Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 1348–1356

polymer

www.elsevier.com/locate/polymer

Effects of moisture on the thermomechanical properties of a polyurethane shape memory polymer

B. Yang, W.M. Huang *, C. Li, L. Li

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

Received 3 June 2005; received in revised form 1 November 2005; accepted 11 December 2005
Available online 9 January 2006

Abstract

The glass transition temperature of an ether-based polyurethane shape memory polymer (SMP) has been found to decrease significantly after immersion in water. In order to get a better understanding of the mechanism behind this phenomenon, a systematic study on the effects of moisture on the glass transition temperature and thermomechanical properties of this SMP was carried out. The results reveal that the hydrogen bonding between N–H and C=O groups is weakened by the absorbed water. Furthermore, the water absorbed into the SMP can be separated into two parts, i.e. the free water and the bound water. Each part inside the SMP was quantified. Bound water significantly reduces the glass transition temperature in an almost linear manner and has a significant influence on the uniaxial tensile behavior, while the effect of free water is negligible. In addition, the recovery stress and recovery strain in constrained/free recovery induced by water were investigated and compared with that induced thermally.

Keywords: Shape memory polymer; Hydrogen bonding; Thermomechanical

1. Introduction

Thermoresponsive shape memory polymers (SMPs) have attracted considerable attention due to their unique recovery phenomenon, i.e. the ability to return to their original shapes upon heating [1–3]. Among the commercially available thermoresponsive SMPs, polyurethane SMP is a multi-block copolymer consisting of both hard and soft segments. Compared with other SMPs, apart from the advantage of easier processing, polyurethane SMPs also have a wider range of shape recovery temperature (from 30 to 70 °C), higher recoverable strain (maximum recoverable strain >400%), and better biocompatibility [3–5]. Previous studies have focused more on polymerization, structure and thermomechanical properties of polyurethane SMPs [3–8]. The effects of moisture on its glass transition temperature reported in [9] reveal its two new features. One is the functionally gradient in the glass transition temperature, and the other is the actuation of the material triggered by water [10]. In Fig. 1, the left upper part of the polyurethane SMP wire has a lower glass transition temperature than its right lower part. The functionally gradient in the glass transition temperature is produced by immersing the left part of the wire in water for about 1 h while keeping the right part dry. The functionally gradient SMP can recover from the pre-deformed 'Z' shape sequentially after immersion in room temperature water as shown in Fig. 1.

The formation of hydrogen bonding in polyurethane is generally known to have a major effect on its morphology and overall properties [11–14]. The primary bands in polyurethane, the N–H stretching as a proton donor and the carbonyl stretching as a proton acceptor, are sensitive to hydrogen bonding. The shift of the Fourier transform infrared (FTIR) absorbance peak to a lower frequency is evidence of the formation of hydrogen bonding. The magnitude of the shift is a measure of the strength of the hydrogen bonding [11–17]. The degree of bonding can be estimated by measuring the ratio of infrared band intensity of the bonded group to that of the free group. Furthermore, the strength of hydrogen bond varies with temperature. This paper aims to identify the possible mechanism behind the effects of moisture on the glass transition temperature of SMP as reported in Ref. [9], in particular, the interaction of water with polyurethane SMP.

This paper comprises two parts. One part investigates the effects of moisture on the glass transition temperature of the polyurethane SMP. In order to understand the behind mechanism, the interaction of water with polymer is studied

---

* Corresponding author. Tel.: +65 679 04859/11859.
E-mail address: mwmhuang@ntu.edu.sg (W.M. Huang).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.12.051

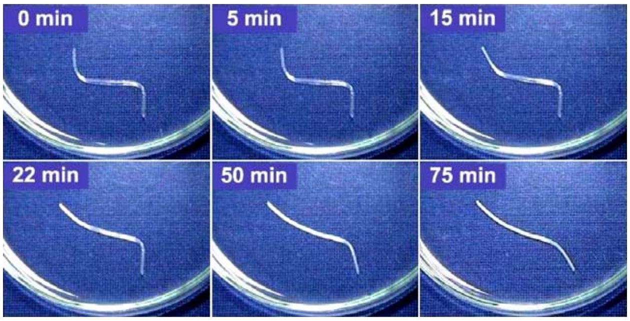

Fig. 1. Recovery of functionally gradient SMP actuated by water in a sequence [10].

with the infrared spectroscopy. The other is to study the influence of moisture on its thermomechanical properties. Together, these two parts provide a foundation for utilizing the new features of this SMP.

2. Material and sample preparation

An ether-based polyurethane SMP in pellet form bought from Mitsubishi Heavy Industries (MHI) was used in the course of this study. It is prepared from diphenylmethane-4,4′-diisocyanate, adipic acid, ethylene glycol, ethylene oxide, polypropylene oxide, 1,4-butanediol and bisphenol A. According to the data provided by MHI, it has a glass transition temperature of 35 °C and a melting point at around 200 °C. Before sample preparation, the SMP pellets were kept in a vacuumed oven at 80 °C for 12 h for drying. Two types of samples were prepared for the different tests. One is a thin sheet with a thickness of 1.0 mm produced by hot pressing at 200 °C on a Teflon mold. The other is a wire with a diameter of 1.0 mm by extrusion at 200 °C.

3. Effect of moisture on glass transition temperature

3.1. Water absorption

In order to quantify the content of water absorption in the samples, thermogravimetric analysis (TGA) was conducted using a TGA 2950 (TA Instruments). The polyurethane SMP sheets were first immersed in deionized water at room temperature (around 25 °C) for different periods. The sheets were then cut into pieces, about 20–25 mg each, and heated from 30 to 350 °C at a constant rate of 20 °C/min.

Fig. 2 shows the TGA results of samples after immersion in water for up to 240 h. All samples start to decompose at about 260 °C, as evidenced by the rapid decrease in weight. Before decomposition, however, samples that have been immersed in water lose dramatic amount of weight between 80 and 180 °C. This should be the result of the evaporation of absorbed water in the polymer. As expected, weight loss becomes significant with the increase in immersion time. The sample is saturated after a 240 h immersion, as indicated by the resultant TGA curve, which becomes pretty stable. For convenience, we choose the weight fraction at 240 °C as the reference for comparison of results in the following study. That is to say, we take the weight loss at 240 °C as the total amount of water absorbed in the polymer, despite the fact that a limited amount of water does evaporate continuously to beyond 240 °C.

