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Molecular engineering and properties of chitin based shape memory polyurethanes

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ABSTRACT

Shape memory polyurethanes (SMPUs) are playing a prominent role in biomedical, self repairing, aerospace and smart materials. Shape memory polyurethanes (SMPUs) were prepared from polycaprolactone diol 4000 (PCL4000), 1-4-butanediol (BDO), chitin, dimethylol propionic acid (DMPA), triethylamine (TEA), and 4, 4′-diphenylmethane diisocyanate (MDI). Trifunctional characteristics of chitin enhanced the thermal and mechanical properties of SMPUs. DMPA was used to obtain higher recovery and lower residual strain. The morphology, microstructure, mechanical, thermo-mechanical, and shape memory properties of synthesized SMPUs were investigated using Fourier transform infrared (FT-IR), differential scanning calorimetry (DSC), dynamic mechanical thermal analyzer (DMTA) and tensile testing techniques. The results showed that crosslinked SMPUs have better thermal and thermo-mechanical properties, and a good shape memory effect.

1. Introduction

Segmented polyurethanes, consisting of hard and soft segments are known to have microphase separated structure, which brings it to be used in various ways such as adhesives, coatings, biomedical materials and elastomers (Barikani & Hepburn, 1986; Barikani & Hepburn, 1987). Polyurethanes have potential array of commercial applications as they can be molded, injected, extruded and recycled (Zia, Bhatti, & Bhatti, 2007). Attempts have also been made to synthesize biodegradable PU through chemical modification of final PU structure via e.g. the incorporation of starch (Barikani & Mohammadi, 2007; Swamy & Siddaramaiah, 2003), chitosan (Silva, Menezes, & Garcia, 2003; Yang, Yang, Lin, Wu, & Chen, 2007; Yu et al., 2006).

Shape memory refers to the ability of materials to remember the shape on demand even after rather severe deformation. During the past few decades shape memory polymers are gaining more and more attention because of their low cost, low density, high shape recoverability and easy processability (Hayashi, Kondo, Kapadia, & Ushioda, 1995; Liang, Rogers, & Malafeew, 1997; Nakyama & Kanetsuna, 1977). Shape memory polymers (SMP) are polymer networks equipped with suitable molecular switches, which are sensitive to an external stimulus. Polymer networks consist of chain segments and net points. The net points crosslink the chain segments and determine the permanent shape of the polymer. The crosslinks can be either of a chemical nature (covalent bonds) or of a physical nature (intermolecular interactions). Among various SMPs, shape memory polyurethanes (SMPUs) are receiving much attention for their easy control of glass transition temperature (T_g) around the room temperature and excellent shape memory effect even at the room temperature. Shape memory polyurethane (SMPU), a novel class of functional materials, has been extensively researched since its discovery by Mitsubishi in 1988 and attracting a great deal of attention recently, due to their unique properties such as the wide range of shape recovery temperatures (from −30 to 70 °C), high shape recoverability, good process ability and excellent biocompatibility (Chen & Lin, 1998a; Chen & Lin, 1998b; Hu, Yang, Yeung, Ji, & Liu, 2005; Lee, Chun, Chung, Sul, & Cho, 2001; Lide, 1996; Ota, 1997). Magnetite-polyurethane (PU) shape memory polymer (SMP) composites containing 10–40 vol.% magnetite have also been reported and their mechanical properties in a temperature range from 255 to 355 K have been investigated (Razzaq, Anhalt, Frormann, & Weidenfeller, 2007). As compared with shape memory alloys, the main advantages of shape memory polyurethanes (SMPUs) are their low cost and light weight. These SMPUs basically consist of two phases, the frozen phase and the reversible phase. Hard segments in polyurethanes can be formed via hydrogen bonding and crystallization, acting as frozen phase below the melting temperature. The reversible phase, transformation of the soft segment, is responsible for the shape memory effect (Lee et al., 2001). This shape memory effect can be controlled via the molar ratio of the hard and soft segments, the molecular weight of the soft segment, and the polymerization process. A series of SMPUs from polycaprolactone diol, 1,4-butanediol (BDO), dimethylol propionic acid (DMPA),

