 127.
3. Lin, J. R.; Chen, L. W. J Appl Polym Sci 1998, 69, 1563.
4. Lin, J. R.; Chen, L. W. J Appl Polym Sci 1998, 69, 1575.
5. Wei, Z. G.; Sandstrom, R.; Miyazaki, S. J Mater Sci 1998, 33, 3743.
6. Lendlein, A.; Kelch, S. Angew Chem Int Ed 2002, 41, 2034.
7. Yang, J. H.; Chun, B. C.; Chung, Y. C.; Cho, J. H. Polymer 2003, 44, 3251.
8. Hu, J. L.; Ji, F. L.; Wong, Y. W. Polym Int 2005, 54, 600.

9. Liang, C.; Rogers, C. A. J Intell Mater Syst Struct 1997, 8, 285.
10. Kim, B. K.; Lee, S. Y.; Xu, M. Polymer 1996, 37, 5781.
11. Kim, B. K.; Lee, S. Y. Polymer 1998, 39, 2803.
12. Ichji, W. Application No. 09–095866, Japan (1995).
13. Akira, S.; Hitotoku, Y. Application No. 06–283155, Japan (1994).
14. Zhu, Y.; Hu, J. L.; Yeung, L. Y.; Liu, Y.; Ji, F. L.; Yeung, K. W. Smart Mater Struct 2006, 15, 1385.
15. Ji, F. L.; Zhu, Y.; Hu, J. L.; Liu, Y.; Yeung, L. Y.; Ye, G. D. Smart Mater Struct 2006, 15, 1547.
16. Lee, B. S.; Chun, B. C.; Chung, Y. C.; Sul, K. I.; Cho, J. W. Macromolecules 2001, 34, 6431.
17. Li, F. K.; Zhang, X.; Hou, J. A.; Xu, M.; Luo, X. L.; Ma, D. Z.; Kim, B. K. J Appl Polym Sci 1996, 64, 1511.
18. Fourne, F. Synthetic Fibers Machines and Equipment, Manufacture, Properties; Hanser Publishers: Munich, 1999.
19. Mark, H. F.; Atlas, S. M.; Cernia, E. Man-Made Fibers Science and Technology, Vol. 3; Wiley: New York, 1968.
20. ISO Standard Handbook, International Organization for Stardardization, Geneva, Switzerland, 1989. ISO 2076, 12.89.
21. Yoshihaya, N.; Ishihara, H.; Yamada, T. Polym Eng Sci 2003, 43, 1740.
22. Fabricius, M.; Gries, T.; Wulfhorst, B. Chem Fibers Int 1995, 45, 1995.
23. Bhat, G.; Chand, S.; Yakopson, S. Thermochim Acta 2001, 367/368, 161.
24. Luo, N.; Wang, D. N.; Ying, S. K. Polymer 1996, 37, 3577.
25. Crescenzi, V.; Manzini, G.; Calzolari, G.; Borri, C. Eur Polym J 1972, 8, 449.
26. Korley, L. T. J.; Pate, B. D.; Thomas, E. L.; Hammond, P. T. Polymer 2006, 47, 3073.
27. Hu, J. L.; Yang, Z. H.; Yeung, L. Y.; Ji, F. L.; Liu, Y. Q. Polym Int 2005, 54, 854.