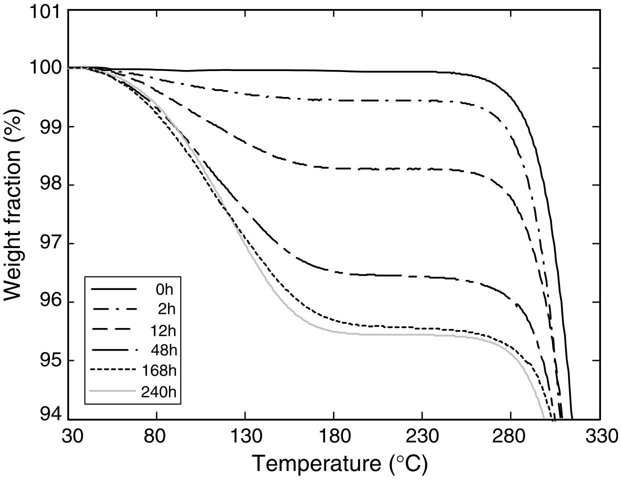

Fig. 2. TGA results after samples immersed in water for different hours.

3.2. Evolution of glass transition temperature

Samples, about 10–15 mg in weight, were cut from the polyurethane SMP sheets. Differential scanning calorimeter (DSC) test (DSC 2920, TA Instruments) was carried out on them at a heating rate of 20 °C/min.

In Fig. 3, we plot the DSC results of the samples after different immersion hours. The glass transition temperature of each sample was determined as the median point in the glass

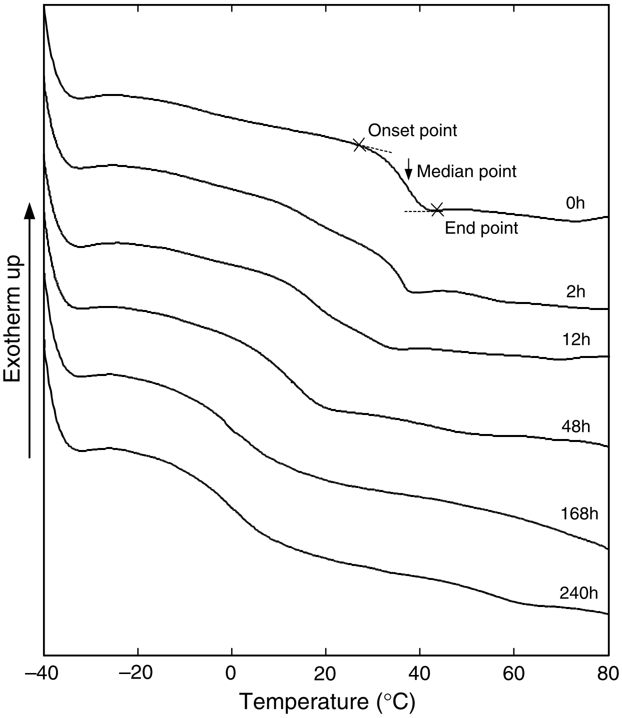

Fig. 3. DSC results after immersion in water for different hours.

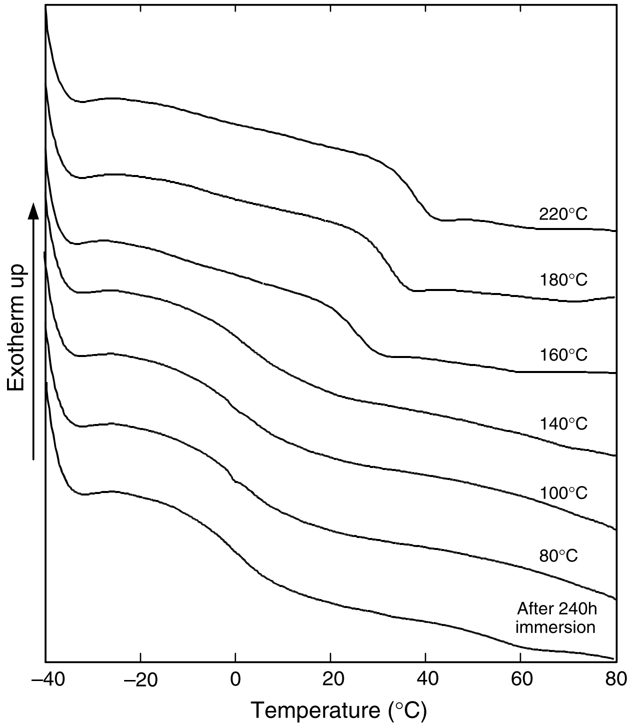

Fig. 4. DSC curves of saturated samples (240 h of immersion) after preheated to different temperatures.

transition region as demonstrated in Fig. 3. As we can see, with the increase in immersion time the glass transition temperature decreases significantly (dropped by about 35 °C after 240-h immersion). The decrease is rapid at the beginning and becomes moderate over a period of prolonged immersion. After about 168 h of immersion, the sample is close to saturation, since the change in the transition temperature becomes negligible. It also reveals that the transition range is widened from about 10 to 40 °C with the increase of immersion hour.

In order to check whether the glass transition temperature is thermally reversible, the polyurethane SMP samples were, after being subjected to different hours of immersion, placed on a digitally controlled hot plate and heated to different temperatures at a constant heating rate of 10 °C/min. Upon reaching a predetermined temperature, the samples were rapidly cooled down to room temperature in 3 min for subsequent DSC tests. One typical DSC result of the sample immersed for 240 h is shown in Fig. 4. It reveals that with the increase in the heating temperature the glass transition temperature gradually approaches its original one (~35 °C). The increase is more significant in the heating temperature range of 100–180 °C, which almost coincides with the temperature range in Fig. 2, in which the evaporation of water takes place. Further increase in the heating temperature reveals a comparably small effect on the glass transition temperature. Therefore, we may conclude that the glass transition temperature of this SMP is thermally reversible upon heating to 180 °C.

3.3. Interactions between water and SMP

At this point, we have demonstrated that moisture has a strong influence on the glass transition of the polyurethane SMP. However, the mechanism behind this phenomenon remains unknown.

