Uniqueness of shape memory fibers in comparison with Existing man-made fibers

Jinlian Hu^a^{*}, Yong Zhu^a, Jing Lu^a, Lap-yan Yeung^a, Kwok-wing Yeung^b

 ^a Institute of Textiles and Clothing, Hong Kong Polytechnic University, Kowloon, Hong Kong, P. R. China
^b Clothing Industry Training Authority, Kowloon, Hong Kong, P. R. China

Abstract

To understand the unique properties of shape memory polyurethane (SMPU) fibers, a series of shape memory polyurethanes having various hard segment contents was synthesized by using pre-polymerization method. Dynamic mechanical analysis (DMA) was used to pinpoint the transition area of SMPU fibers and compare the SMPU fibers with other existing man-made fibers. The shape memory effect of SMPU fibers was studied by the cyclic tensile testing. The fixity for temporary elongation and the recovery to the original length of SMPU fibers were detected with cyclic tensile test, suggesting that SMPU fibers can effectively fix the temporary elongation and subsequently can retrieve the original length with the stimulus of external heating.

Keywords: Shape Memory; Polyurethane; Fiber; Man-made Fibers

1. Introduction

Since the Nagoya Research and Development Center of Mitsubishi Heavy Industry (MHI) developed a series of SMPUs in 1988[1], some progress about the application of SMPU has been made in the past decades. It is due to the following advantages of this kind of smart materials: the forming processes used for other thermoplastic polymers could be utilized directly; the shape recovery temperature could be set at any value within 50 K around the room temperature; there are the large differences of mechanical properties, optical property and water vapor permeability at the temperatures above and below the designed switch temperature. Based on these advantages, the SMPU has been expected to be used as self-repairing, and smart materials or biomaterials. The use area can be divided into the following classes: use of variation in modulus of elasticity; use of shape fixity and shape recoverability; use of variation in moisture permeability, volume expansion and refractive index and high damping[2]. In textile area, the shape memory polyurethane was reported to be used in coating on the fabric surface to offer the temperature dependence of water vapor permeability to improve the comfort sense of fabric[3]. The smart water vapor permeability dependent on temperature arises from the increased free volume in soft segment domains, which allow water vapor molecules with an average diameter of 3.5Å to be easily transmitted through the polymer thin film[4]. Since 2003, the Shape Memory Textile Centre in The Hong Kong Polytechnic

University has applied shape memory polyurethane in fiber spinning, fabric finishing, garment finishing with various techniques so as to impart shape memory function into fiber and garment products[5-16]. In principle, SMPU consists of a rigid fixed and a soft reversible phase. The reversible phase having a melting or glass transition temperature of the soft segments as the transition temperature is used to hold the temporary deformation, whereas the fixed phase is referred to the hard segments covalently coupled to the soft segments. Hereinto, the fixed phase inhibits plastic slip of the molecular chains by having physical cross-linkage points among them and can be responsible for memorizing the permanent shape [17-21]. In this study, the glass transition (T_g) of amorphous soft segment phase was used as switch temperature to control the fixity of temporary elongation and recovery temperature. Whereas, the physical cross-link of hard segment phase was responsible for memorizing the original length of fibers. In this way, the fabric composed of SMPU fibers was designed to possess the following advantages: When the garment with given size is enlarged to fit different wears' figures, the fixity ability to temporary deformation caused in wearing process was expected to diminish most of pressure sensation to wearer as shown in Figure 1. After wearing, heating in washing or drying process will give rise to the recovery of the original size. The mentioned mechanism stems from the shape memory function of SMPU fibers, which was expected to be imparted into fabric, garment in this study.

* Corresponding author: Jinlian Hu, Email: tchujl@inet.polyu.edu.hk This work is being supported by Hong Kong ITF research project 'High Performance Advanced Materials for Textile and Apparel' (No. GHS/088/04)

2. Tables and figures

2.1 Tables

As shown in Table 1, the SMPU fibers are nomenclated by four alphabets followed by numbers. The alphabet denotes the samples belong to shape memory polyurethane fibers; the number represents the hard segment content containing isocyanate and chain extender. SMPU were synthesized by pre-polymerization, spun by wet spinning method and treated with high pressure steaming as described in our reported literature[8, 11, 22].