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and 4,4-diphenylmethane diisocyanate (MDI) or toluene diisocyanante (TDI) were introduced (Han, Boung, & Byung, 2001; Hu et al., 2005; Jeong, Lee, Lee, & Kim, 2000; Kim et al., 1998; Kim, Lee, & Xu, 1996; Li, Chen, Zhu, Zhang, & Xu, 1998; Li et al., 1996a,b). The effect of their structures, including the ionization of SMPUs, and their thermo-mechanical and shape memory properties have been extensively investigated and well documented in the literature (Yang, Huang, Li, Lee, & Li, 2004). Up to the present, most SMPUs are prepared from linear polyurethane, which have physically crosslinked segments. However, these linear SMPUs cannot endure repeated changes in shape memory, and the retention and recovery of shape memory will decrease after several cycles of shape memory recovery; some studies have even found that the shape retention and shape recovery of SMPUs decrease dramatically after first cycle (Kim et al., 1998). In order to fulfill the various needs regarding the physical properties and enhancement of the shape memory function, in this paper, we have synthesized and characterized chitin based polyurethane with pronounced shape memory effect and thermo-mechanical properties by introducing one series of shape memory polyurethane, some of which were crosslinked using chitin. Due to very limited number of papers concerning the study of crosslinked shape memory polyurethane, we in this manuscript have introduced chitin based shape memory polyurethane (SMPU) with on going investigation into their shape memory effect and thermo-mechanical properties. The molecular characterization and thermal properties of the synthesized SMPU were analyzed by FTIR, DSC, and DMTA studies. After characterization the intended outcome of the samples shape memory effect was investigated and discussed.

2. Experimental

2.1. Materials

4,4′-Diphenylmethane diisocyanate (MDI), dimethylol propionic acid (DMPA) and 1,4-butane diol (BDO) were purchased from Sigma–Aldrich Chemical Co. Polycaprolactone polyol, CAPA 240, (molecular weight 4000 from Solvay Chemicals) and BDO were dried at 70 °C under vacuum for 24 h before use to ensure the removal of all air bubbles and water vapors that may otherwise interfere with the isocyanate reactions. Molecular weight of CAPA 240 was confirmed by applying the procedure reported in ASTM D-4274C. MDI and all other materials were used as received. Dimethylformamide (DMF) and triethylamine were used after being dehydrated with a 4 Å molecular sieve for 2 days. Chitin ($M_v = 6.067 \times 10^5$) was kindly supplied by Iran Polymer and Petrochemical Institute, Iran. Chitin was purified according to already established methods in literature (Muzzarelli, 1997; Wang, Qin, & Bo, 1991). Its molecular weight was deduced from the intrinsic viscosity, as described in the literature (Chen, Sun, Fan, & Zhang, 2002). All the reagents used in this work were of analytical grade.

2.2. Synthesis of shape memory polyurethane (SMPU6)

Into a four-necked reaction kettle equipped with mechanical stirrer, heating oil bath, reflux condenser, dropping funnel and N_2 inlet and outlet was placed PCL 4000 (3 mmol) and the temperature of the oil bath was increased to 60 °C. Then MDI (5 mmol) and 80 ml DMF were charged to the dried flask and reacted for about 2 h at 80–85 °C; then, DMPA (2 mmol) and MDI (2 mmol) were successively added, and lasted the reaction at the same temperature. Two hours later, BDO (5 mmol) and MDI (6 mmol) were added for another 2 h. Then chitin (3 mmol) was added for another 1 h. At last, the neutralization reaction was carried out at 50 °C for 0.5 h, with the addition of TEA (2.2 mmol). The solid content of the product is about 15–20%. The formulation of the prepared SMPU samples is listed in Table 1. The liquid polymer was casted into a Teflon plate to form a uniform sheet. The synthesized polymer was then placed in a hot air circulating oven at 100 °C and cured for 24 h. The cured sample sheets were then stored for one week at ambient temperature (25 °C) and 40% relative humidity before testing.

Films for the measurement of tensile properties were prepared by casting the SMPU solution in DMF in a mould. After evaporation of DMF at 80 °C for 24 h, the films were further dried at 60 °C under a vacuum for another 48 h. Tensile tests were conducted using a tensile tester, attaching a constant-temperature heating chamber. The micro tensile test specimens had dimensions of 40 × 5 × 0.5 mm. The general structure of the chitin based SMPU is shown in Fig. 1.

