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Synthesis and Properties of Reversible Disulfide Bond-based Self-healing Polyurethane with Triple Shape Memory Properties

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Abstract A reversible disulfide bond-based self-healing polyurethane with triple shape memory properties was prepared by chain extending of random copolymer poly(lactide-co-caprolactone) (PCLA), hexamethylene diisocyanate (HDI), polytetrahydrofuran (PTMEG), and 4,4'-aminophenyl disulfide. The chemical structures were characterized using ¹H nuclear magnetic resonance (¹H-NMR) spectroscopy, Fourier transform infrared spectroscopy (FTIR), and gel permeation chromatography (GPC). The thermal properties, self-healing properties, triple-shape memory effect, and quantitative shape memory response were evaluated by differential scanning calorimetry (DSC), tensile tests, two-step programming process thermal mechanical experiments, and subsequent progressive thermal recovery. The self-healing mechanism and procedures were investigated using polarizing optical microscopy (POM) and an optical profiler. It was concluded that self-healing properties (up to 60%) and triple-shape memory properties around 35 and 50 °C (with shape fixation ratios of 94.3% and 98.3%, shape recovery ratios of 76.6% and 85.1%, respectively) were integrated to the shape memory polyurethane. As-prepared polyurethane is expected to have potential applications in multi-shape coatings, films, and step-by-step deploying structures.

Keywords Self-healing; Reversible disulfide bond; Triple shape memory; Polyurethane

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INTRODUCTION

The self-healing material is one of the smart materials that can automatically restore some or all of its functions after suffering external mechanical damage under stimuli such as heat^[1–3] and irradiation.^[4] Over the last decades, several kinds of self-healing materials, such as concretes,^[5] metals,^[6] ceramics,^[7] and polymeric materials,^[1–4,8] have been reported. Among them, self-healing polymeric materials have attracted the greatest research interests due to their promising applications in biomedical fields,^[9] aeronautic areas,^[10] adhesives,^[11] electronics,^[12] and so on.

According to the healing mechanism, self-healing polymers can be classified into extrinsic self-healing polymers and intrinsic self-healing polymers. For the extrinsic self-healing polymers, the encapsulated healants in microcapsules, microvascular networks, and microballons can be released and polymerized upon crack intrusion to heal the microcracks.^[8] The intrinsic self-healing polymers utilize reversible covalent bonds or non-covalent interactions, such as dynamic transesterification,^[13] reversible Diels-Alder (D-A) bonds,^[1] dynamic disulfide bonds,^[3,14] or hydrogen bonds,^[15,16] for microcrack mending. Thereinto, disulfide

exchange can be activated at a moderate temperature with a reasonable level of bond strength.^[3,14] The healing of polymers containing disulfide bonds is achieved by cleavage and re-bonding of the disulfide bonds.^[14] Self-healing poly(urea-urethane) elastomers based on aromatic disulfide metathesis with high healing efficiency were reported by Rekondo *et al.*^[17] A reversible shape-memory adhesive with two-level reversible adhesion containing dynamic disulfide bonds was developed by Michal *et al.*^[11] Polyurethanes (PUs) possess tunable physical and chemical properties due to the possibility of modifying their structures by controlling the ratio or composition of their hard segments and soft segments and have attracted great attention in science and industry areas. A variety of self-healing polyurethanes based on disulfide bonds have been reported. The healing efficiency of poly(ethylene glycol) (PEG) polyurethanes based on disulfide bonds at a moderate healing temperature was over 90% with excellent healing repeatability.^[14] Ling *et al.* reported a self-healing poly(tetramethylene glycol) (PTMEG) polyurethane based on disulfide bonds with excellent mechanical properties. The healing efficiency, breaking strength, and elongation at break were as much as 90%, 31.91 MPa, and 1156%, respectively.^[18] Transparent self-healing elastomers with remarkable mechanical properties, transparency, and superior toughness were also reported.^[12,19] Shape memory-assisted self-healing polycaprolactone-based polyurethane was investigated by Chen *et al.* A maximal

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healing efficiency of about 97% could be achieved.^[20] Zhang *et al.* investigated how the location of dynamic covalent bonds could affect the triggering temperature of self-healing procedure. The dynamic and mechanical properties of the materials could be controlled by tailoring the nature of the hard phase.^[21]

Poly(lactide-*co*-caprolactone) (PCLA) is a random copolymer from lactide (LA) and ϵ -caprolactone (CL) with a broad transition temperature which could be tuned by controlling the molar ratio of LA to CL.^[22] PCLA-based polyurethane exhibited shape memory properties with high shape fixity ratios above 98% and shape recovery ratios above 82%.^[22] The shape memory behavior of the polymers was expected to help the closure of cracks and assist the self-healing of polymers.^[23] The main purpose of this work was to integrate the shape memory properties and the dynamic exchangeable properties of disulfide bonds into the PCLA-based polyurethane. PTMEG was incorporated to endow the polyurethane with triple shape memory properties. The structures, shape memory properties, self-healing properties, and mechanism of the synthesized system were investigated. As-prepared self-healing polyurethane exhibited good self-healing properties and triple shape memory properties. The combination of triple shape memory with self-healing properties could meet the increasing requirements in multi-shape coatings, films, and step-by-step deploying structures.