Mechanical properties testing of SMPU fibers were conducted with Instron4411 according to the ASTM D2256. Testing for each fiber was repeated 10 times under the same testing condition so as to obtain the reliable average resulting data including tenacity and maximum strain.

Table 1 Mechanical properties of SMPU fibers

| Sample code | Hard segment Content (%) | Linear Density (tex) | Maximum Strain (%) | Tenacity (cN/tex) |
|----------------|-----------------------------|-------------------------|-----------------------|----------------------|
| SMPU64 | 64.1 | 7.18 | 147.0 | 7.4 |
| SMPU55 | 54.7 | 5.28 | 172.4 | 7.5 |
| SMPU48 | 47.7 | 5.14 | 215.9 | 8.7 |

2.2 Figures



Fig. 1. SMPU fabric, garment fits different wearer's figure without tension

Dynamic mechanical properties of the samples were determined by using a Perkin-Elmer DMA at frequency of 2 Hz. The heating rate is 2 °C/min and temperature is scanned from -150 to 200 °C. The length for each fiber sample between crossheads is 15mm and a bunch of 100 fibers was used in each testing process. As shown in Figure 2 and Figure 3, all the resulting data about the storage modulus was normalized with the linear density of the fiber so as to make the comparison among them. Other man-made fiber specimens were commercial products. Figure 4 illustrates the temperature dependence of loss tangent, which was used to pinpoint the glass transition temperature of SMPU fiber.

As shown in Figure 5, cyclic tensile test was performed using an INSTRON 4466 tensile tester equipped with a temperature control chamber. The fiber with the length 30mm was initially stretched to 50% elongation ratio (ε_m) at room temperature (22°C) with a constant elongation rate 5.5×10^{-3} s⁻¹ and the ε_m was kept with the strain for 60 second; then the clamps of tensile tester was retracted to -50% of the original length of fibers to cause the sample to bend; after that, the fibers was heated up to 75 °C (T_{hieh}) in 900 seconds to recover the original length; subsequently, the cool air is vented passively into the chamber to cool down the sample to 22 °C (T_{low}) in 1200 seconds. Each complete thermal cycle for the sample will be repeated three or more times for assessing the shape memory effect. Detailed parameter definitions such as shape recovery ratio or shape fixity ratio used to characterize the shape memory effect was defined in the reported literature [17, 23].



Fig. 2. Temperature dependence of storage modulus (*E'*) of existing man-made fibers



Fig. 3. Temperature dependence of storage modulus (*E'*) of SMPU fibers



Fig. 4. Loss tangent (tanb) of SMPU fibers





Fig. 5. Cyclic tensile test for evaluating shape memory effect of SMPU fibers



Fig. 6. Testing cylinder of *Testing sensor: Novel Pliance -X* system for pressure detection



Fig. 7. Pressure (vertical direction to fabric surface) of enlarged fabrics to 'wearer' (testing cylinder) (SMF1, SMF2, SMF3, SMF4 made with SMPU fibers with different composition)

The pressure in vertical direction to testing cylinder surface of enlarged fabrics was detected with *Testing sensor: Novel Pliance -X system* offered by Intimate Apparel Institute of The Hong Kong Polytechnic University. The fabric column specimens made with SMPU fibers and other commercial fiber products were firstly enlarged with various elongation ratios in perimeter and then fixed in the deformed size for 10 mins. After that, specimens were set onto the testing cylinder surface. The Pliance-X system recorded the average pressure. The whole testing setup and resultant data were illustrated in Figure 6 and Figure 7.

3. Discussion

The resultant data of DMA show that a difference between SMPU fiber and conventional man-made fibers is the variation of E' in normal using temperature range. For SMPU fibers, the variation of E' is very significant. Namely, when the temperature was increased above the T_g , the E' will sharply decrease and the rubbery state plateau will appear and be extended to above 160°C as shown in Figure 3. However, for other types of man-made fibers such as polyester and Lycra, though in the entire heating scan range, there are sharp transition area of E', such as -40°C for Lycra[24], 100-105°C for Polyester fibers and yarns[25], the elastic modulus is almost the constant and change little with the increase of temperature in normal using temperature range. Therefore, this point imparts the heating responsive shape memory properties to the SMPU fiber in normal using temperature just as reported T_g used as the switch temperature in the shape memory polyurethane film[20, 21, 26-28].