In this study, FTIR spectroscopy was used to study the interaction of water with the polyurethane SMP and identify other possible factors. The samples used for FTIR test were thin polyurethane SMP sheets with a thickness of 1.0 mm. FTIR spectra were collected by averaging 70 scans at a resolution of 4 cm^{-1} in a reflection mode from a FTIR spectrometer (Nicolet Magna IR-560).

The full FTIR spectrum of the polyurethane SMP at room temperature without immersion in water is presented in Fig. 5. Some peaks of this spectrum that are relevant to this study have been marked out and identified according to some references [11–13]. On the one hand, the infrared band of the bonded N–H stretching occurs at 3289 cm^{-1} while that of the free N–H

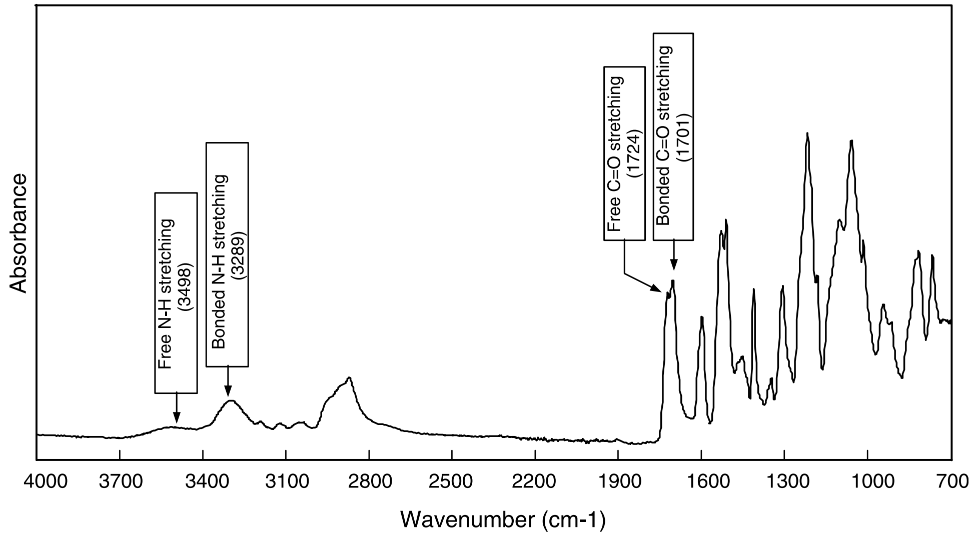

Fig. 5. FTIR spectra of polyurethane SMP without immersion.

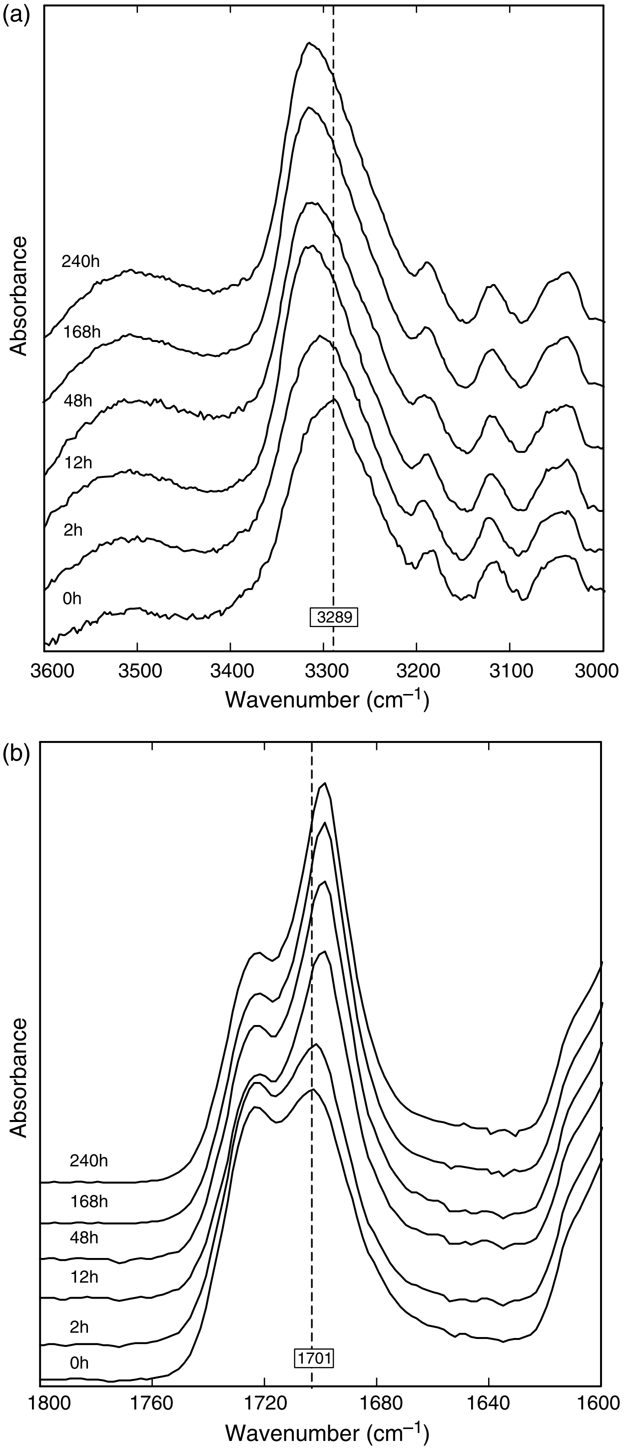

Fig. 6. FTIR spectra of polyurethane SMP after different immersion hours. (a) N–H stretching region, (b) C=O stretching region.

stretching occurs at 3498 cm^{-1}. On the other hand, the infrared band of free C=O stretching at 1724 cm^{-1} shifts to that of the bonded one at 1701 cm^{-1}. As such, the strong hydrogen bonding in the SMP is apparent.