2.3. Characterization

Infrared measurements were performed on a Bruker-IFS 48 Fourier Transform Infrared (FT-IR) Spectrometer (Ettlingen, Germany). Differential scanning calorimetry (DSC) was recorded on a Stanton Redcraft STA-780 (London, UK). The dynamic mechanical measurements (DMTA) were performed on a UK Polymer Lab Dynamic Mechanical Thermal Analyzer (Model MK-II) over a temperature range of −150 to 200 °C, using a bending mode at heating rate of 10 °C/min and frequency of 1 Hz. The dimensions of samples were 30 × 10 × 1 mm. The values of the storage modulus versus temperature were recorded for each sample.

2.4. Analysis of shape memory effect

Thermo-mechanical cycle tests were performed to investigate the shape memory effect of the final polyurethane material. Shape retention (%) and shape recovery (%) were calculated following the relationship developed earlier (Kim et al., 1998; Kim et al., 1996):

$$\text{Shape retention } (\%) = \varepsilon_u \times \frac{100}{\varepsilon_m} \tag{1}$$

$$\text{Shape recovery } (\%) = (\varepsilon_m - \varepsilon_p) \times \frac{100}{\varepsilon_m} \tag{2}$$

Table 1
Sample code designation and formulation of shape memory polyurethane

S. code	[b]MDI (mol)	[c]PCL4000 (mol)	[d]BDO (mol)	[e]DMPA (mol)	Chitin (mol)
[a]SMPU1	10	6	4	–	–
SMPU2	10	4	2	4	–
SMPU3	10	3	5	2	–
SMPU4	11	3	5	2	1
SMPU5	12	3	5	2	2
SMPU6	13	3	5	2	3

[a] SMPU1 = shape memory polyurethane.
[b] MDI = 4,4′-diphenylmethane diisocyanate.
[c] PCL4000 = polycaprolactone polyol, CAPA 240.
[d] BDO = 1,4-butane diol.
[e] DMPA = dimethylol propionic acid.

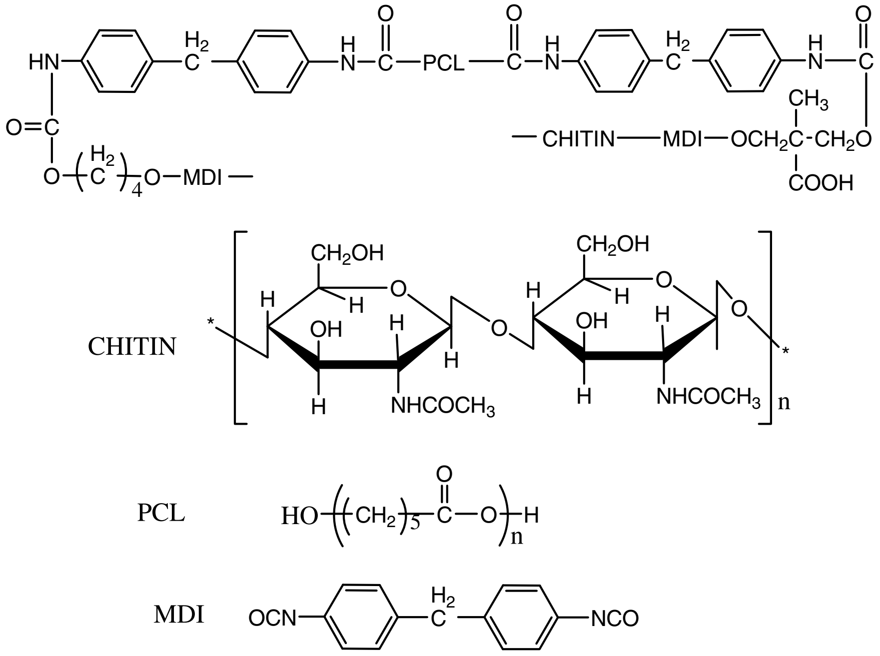

Fig. 1. General structure of the chitin based shape memory polyurethanes.