Figure 4 demonstrates that the T_g of soft segment reflected by the peak of tan δ can be controlled with solely changing hard segment content. It will be used in fabricating SMPU fiber with different 'switch' temperature.

In Figure 5, it can be observed that the fixity ratio to temporary elongation decreases with the decrease of hard segment content. It might be due to the decreasing trend of T_g of soft segment with the decrease of hard segment content. In our testing routine, the fixity temperature is 22 °C (T_{low}) and higher than transition temperature of the samples: SMPU55 and SMPU48, which can be detected from the peak of tano. For SMPU64, most of elongation can be fixed temporarily in each stretching cycle. In the subsequent heating process, all stretched specimens can recover the original length with the recovery ratio 90% or more. Instead, Spandex or Lycra provides the desired stretch-effect with enough high elongation at break of 500-600% depending on the molecular weight of the soft segment (between 1000-3000). The high value of recovery ability (90%)[29] after several times elongation represents the elastic properties of the yarn and the flat shaped article. Non-elastic, hard fibres such as Nylon6 or Polyester filaments could be characterized with the very small elongation at break, very high tensile strength and modulus. Therefore, it can be found the uniqueness of SMPU fiber compared with the existing man-made fiber is the ability to fix the temporary deformation and the thermal responsive shape recovery.

The vertical pressure/tension exerted by the deformed fabric column to the testing cylinder surface was detected with the facilities shown in Figure 6. Although the effect of fabric structure of used fabric specimens was tentatively ignored, the

resultant data shown in Figure 7 illustrates that the fabric made with SMPU fibers after stretching with various elongation ratio can effectively diminish the pressure in vertical direction in comparison with fabrics made with Lycra or PA/Lycra. Hence, through this study, it is expected to offer a novel smart textile material to automatically fit customized size without uncomfortable tension to wearers.

4. Conclusion

The uniqueness of SMPU fibers were described in comparison with other existing man-made fibers. The switch temperature for shape memory function was located with DMA testing and the shape memory effect was quantitatively characterized with cyclic tensile testing method. It was found that the ability to fix the temporary deformation and the thermal responsive shape recovery are characteristics for SMPU fibers. Subsequently, the fabric made with these fibers was observed to be able to adapt to various customized size with relative low vertical tension. Instead, the tension caused by deformed traditional elastic fabric is very high. Therefore, the fabric made with SMPU fibers potentially was used to improve the comfort sensation of textile products such as intimate apparel.

Acknowledgements

The authors would like to acknowledge the support from the Hong Kong ITF research project 'High Performance Advanced Materials for Textile and Apparel' (No. GHS/088/04) and gratefully thank the Intimate Apparel Institute of The Hong Kong Polytechnic University for using *Testing sensor: Novel Pliance -X system*.

References

- liang, C., C.A. Rogers, and E. Malafeew, *Investigation of shape memory polymers and their hybrid composites*. Journal of intelligent material systems and structures, 1997. 8(4): p. 380-386.
- Tobushi, H., et al., *Thermomechanical properties in a thin film of shape memory polymer of polyurethane series*. Smart Materials and Structures, 1996. 5: p. 483-491.
- Hayashi, S. and N. Ishikawa, *High Moisture Permeability Polyurethane for Textile Application*. Journal of Coated Fabrics, 1993. 23: p. 74-83.
- Hu, J.L., et al., Shape Memory Polymers and Their Applications to Smart Textile Products. Journal of Dong Hua University (Eng Ed), 2002. 19(3): p. 89.
- Zeng, Y.M., J.L. Hu, and H.J. Yan, *Temperature Dependency* of Water Vapor Permeability of Shape Memory Polyurethane. Journal of Dong Hua University (Eng Ed), 2002. 19(3): p. 53.
- Hu, J.L. and S. Mondal, Structural characterization and mass transfer properties of segmented polyurethane: influence of block length of hydrophilic segments. Polymer International, 2005. 54(5): p. 764-771.
- Hu, J.L., et al., Crosslinked polyurethanes with shape memory properties. Polymer International, 2005. 54: p. 854-859.
- Zhu, Y., et al., Development of Shape Memory Polyurethane Fiber with Complete Shape Recoverability. Smart Materials & Structures, 2006. 15: p. 1385-1394.
- 9. Mondal, S., J.L. Hu, and Y. Zhu, Free volume and water

vapor permeability of dense segmented polyurethane membrane. Journal of Membrane Science, 2006. **280**(1-2): p. 427-432.