Fig. 6(a) and (b) present the FTIR spectra in the N–H and C=O stretching regions in samples after different immersion hours, respectively. Fig. 6(a) shows that the infrared band intensity of hydrogen-bonded N–H stretching has only a small change compared with that of the free N–H stretching. However, with the increase of immersion time the infrared band of hydrogen-bonded N–H stretching shifts to a higher frequency. The shift is more significant at a short immersion period and becomes almost negligible after more than 48 h of immersion. Fig. 6(b) shows that after immersion the infrared band of the hydrogen-bonded C=O stretching shifts slightly to a lower frequency. Furthermore, with the increase of

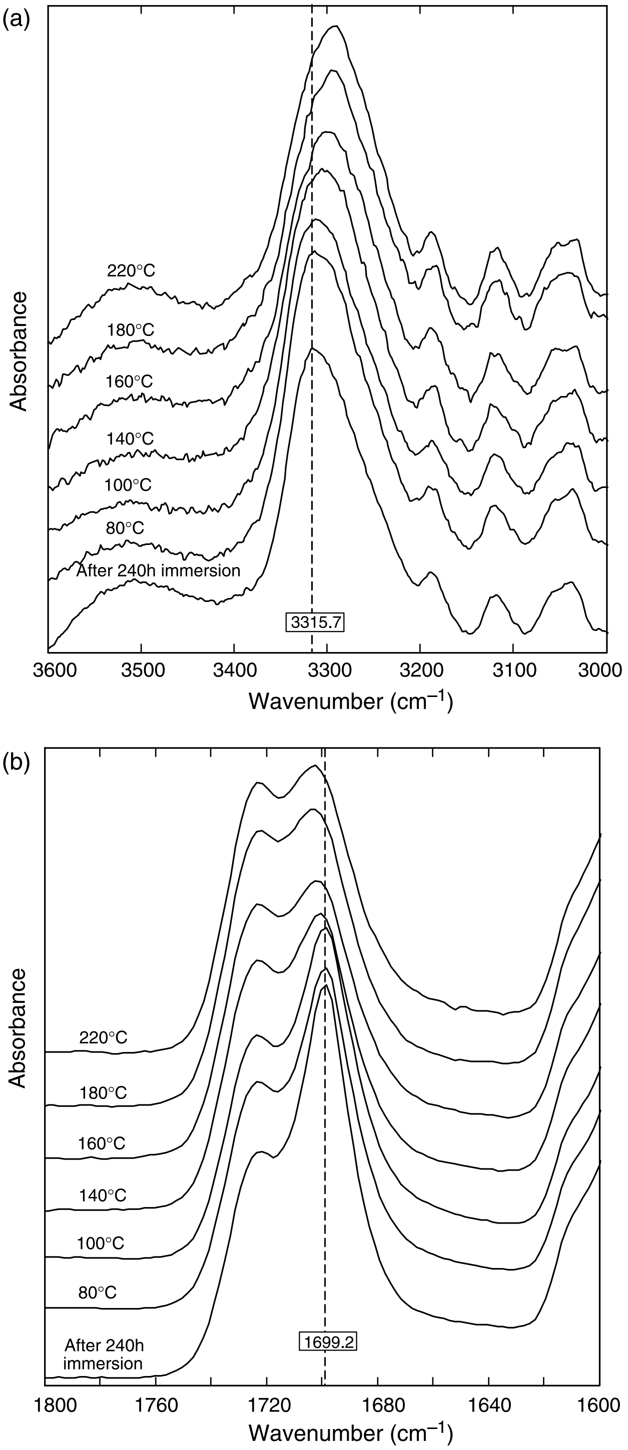

Fig. 7. FTIR spectra of saturated samples (240 h immersion) after heated to different temperatures. (a) N–H stretching region, (b) C=O stretching region.

immersion time the infrared band intensity of the bonded C=O stretching becomes more striking compared with that of the free C=O stretching, which indicates that a longer immersion time triggers more C=O groups involved in hydrogen bonding.

The heating process mentioned above has a direct influence on the absorbed water in the polymer. Fig. 7 shows the FTIR spectra of the saturated polyurethane SMP sample (240 h immersion) after heated to different temperatures. In Fig. 7(a), with the increase of heating temperature, both the infrared band position and intensity of the hydrogen-bonded N–H stretching return to their original values [the dry sample, as shown in Fig. 6(a)]. Meanwhile in Fig. 7(b), the infrared band of the bonded C=O stretching not only shifts to a higher frequency almost identical to that of the dry sample but also regains its dominance in terms of intensity (Fig. 6(b)).

3.4. Correlations among water absorption, glass transition temperature and hydrogen bonding

Utilizing the data obtained from previous tests, namely the TGA and DSC tests, we can determine the relationship between the glass transition temperature and water ratio in wt% in the water immersion and heating processes (Fig. 8). A series of similar slant L-shaped curves indicating the relationship between transition temperature and water content upon heating are obtained. The evolution in the glass transition temperature upon heating is obviously divided into two stages. At a lower heating temperature, the transition temperature is kept almost as a constant, despite the continuous reduction of water content. However beyond a critical temperature, the glass transition temperature starts to increase linearly with further decrease in water content. Note that there is a turning point in the L-shaped curve during heating process in Fig. 8. Referring to the water ratio in weight percent at this turning point in the TGA heating curve in Fig. 2, the critical temperature can be found to be about 120 °C.

The critical heating temperature (120 °C) discovered in Figs. 2 and 8 has physical significance. Subsequently, the total absorbed water in the SMP can be divided into two parts, namely, free water and bound water [18,19]. Bound water can be removed from the polymer only at a higher heating temperature (over 120 °C in this SMP). The glass transition temperature depends linearly on the amount of the bound water. Further heating to about 180 °C is required for a full removal of water (zero water ratio and glass transition temperature ∼35 °C). The horizontal segment in Fig. 8 indicates that free water has negligible effect on the glass transition temperature and it can be fully removed at about 120 °C.

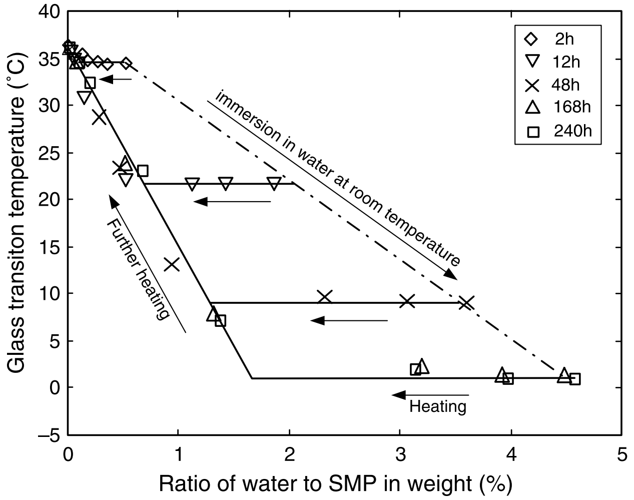

Fig. 8. Glass transition temperature vs. ratio of water to SMP in weight percent.