Where ε_m is the maximum strain, ε_u is the retention strain and ε_p is the recovery strain

3. Results and discussion

For this investigation, SMPU was prepared from PCL4000, MDI, BDO, DMPA, TEA and chitin. PCL4000 acts as the soft segment and others act as the hard segment. DMPA was used for preparing the SMPU, since DMPA can give higher recovery strain and lower residual strain (Kim et al., 1998). At the same time chitin was used as crosslinking agent for enhancing the thermal and mechanical properties of SMPU.

3.1. FT-IR analysis

FTIR spectra of original chitin and polyurethane extended with 100% BDO (SMPU1) and having different contents of chitin in their formulation (SMPU4, SMPU5 and SMPU6) are shown in Fig. 2a–e. FT-IR spectra of original chitin (Fig. 2a) and PU extended with 100% BDO (SMPU1) have already been explained in our previous study (Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008). FTIR spectra of SMPU6 (Fig. 2e) showed an absorption peak of NH stretching vibration at 3339 cm^{-1}. The CH symmetric and asymmetric stretching vibrations of CH2 groups were observed at 2935, and 2865 cm^{-1}, respectively. The other peaks were assigned as: 1726, 1645 cm^{-1} (C=O bond); 1597, 1534 cm^{-1} (NH deformations); 1460 cm^{-1} (CH_2 bending vibration); 1412 cm^{-1} (CH bending vibration); 1306 cm^{-1} (CH_2 wagging). By extending prepolymer with different proportions of chitin/BDO, the FT-IR spectra showed a very strong, new peaks at about 1728 cm^{-1} which were assigned to C=O stretching of soft segment of PCL. Another new peak was also observed at about 1460 cm^{-1} which was assignable to urethane —NH group. It was observed that the intensity of hydrogen-bonded-NH increased as the chitin content increased, suggesting that the hydrogen bonds of chitin were broken and new hydrogen bonds between chitin and NCO terminated prepolymer were formed. Moreover, with increasing chitin content, the peak of urethane carbonyl groups at around 1728 cm^{-1} decreased and shifted to lower wave number while the band around (1642–1649 cm^{-1}) for hydrogen-bonded carbonyl of chitin increased and shifted to higher wave number. This implies that stronger inter chain interactions arises between chitin and NCO terminated prepolymer in chitin based PU in comparison with BDO based PU. The

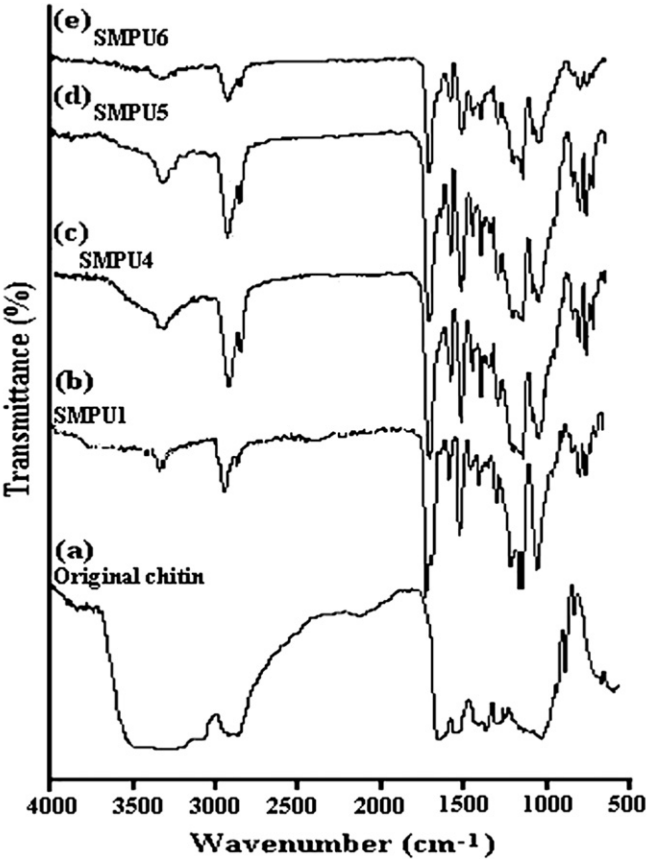

Fig. 2. FTIR spectra of (a) original chitin; (b) PU extended with 100% BDO; (c, d and e) PU having 1, 2 and 3 mol. of chitin in their formulation, respectively.