- Liu, Y.Q., et al., Surface modification of cotton fabric by grafting of polyurethane. Carbohydrate Polymers, 2005. 61: p. 276-280.
- 11. Ji, F.L., et al., *Smart polymer fibers with shape memory effects.* Smart Materials and Structures, 2006. **15**(6): p. 1547-1554.
- 12. Hu, J.L., *Shape memory textiles*, in *Shape Memory Polymers and Textiles*. 2007, Woodhead Publishing Limited: Cambridge.
- Mondal, S., Studies of structure and water vapor transport properties of shape memory segmented polyurethanes for breathable textiles, PhD thesis, in Institute of Textiles and Clothing. 2006, The Hong Kong Polytechnic University: Hong Kong.
- 14. Ding, X., *Microstructure and water vapor transport* properties of temperature sensitive polyurethanes, *PhD* thesis, in Institute and Textiles and Clothing. 2004, The Hong Kong Polytechnic University: Hong Kong.
- Hu, J.L., Y.M. Zeng, and H.J. Yan, *Influence of Processing* Conditions on the Microstructure and Properties of Shape Memory Polyurethane Membranes. Textile Research Journal, 2003. 73(2): p. 172-178.
- Ding, X.M., J.L. Hu, and X.M. Tao, *Effect of Crystal Melting on Water Vapor Permeability of Shape-Memory Polyurethane Film.* Textile Research Journal, 2004. 74(1): p. 39-43.
- Kim, B.K., S.Y. Lee, and M. Xu, *Polyurethane having shape* memory effects. Polymer, 1996. **37**(26): p. 5781-5793.
- Hou, J.A., et al., Thermally Simulated Shape Recovery Effect of Segmented Polyurethane, in The International Symposium on Polymer Alloys and Composites, C.L. Choy and F.G. Shin, Editors. 1992, Hong Kong Polytechnic University: Hong Kong Polytechnic University, Hong Kong. p. 211.
- Li, F.K., et al., Studies on Thermally Stimulated Shape Memory Effect of Segmented Polyurethanes. Journal of Applied Polymer Science, 1997. 64: p. 1511-1516.
- Lin, J.R. and L.W. Chen, Study on Shape-Memory Behavior of Polyether-Based Polyurethanes. I. Influence of the Hard-Segment Content. Journal of Applied Polymer Science, 1998. 69: p. 1563-1574.
- Lin, J.R. and L.W. Chen, Study on Shape-Memory Behavior of Polyether-Based Polyurethanes. II. Influence of Soft-Segment Molecular Weight. Journal of Applied Polymer Science, 1998. 69: p. 1575-1586.
- 22. Zhu, Y., et al., *Effect of steaming on shape memory polyurethane fibers with various hard segment contents.* Smart Materials & Structures, 2007. In revision.
- Lendlein, A. and S. Kelch, *Shape-Memory Polymers*. Angewandte Chemie-International Edition, 2002. 41: p. 2034 - 2057.
- 24. Meyer, R.V., E. Haug, and G. Spilgies, *Sources of stretch*. Textile Asia, 1994: p. 40-45.
- Manich, A.M., et al., *Thermal Analysis and Differential Solubility of Polyester Fiber and Yarns*. Textile Research Journal, 2003. **73**(4): p. 333-338.
- Lee, B.S., et al., Structure and Thermomechanical Properties of Polyurethane Block Copolymers with Shape Memory Effect. Macromolecules, 2001. 34: p. 6431-6437.
- Jeong, H.M., S.Y. Lee, and B.K. Kim, Shape memory polyurethane containing amorphous reversible phase. Journal of Materials Science, 2000. 35: p. 1579-1583.

- Hu, J.L., F.L. Ji, and Y.W. Wong, Dependency of the shape memory properties of a polyurethane upon thermomechanical cyclic conditions. Polymer International, 2005. 54: p. 600-605.
- Zhang, J. and Y. Zhao, Production and Application of Polyurethane Elastic Fibers. Polyurethane Industry, 2000. 15(4): p. 11-14.