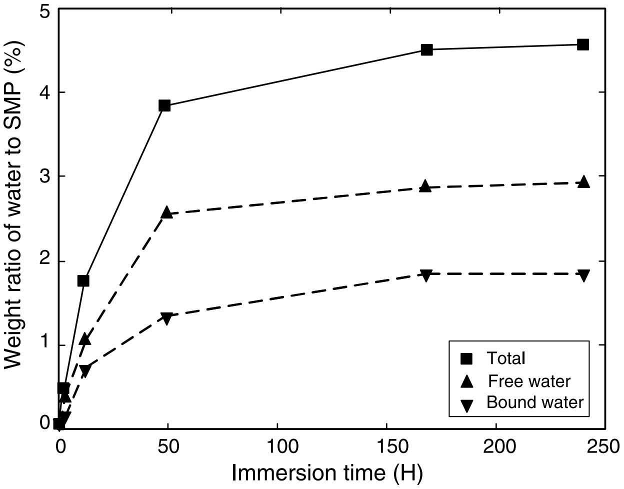

Fig. 9. Ratio of water to SMP in weight vs. immersion time.

Now we can further quantitatively identify the amounts of free and bound water during immersion according to Fig. 8. With the two segments in the slant L-shape curves, the ratios of the free, bound and total absorbed water in the polymer can be worked out as functions of immersion time as presented in Fig. 9. Fig. 9 reveals that water absorption increases dramatically in the first 48 h immersion and more free water is absorbed than bound water at any instant.

FTIR results in Figs. 6 and 7 reveal the role of hydrogen bonding behind the change of the glass transition temperature in the SMP. The shift of infrared bands in the hydrogen-bonded N–H and C=O groups is significant in the first 48 h immersion and then flattens out. The water content in the SMP also increases with the immersion time in a similar manner (cf. Fig. 9). It reveals that water has direct effects on the hydrogen bonding in the polyurethane SMP, which can be explained by the schematic model in Fig. 10 [20]. Some water molecules absorbed in the polyurethane SMP upon immersion in water may bridge the gaps between the hydrogen-bonded N–H and C=O groups (site ‘a’ in Fig. 10). The loosely bound water directly weakens the hydrogen bonding, which is evidenced by the shift of infrared band of the hydrogen-bonded N–H to a higher frequency. Together with the function of water as a plasticizer the glass transition temperature is reduced. On the other hand, some absorbed water molecules can form double hydrogen bonds with two already hydrogen-bonded C=O groups (site ‘b’ in Fig. 10). Due to the hydrogen bonding in site ‘a’ the infrared band of bonded C=O stretching shifts up

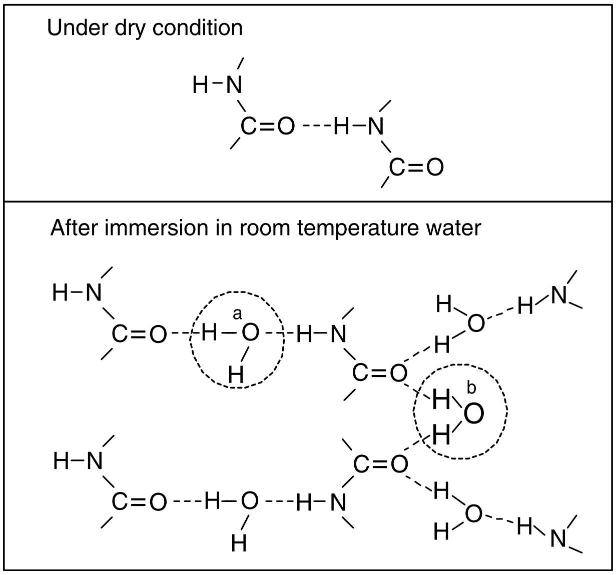

Fig. 10. Effects of water on the hydrogen bonding in polyurethane SMP (modified from [20]).

to a higher frequency while the hydrogen bond in site ‘b’ brings it down to a lower frequency. These two hydrogen bonds may work together and counteract. According to the study of Puffr and Sebenda, water in site ‘b’ is more firmly bounded than that in site ‘a’ [20,21]. Consequently, the infrared band of hydrogen-bonded C=O shifts to lower frequencies (cf. Fig. 6).

Fig. 7 shows that both the N–H and C=O infrared bands change remarkably in the temperature range from 100 to 180 °C, a range that is coincident with the temperature range of significant water loss in Fig. 2. With the evaporation of water, especially the bound water (cf. Fig. 8) upon heating, the interaction between water and polymer vanishes. The hydrogen bonding between N–H and C=O gradually reverts to its original state. On the other hand, water as a plasticizer is removed upon heating. Therefore, SMP finally recovers its original glass transition temperature.

4. Effect of moisture on mechanical properties

This section investigates the effects of moisture on the mechanical properties of the polyurethane SMP. The focus is on the understanding of the mechanical behaviors, which are vital to any attempt to design functionally gradient and/or water actuatable SMPs as demonstrated in Fig. 1.

4.1. Uniaxial tensile test

Uniaxial tensile tests were carried out on polyurethane SMP wires with diameters of 1.0 mm by an Instron 5565 with a 100 N load cell at a constant strain rate of $5\times10^{-3}\ \mathrm{s}^{-1}$. The gauge length was 40.0 mm. A hot chamber with a tolerance of ±0.5 °C was attached to the Instron for temperature control. Two different testing temperatures were chosen, i.e. room temperature (25 °C) and the glass transition temperature +25 °C at which the polyurethane SMP is in the rubber state. In these experiments, the glass transition temperature of an individual sample was determined by the DSC test. Note that we present all results using the engineering stresses and strains in the current study.