FT-IR spectrum of the SMPUs showed the growth in the transmittance peaks of the crosslinked SMPUs at 1720–1730 and 1596 cm^{-1}. Usually, the hydrogen bonding among hard segments plus dipole–dipole interaction between carbonyl groups will primarily affect C=O stretching vibration. The carbonyl stretch peak at 1720–1730 cm^{-1} suggests that more extensive interactions are made not only with the increase of hard segment content but also with the increase in crosslinking, moreover, the later is also responsible for the increase of the hydrogen bonds in this series. Based on these results of FT-IR spectrum, it was thought that chitin had already effectively crosslinked with polyurethane, which greatly affected on the properties of the SMPU.

3.2. Thermal analysis

The DSC data of all the samples are listed in Table 2. The results of the DSC showed that the soft segment content has a positive effect on the thermal properties: the higher the soft segment content, the higher should be the melting temperature and melting enthalpy, which suggests that more ordered polymer packaging can be obtained with a higher percentage of soft segment. From these samples, it was found that SMPU2 has an abnormally higher melting temperature and melting enthalpy, which suggests that DMPA has an effect on the thermal property, since the microphase separation increases with the DMPA in SMPUs (Kim et al., 1998). The sample with a high content of chitin implied that its crosslinked density was high in molecular structure. If we compare the thermal properties of SMPU1, SMPU4, SMPU5, and SMPU6 it can be found that chitin also affects the thermal property of SMPUs. The increase in chitin contents results to decrease in the melting temperature of the soft segment and the melting enthalpy, which is probably because crosslinking increases the miscibility of the soft segment and the hard segment as the crystallization of the soft segment decreases: the more chitin is used, the less crystallization enthalpy is needed.

Fig. 3 shows the storage modulus of prepared SMPUs. A gradual decrease in *E* in the temperature range between the glass transition temperature of the soft segment and the melting temperature of the soft segment, and a sudden drop in *E* at T_m can be observed. Generally, the crosslinked SMPUs have a higher storage modulus even above the T_m region. The thermal properties of SMPU1, SMPU4, SMPU5, and SMPU6, clearly show that a higher storage modulus can be obtained with an increase in crosslinking, when they are above T_m and under these conditions; SMPU6 has the highest storage modulus. This is due to the higher thermal stability of chitin polymeric structure in comparison to BDO molecular structure because the molecular chain of chitin is composed of *N*-acetyl-D-glucosamine monomers (Fig. 1) (Moussian, Schwarz, Bartoszewski, & Nusslein-Volhard, 2005). The linked glucosamine rings on chitin had better miscibility with linked double rings in the hard segment of PU and can establish the formation of H-bonds between soft segment and NH group in the hard segment. Therefore shift of thermogravimetric values for SMPU6 is more obvious than that of SMPU1. This behaviour may also imply that chitin; a crystalline polymer of *N*-acetyl-D-glucosamine monomers do not melt but degrade at elevated temperature (Chen, Sun, & Zhang, 2004) and can play a role in enhancement of thermal properties. Moreover, Lundberg and Cox (1969) established the fact that polyurethane with high cross-linking density has good thermal stability.

Table 2
DSC data of SMPU samples

S. code	[a]ΔH_m (J_g^{-1})	[b]T_m (°C)	Soft segment (%)
SMPU1	59.3	53.5	89.35
SMPU2	63.2	54.7	83.26
SMPU3	47.7	49.6	78.85
SMPU4	41.3	46.9	76.57
SMPU5	34.9	43.6	74.42
SMPU6	25.5	40.2	72.39

[a] ΔH_m (J_g^{-1}) = melting enthalpy.
[b] T_m = melting temperature.