EXPERIMENTAL

Materials

D,L-lactide (D,L-LA) was purchased from Jinan Daigang Biological Engineering Co., Ltd. and used after solution-recrystallization purification. ϵ -Caprolactone (CL, 99%) was supplied by Acros Organics and used as received. Stannous(II) octoate ($\text{Sn}(\text{Oct})_2$, 95%), butanediol (BDO, AR), and hexamethylene diisocyanate (HDI, 99%) were purchased from Aladdin Reagents (Shanghai) Co., Ltd. and used as received. 4,4'-Aminophenyl disulfide (98%) was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. and used as received. Dichloromethane (AR) and *n*-hexane (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. Poly(tetramethylene glycol) (PTMEG, number-average molecular weight (M_n) $\approx$ 2000 g·mol⁻¹) purchased from Aladdin Reagents (Shanghai) Co., Ltd. was used after 6 h of drying under vacuum at 80 °C. *N,N*-dimethylformamide (DMF, 99.5%) purchased from Sinopharm Chemical Reagent Co., Ltd. was dried with anhydrous sodium sulfate for 24 h and filtrated for further use.

Synthesis of Self-healing Polyurethane

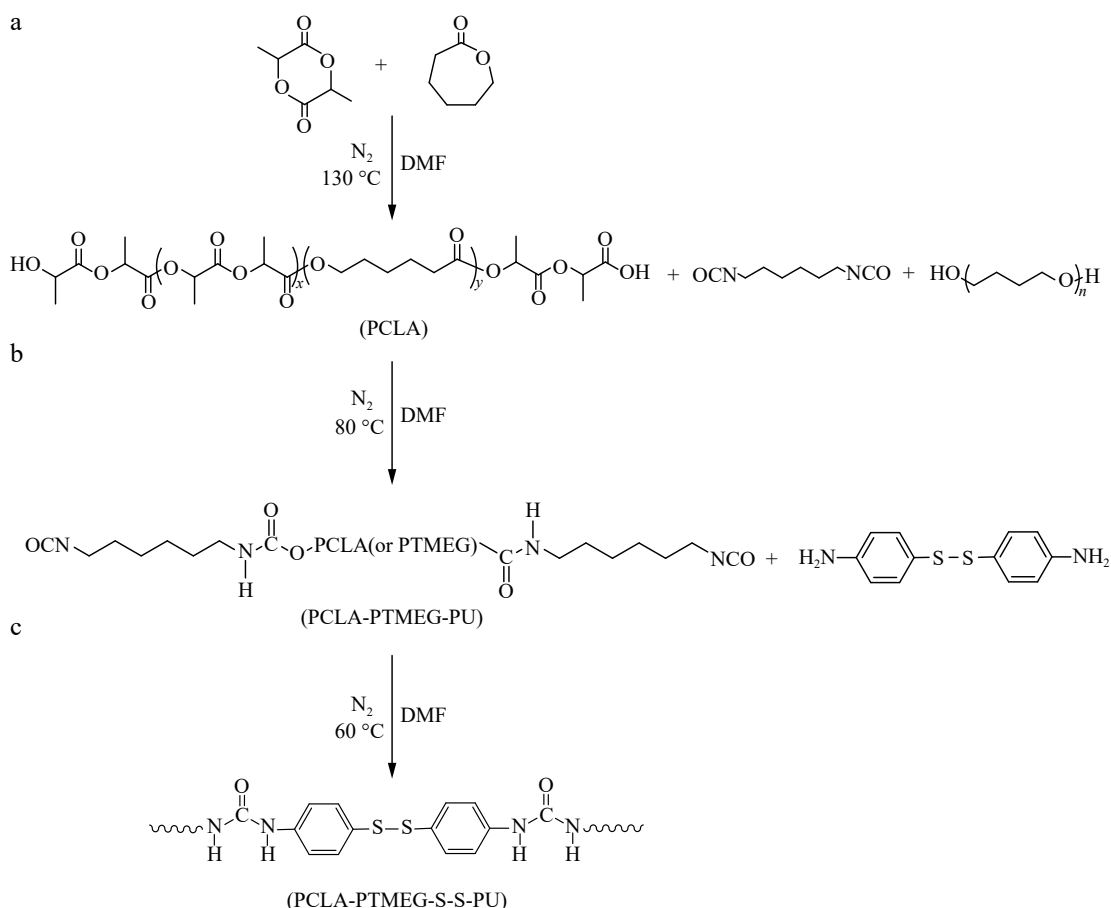
Random copolymer PCLA was synthesized *via* ring-opening polymerization (ROP) with D,L-LA and ϵ -CL, catalyzed by $\text{Sn}(\text{Oct})_2$ as shown in Scheme 1(a). D,L-lactide (18.335 g, 0.127 mol), ϵ -caprolactone (1.615 g, 0.014 mol), BDO (31.5 μL , 0.355 mmol), and 142 μL of $\text{Sn}(\text{Oct})_2$ solution in toluene (0.001 mol·mL⁻¹) were added into a round-bottom flask. The air in the flask was exchanged with N_2 . The mixture was heated to 130 °C and kept isothermal for 48 h under N_2 protection. The obtained crude product was dissolved in a