Fig. 11(a) plots a series of stress–strain curves of SMP wires tested at room temperature. It shows two types of distinct behaviors. When the immersion time is shorter than 12 h, the SMP behaves like a crystalline material, in which a linear stress–strain relation can be found prior to yielding followed by hardening. When the immersion time exceeds 12 h, the stress–strain curve is similar to those of rubbers. This curve has no apparent yielding point and shows that a large deformation can be achieved at a low level of stressing. The rubber-like behavior becomes more pronounced over a prolonged immersion period due to the increased mobility of polymer chains. On the other hand, if the uniaxial tensile test is carried out at 25 °C above the glass transition temperature, the SMP becomes more rigid after a longer immersion period as shown in Fig. 11(b).

We are also interested in the individual roles of free water and bound water on the stress–strain relation. The uniaxial

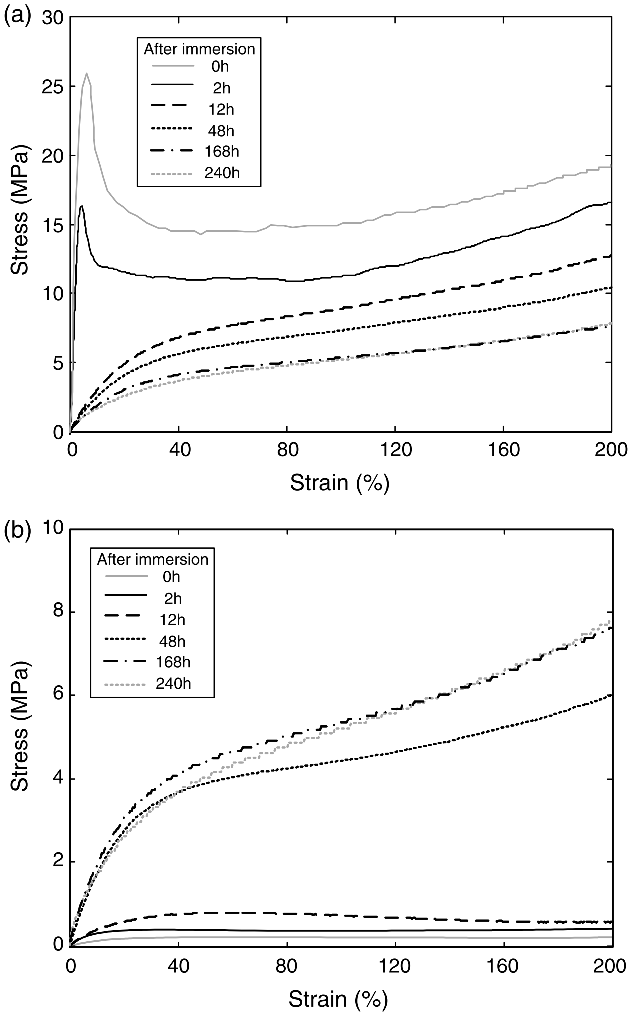

Fig. 11. Stress–strain relation after different hour of immersion. (a) At room temperature, (b) at glass transition temperature +25 °C.

tensile test was conducted after the following processes. The SMP wires were immersed in water for different hours, and then heated in air up to 80 and 120 °C, respectively, at a constant rate of 10 °C/min. Subsequently, wires were cooled down to room temperature in 3 min. No apparent change in the stress–strain behavior was found in the SMP wires pre-heated to 80 °C. The stress–strain curves of SMP wires after heated to 120 °C are presented in Fig. 12. Note that according to Fig. 8, 120 °C is the critical point for a full removal of the free water from the SMP. In Fig. 12(a), a remarkable change can be found in comparison with the results in Fig. 11(a). All samples exhibit a linear stress–strain relation followed by hardening regardless of how long samples are immersed in water. The stiffness of the wires is obviously increased by the removal of the free water. This removal results in a narrower glass transition temperature range and a very slight increase in the glass transformation temperature after heating to 120 °C (cf. Fig. 5). However, in the tensile test conducted at transition temperature +25 °C (Fig. 12(b)), the removal of free water has no other significant influence but that of the wires becoming stiffer after a longer immersion period (>12 h). To sum up, we may conclude that free water only has a very limited effect on the tensile behavior of the SMP, while bound water has a very strong influence.

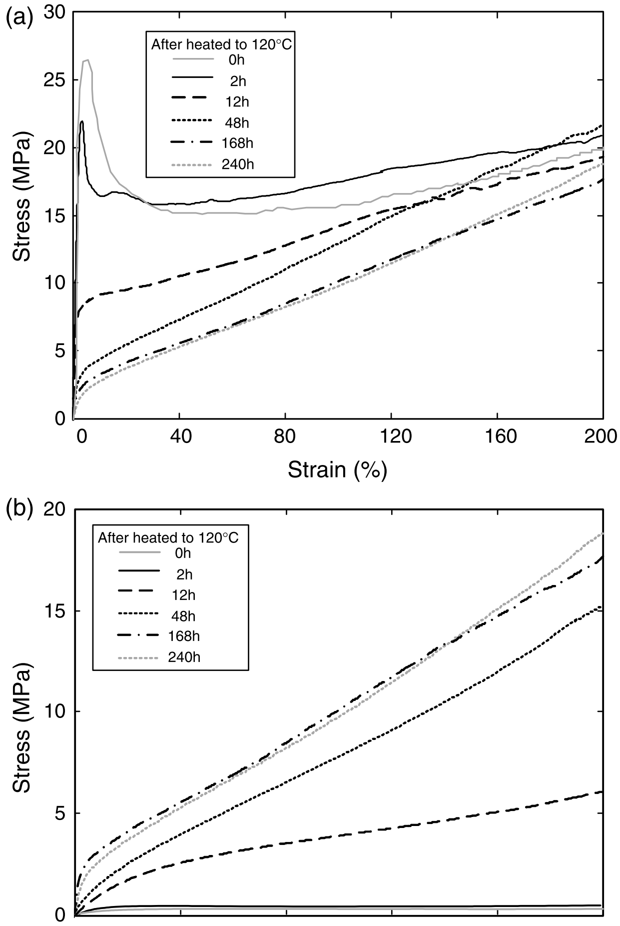

Fig. 12. Stress–strain relation after different hour of immersion and heated to 120 °C. (a) At room temperature, (b) at glass transition temperature +25 °C.