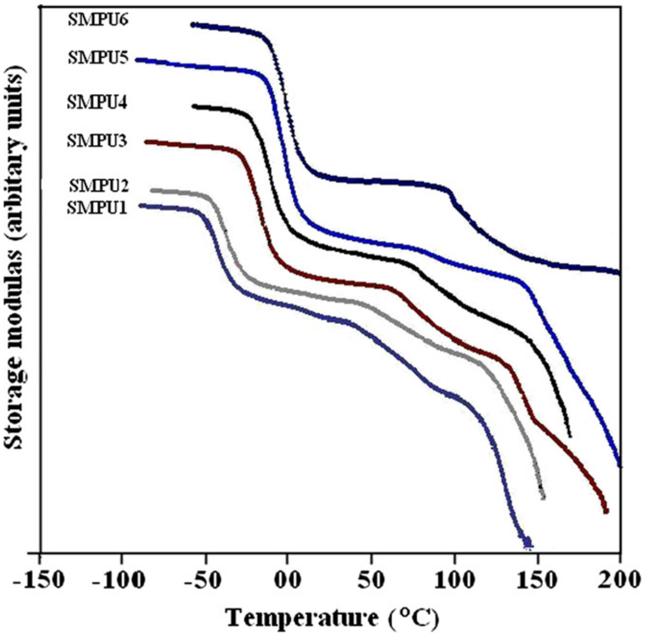

Fig. 3. Storage modulus vs. temperature curves of PU samples.

3.3. Mechanical analysis

The data on the tensile analysis of SMPUs with various soft segment contents or crosslinking are listed in Table 3. The elongation at break (%) in different temperatures first decreases with a significant decrease in the soft segment, then increase with the crosslinking (Table 3). At room temperature, the elongation of each of samples SMPU1, SMPU2, and SMPU6 is more than 665%, while above T_m only SMPU6 showed an elongation of 532%, 400% and 250% at T_m + 5 °C, T_m + 10 °C, T_m + 15 °C, respectively, which means that only SMPU6 can meet the fundamental demand of the shape memory effect under these conditions. In Table 3, the maximum stress also showed a similar trend compared with the strain at room temperature. For example, both SMPU1 (39.90 MPa) and SMPU6 (53.20 MPa) showed a higher maximum stress, while above T_m, the maximum stress of the sample increases with both a decrease in the soft segment and an increase of the crosslinking. SMPU1 showed poor maximum stress; in contrast, SMPU6 has a maximum stress among these products. The following two reasons may be explain the results: first, with the increase in the hard segment content, SMPUs can endure higher level of stress of above T_m with more physical crosslinking points; second, as chemical crosslinking increases, the mechanical properties of the hard segment also increases, especially when they are in a rubbery state. Comparing samples of SMPU3, SMPU4, SMPU5, and SMPU6, which have similar components but which differ in their degree of crosslinking, it can be found SMPU6 has a best mechanical property, while SMPU3 also has the better mechanical properties than SMPU4 and SMPU5. From these results, it was suggested that the degree of crosslinking is also very important to the mechanical properties of SMPUs and that only suitable crosslinking in SMPUs can lead to better mechanical properties. This result is also in accordance with the thermal properties mentioned above.

Table 3
Tensile properties data of the shape memory polyurethane samples

S. code	$^{a}T_m + 15$ °C		$T_m + 10$ °C		$T_m + 5$ °C		Room temperature	
	$^{b}\sigma_m$ (MPa)	$^{c}\varepsilon_m$ (%)	σ_m (MPa)	ε_m (%)	σ_m (MPa)	ε_m (%)	σ_m (MPa)	ε_m (%)
SMPU1	0.58	133	0.65	135	0.70	138	39.90	665
SMPU2	0.81	107	0.93	113	1.05	120	31.92	798
SMPU3	3.50	53	3.97	41	4.43	41	23.94	106
SMPU4	0.65	33	0.69	42	0.74	53	27.93	33
SMPU5	1.40	106	1.75	82	2.09	67	29.26	133
SMPU6	6.29	279	9.01	400	12.23	532	53.20	788

[a] T_m = melting temperature.
[b] σ_m = maximum stress in MPa.
[c] ε_m = maximum strain in %.

Table 4
Cyclic tensile behavior of SMPU6

Cyclic tensile behavior at maximum strain (ε_m) of	Retention strain (ε_u)	Recovery strain (ε_p)	Shape retention (%)	Shape recovery (%)
100%	89	13	89	87
200%	182	22	91	89

Then, based on the thermal and mechanical properties, it was thought good SMPUs should have a higher storage modulus when they are above T_m in order to allow these samples to have enough elasticity to recover to their original shape when they are heated to T_m. Combining the above results including the thermal and mechanical, we can conclude that crosslinking decreases the crystallization of the soft segment and increases the chemical crosslinking point of the hard segment, which greatly affects the mechanical properties, especially when these SMPUs are above T_m.