small amount of dichloromethane and precipitated in an excessive amount of cold hexane. The precipitates (PCLA) were vacuum-dried under 40 °C for 48 h and reserved for further use. PCLA (3.8 g, 0.082 mmol) was dissolved in 8.75 mL of DMF in a 50 mL glass flask and heated to 80 °C for 30 min. HDI (0.2 g, 1.187 mmol) and 50 μL of $\text{Sn}(\text{Oct})_2$ (0.001 mol·mL⁻¹) were added into the flask after the solution was cooled to room temperature ($-\text{NCO}:-\text{OH} = 2.04:1$). The mixture was then re-heated to 80 °C and stirred for 10 min. PTMEG (1 g, 0.5 mmol) was added and kept stirring at 80 °C for 6 h. All the procedures were protected under N_2 . Then PCLA-PTMEG polyurethane named as PU0 was obtained. The synthesis scheme is presented in Scheme 1(b). For the synthesis of self-healing polyurethane, 4,4'-aminophenyl disulfide (0.216 g, 0.870 mmol) was dissolved in 10 mL of DMF and introduced into the above solution (PU0). The molar ratio of $-\text{NH}_2:-\text{NCO}$ was 1.39:1. Then the mixture was stirred under N_2 at 60 °C for 16 h. Finally, as-prepared polyurethane was poured into the Teflon molds and volatilized at 80 °C for 48 h to obtain polyurethane films (named as PU1) as shown in Scheme 1(c). PU0 without disulfide bonds was used as the control sample.

Characterizations

¹H-NMR spectra were recorded using a Bruker DMX 500 NMR spectrometer at room temperature (25 °C). CDCl_3 was selected as the solvent. Tetramethylsilane (TMS) was used as the internal standard for the analysis of chemical shifts. The chemical structures of PU0 and PU1 were characterized by Fourier transform infrared spectroscopy (FTIR) with a BRUKER AVATAR 360 ESP FT-IR using ART mode at room temperature (25 °C). All samples were scanned in the range of 4000–400 cm⁻¹. The molecular weight and molecular weight distribution of PU0 and PU1 were measured by gel permeation chromatography (GPC, Waters-150, USA) using tetrahydrofuran as the eluent. Differential scanning calorimetry (DSC) analyses were carried out using a thermal analyzer (TA Q100, USA). The specimens (about 5 mg) were heated to 180 °C at a rate of 40 °C·min⁻¹, kept isothermal for 10 min, and then cooled to 0 °C at a rate of 10 °C·min⁻¹. Then the specimens were re-heated to 180 °C at a rate of 10 °C·min⁻¹. The transition temperatures and heat flow of the cooling scan and the second heating trace were recorded. X-ray diffraction measurements (XRD) were carried out on a Rigaku X-ray diffractometer (D/max 2550 VB3 +/PC, Japan, Cu K α , $\lambda = 0.154$ nm) at a scanning rate of 5 (°)·min⁻¹ from 5° to 50°. Stress relaxation behaviors of PU0 and PU1 were evaluated in a tensile mode. After being heated to 50 °C at a heating rate of 3 °C·min⁻¹ and kept isothermal for 5 min, the rectangular samples (20 mm $\times$ 3 mm $\times$ 1 mm) were stretched to a strain of 50% at a strain rate of 3% per second. Then the samples were held at the strain for 60 min and stress values were recorded with time *t*.