4.2. Recovery

One of the unique features of SMPs is the recovery of the original shape upon heating to the glass transition temperature. Since the glass transition temperature is strongly affected by moisture, we can utilize this feature to create a water-actuable and functionally gradient SMP as shown in Fig. 1 [10]. From a thermomechanical point of view, recovery stress and recoverable strain are essential concerns in such applications. We carried out two types of tests, namely, the constrained and free recovery tests, to measure them.

Polyurethane SMP wires with diameters of 1.0 mm and initial gauge lengths of 40.0 mm were stretched at 50 °C uniaxially by the Instron 5565 with a 100 N load cell to three selected strains, 10, 20 and 50%, respectively. They were then rapidly cooled to room temperature in 3 min with their pre-stretched length fixed. After cooling, an unloading process was followed. Note that a constant strain rate of $5\times10^{-3}\ \mathrm{s}^{-1}$ was applied in both loading and unloading. Fig. 13 shows three typical stress–strain curves in these processes. The unloading process is virtually linear elastic. Less than 1% strain is recovered instantly.

In the next step, the pre-strained wires were divided into four groups for two different types of recovery tests (in room temperature water or in air). The wires from one group were immersed in room temperature water with their lengths fixed. This is the so-called constrained recovery test. The recovery stress was measured. In the second group, wires were immersed in room temperature water but without any constraint, so that they could deform freely (free recovery test). Hence, the recovery strain upon immersing in water can be obtained. The third (constrained recovery) and forth (free recovery) groups were carried out in air for comparison.

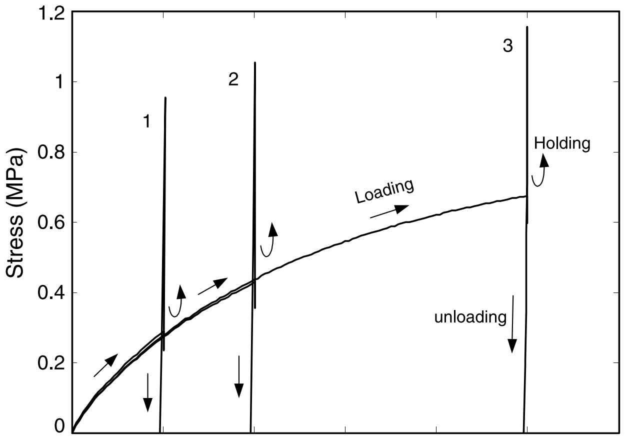

Fig. 13. Stress–strain curves upon loading (at 50 °C) and unloading (at room temperature).

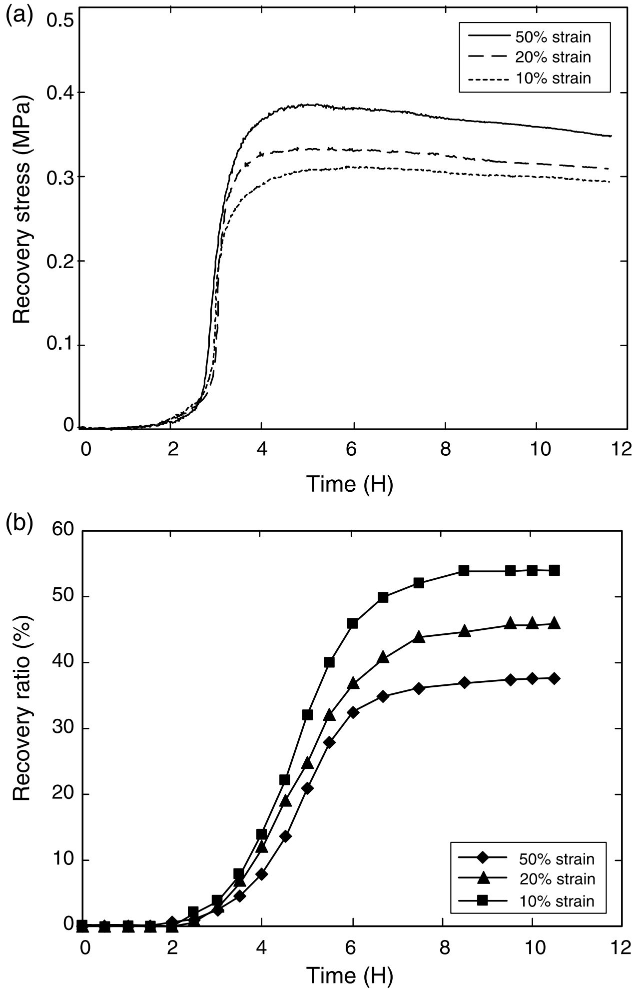

Fig. 14. Recovery in room temperature water. (a) Recovery stress as a function of immersion time, (b) shape recovery ratio as a function of immersion time.

The wires were heated in a hot chamber at a constant rate of 2 °C/min.

Since the pre-loading was carried out at three different strains, namely, 10, 20 and 50%, the recovery ratio, which is defined as the ratio of the measured recovery strain to the pre-strain (10, 20 or 50%), was applied as a measure of the recovery. Fig. 14 presents the evolution of the recovery stress and recovery ratio against the immersion time, and Fig. 15 plots the results of the thermally induced recovery.

Fig. 14(a) reveals that a higher pre-strain results in a higher recovery stress in wires immersed in water. The recovery stress starts to increase dramatically after about 2.5 h of immersion and reaches a maximum in about 4 h. Thereafter, it is reduced but only very slightly. In contrast, the recovery ratio after a 10 h immersion, Fig. 14(b), is lower in the higher pre-strained wires, and significant recovery starts after about 4 h of immersion.

In the thermally induced recovery as shown in Fig. 15(a) and (b), the recovery stress reaches the peak at ∼30 °C and then falls continuously upon further heating, in particular, at temperatures over ∼40 °C. The recovery stress almost vanishes at 60 °C. Similar to that in the water-actuated recovery, a higher pre-strain results in a higher recovery stress. Upon heating to 60 °C, the recovery (without any constraint) is about 100% as shown in Fig. 15(b). In other words, the wires fully regain their original shapes.