3.4. Shape memory effect

Based on the above results of these SMPUs, only SMPU6 has suitable mechanical properties both at room temperature and above T_m. Because of this, SMPU6 was chosen to undergo to a further analysis of the shape memory effect. The results of the cyclic tensile tests to characterize the shape memory effect of SMPU6 are shown in Table 4. Thermo-mechanical cycle (Fig. 4) tests were performed to investigate the shape memory effect of the final polyurethane material. The sample was first elongated at 55 °C ($T_h = T_m + 15$ °C) to 100% or 200% (ε_m) at a constant elongation rate of 10 mm min^{-1}. While maintaining the strain at ε_m, the sample was cooled to 25 °C ($T_1 = T_m + 15$ °C) and unloaded. Upon removing the constraint at 25 °C, a small recovery of the strain to ε_u occurred. The sample was subsequently heated to 55 °C in 10 min, and kept at that temperature for the next 10 min, allowing the strain to recover. This completes one thermo-mechanical cycle ($N = 1$), leaving a strain ε_p, where the next cycle ($N = 2$) starts. It has been found that SMPU6 gives a higher shape recovery and higher shape retention as compared with that reported in literature (Kim et al., 1998). Even after several cycles, SMPU6 still has a shape recovery of around 87% and shape retention of around 89%, while in literature, only about a 75% shape recovery can be obtained (Kim et al., 1998). Comparing cyclic tensile behavior of SMPU6 at strain of 100% and 200%, some difference can be observed. At 100% strain, SMPU6 has a shape recovery of around 87% and shape retention of around 89%; while at 200%, SMPU6 has a shape recovery of around 89% and shape retention of around 91%. The reason may be explained as follows: because there are chemical crosslinking bonds in SMPU6, a suitable elongation is beneficial to its recovery.

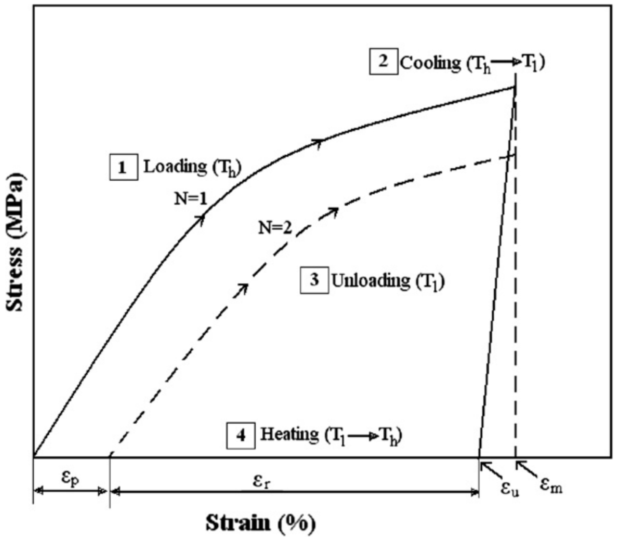

Fig. 4. Schematic representation of the thermo-mechanical cycle: (1) stretching to ε_m at T_h; (2) cooling to T_l while ε_m is kept constant; (3) keeping 5 min at T_l; then the load was taken off; (4) heating up to T_h; then start of the second cycle.

4. Conclusions

In this paper, one series of chitin based shape memory polyurethanes was first prepared and their thermo-mechanical, mechanical and thermal properties were characterized. The shape memory property of sample SMPU6 was also investigated and discussed. The FT-IR result showed that crosslinking could effectively occur in chitin based SMPUs. The analysis of thermal properties showed that the content of the soft segment, chitin and DMPA affect the melting temperature and melting enthalpy of the soft segment. In addition, it showed that the crosslinking decreases the crystallization of the soft segment, which leads to a decrease in the melting temperature and melting enthalpy of the soft segment. As chemical crosslinking bonds existed in the hard segment, the crosslinked SMPUs has better mechanical properties, especially above the T_m of soft segment, while the content of the crosslinking also has a very significant effect on these properties. The analysis of the shape memory effect shows that SMPU6 has a good shape memory effect and that a suitable elongation is important to improve cyclic shape memory retention and shape memory recovery.

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