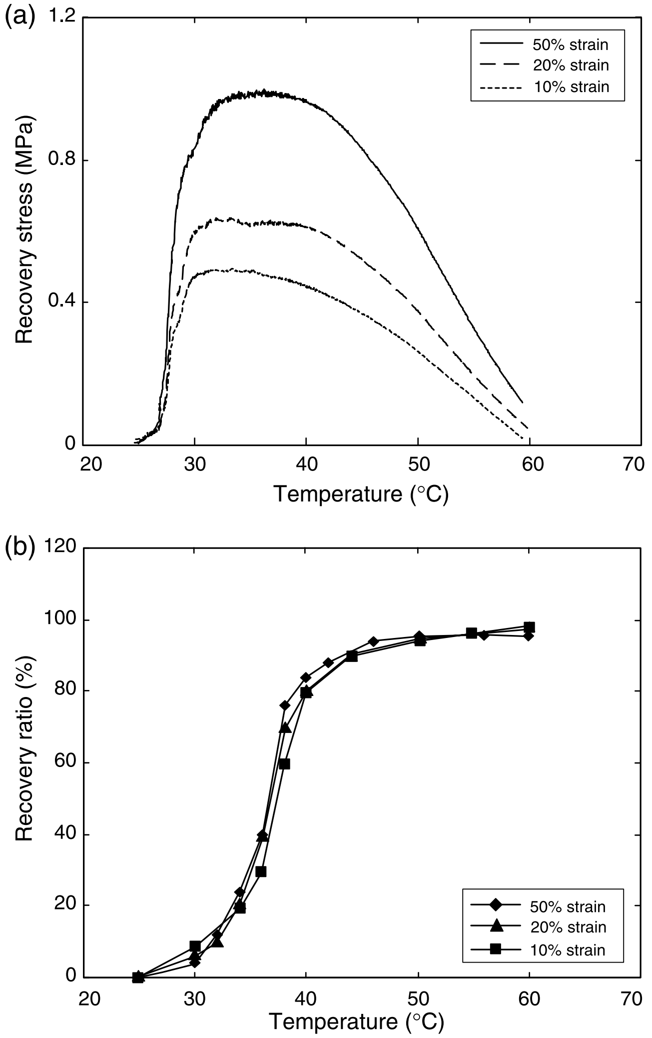

Fig. 15. Recovery upon heating. (a) Recovery stress as a function of temperature, (b) shape recovery ratio as a function of temperature.

As we can see, the SMP can fully recover its original shape or generate a higher maximum recovery stress upon heating. A wider transition temperature range upon immersion in water should be the main reason for the partial recovery or lower maximum recovery stress (Fig. 3).

5. Conclusions

We present a series of experimental studies on the effects of moisture on the glass transition temperature of an ether-based polyurethane SMP and its thermomechanical properties. The main conclusions are:

(1) The glass transition temperature of the SMP decreases with the increase of immersion time in room temperature water. This change is thermally reversible.

(2) Water absorbed in the SMP weakens the hydrogen bonding between N–H and C=O groups, which causes a significant decrease in the glass transition temperature.

(3) Upon heating to 180 °C, the absorbed water can be fully removed and interactions between water and the polymer chains are, therefore, eliminated. Consequently, the glass transition temperature returns to its original value, which is the glass transition temperature of the SMP under dry conditions.

(4) Water absorbed in the SMP can be split into two parts, namely, free water and bound water. Their quantities in the SMP can be determined by the cyclic DSC test. It is found that the free water can be totally removed at around 120 °C through evaporation.

(5) Free water absorbed in the SMP has negligible effects on the glass transition temperature and the uniaxial tensile behavior, while bound water significantly reduces the glass transition temperature in an almost linear manner and has significant influence on the uniaxial tensile behavior.

(6) The polyurethane SMP can partially recover its original shape in room temperature water due to the decrease of its glass transition temperature. A higher pre-strain results in a higher recovery stress (constrained recovery) or less recovery strain (free recovery) upon immersion in water.

References

[1] Lendlein A, Langer R. Science 2002;296:1673–6.
[2] Gall K, Dunn ML, Liu YP, Finch D, Lake M, Munshi NA. Acta Mater 2002;50:5115–26.
[3] Lee BS, Chun BC, Chung YC, Sul KI, Cho JW. Macromolecules 2001;34:6431–7.
[4] Hayashi S, Kondo S, Kapadia P, Ushioda E. Plast Eng 1995;51:29–31.
[5] Wache HM, Tartakowska DJ, Hentrich A, Wagner MH. J Mater Sci, Mater Med 2003;14:109–12.
[6] Yang JH, Chun BC, Chung YC, Cho JH. Polymer 2003;44:3251–8.
[7] Kim BK, Lee SY, Xu M. Polymer 1996;37:5781–93.
[8] Tobushi H, Okumura K, Hayashi S, Ito N. Mech Mater 2001;33:545–54.
[9] Yang B, Huang WM, Li C, Lee CM, Li L. Smart Mater Struct 2004;13:191–5.
[10] Huang WM, Yang B, An L, Li C, Chan SY. Appl Phys Lett 2005;86:114105.
[11] Yen FS, Lin LL, Hong JL. Macromolecules 1999;32:3068–79.
[12] Luo N, Wang DL, Ying SK. Macromolecules 1997;30:4405–9.
[13] Yoon JP, Han CD. Macromolecules 2000;33:2171–83.
[14] Brunette CM, Hsu SL, MacKnight WJ. Macromolecules 1982;15:71–7.
[15] Heintz AM, McKiernan RL, Gido SP, Penelle J, Hsu S, Sasaki S, et al. Macromolecules 2002;35:3117–25.
[16] Teo HS, Chen CY, Kuo JF. Macromolecules 1997;30:1793–9.
[17] Chen TK, Tien YI, Wei KH. Polymer 2000;41:1345–53.
[18] Herrera-Gómez A, Velázquez-Cruz G, Martín-Polo MO. J Appl Phys 2001;89:5431–7.
[19] Moro García R, Alvarez Bartolomé ML, Espina Alvarez A. Thermochim Acta 1993;215:281–9.
[20] Lim LT, Britt IJ, Tung MA. J Appl Polym Sci 1999;71:197–206.
[21] Puffr R, Sebenda J. J Polym Sci C 1967;16:79–93.