Self-healing properties were characterized by tensile tests. Strips of 25 mm $\times$ 5 mm $\times$ 1 mm in dimension were cut from the cast films of PU0 and PU1. A scratch (cut) perpendicular to the tensile axis and about 50% thickness of the strip was generated in the middle of each strip using a razor blade. Then the strips were heated and kept isothermal at 60, 70, and



Scheme 1 Synthesis procedure of the self-healing polyurethane: (a) Synthesis of random copolymer PCLA; (b) Synthesis of PCLA-based polyurethane (PU0); (c) Synthesis of PCLA-based polyurethane with disulfide bonds (PU1)

80 °C for 1, 2, 4, 8, 12, and 24 h, respectively. The tensile strength and elongation at break of the scratched and healed strips were obtained using a universal testing machine (M2502, China) at a strain rate of 10 mm·min⁻¹ at room temperature (25 °C). The cycling tests at 80 °C of PU1 were carried out to investigate the repeatability of healing performance. The scratching and healing procedures were repeated for 1, 2, 3, 4 and 5 cycles, respectively. For the repeatability evaluation, the scratch was cut at the same location on the same sample. The self-healing efficiencies for tensile strength and elongation at break were calculated according to Eqs. (1) and (2), respectively.

$$\text{Healing efficiency for tensile strength (\%)} = \frac{\text{Tensile strength}_{(n)}}{\text{Original tensile strength}} \times 100 \quad (1)$$

$$\text{Healing efficiency for elongation at break (\%)} = \frac{\text{Elongation at break}_{(n)}}{\text{Original elongation at break}} \times 100 \quad (2)$$

Here the original tensile strength and tensile strength_(n) are the tensile strength of the original sample and the healed sample, respectively. Original elongation at break and elongation at break_(n) are the elongation at break of the original sample and the healed sample, respectively. *n* represents the healing cycles.

Surface analyses of the scratched and healed samples were performed using a polarizing optical microscope (POM, Leica, DM LP, Germany) and a Veeco NT9100 optical profiler. Shape memory properties were determined by cyclic thermo-mechanical tensile experiments using DMA-Q800 at force control mode. PU0 strip with a dimension of 20 mm × 3 mm × 1 mm was kept isothermal at 20 °C for 2 min with a pre-load of 0.001 N. The original length was recorded as *L*₀. Then the strip was heated to 50 °C at a heating rate of 3 °C·min⁻¹ and kept isothermal for 5 min before it was stretched to a strain of about 50% at a rate of 0.1 N·min⁻¹. The strip was then cooled to 0 °C and kept isothermal for 5 min with the stress loaded. The length was recorded as *L*₁. The temporary shape with a length of *L*₂ was obtained 5 min later after the release of the load. For the recovery procedure, the strip in the temporary shape was heated to 50 °C and kept isothermal for 30 min, recovering to a length of *L*₃. Shape fixity ratio (*R*_f) and shape recovery ratio (*R*_r) were calculated according to Eqs. (3) and (4), respectively.

$$R_f = \frac{L_2 - L_0}{L_1 - L_0} \times 100\% \quad (3)$$

$$R_r = \frac{L_2 - L_3}{L_2 - L_0} \times 100\% \quad (4)$$

To characterize the triple shape memory properties of

PU1, the cyclic thermo-mechanical tensile experiment was carried out according to the procedure in our previous work.^[24] First, PU1 strip was kept isothermal at 20 °C for 2 min with a pre-load of 0.001 N. The original length was recorded as L_0' . Then the strip was heated to 50 °C at a heating rate of 3 °C·min⁻¹ and kept isothermal for 5 min before it was stretched to a strain about 25% at a rate of 0.1 N·min⁻¹. The stretched strip was cooled to 35 °C and the length was recorded as L_1' after being kept isothermal for 5 min with the stress loaded. The first temporary shape with a length of L_2' was obtained 5 min later after the release of the load. Secondly, the sample in the first temporary shape was stretched further at the same rate to a strain about 50% with length marked as L_3' . Then it was cooled to 0 °C with the stress loaded. The second temporary shape with a length of L_4' was obtained after the release of the stress. For the recovery procedure, the sample in the second temporary shape was first heated to 35 °C, recovering to length of L_5' . Finally, the strip was heated to 50 °C and recovered to its final length L_6' . The shape fixity ratios at 0 °C ($R_f(0^\circ\text{C})$) and 35 °C ($R_f(35^\circ\text{C})$) were calculated according to Eqs. (5) and (6), while the shape recovery ratios at 35 °C ($R_r(35^\circ\text{C})$) and 50 °C ($R_r(50^\circ\text{C})$) were calculated according to Eqs. (7) and (8), respectively.

$$R_f(0^\circ\text{C}) = \frac{L_4' - L_2'}{L_3' - L_2'} \times 100\% \quad (5)$$

$$R_f(35^\circ\text{C}) = \frac{L_2' - L_0'}{L_1' - L_0'} \times 100\% \quad (6)$$

$$R_r(35^\circ\text{C}) = \frac{L_4' - L_5'}{L_4' - L_2'} \times 100\% \quad (7)$$

$$R_r(50^\circ\text{C}) = \frac{L_2' - L_6'}{L_2' - L_0'} \times 100\% \quad (8)$$

RESULTS AND DISCUSSION

Chemical Structures

¹H-NMR spectrum of random copolymer PCLA is presented in Fig. 1. As shown in Fig. 1, signal e (δ : 5.25–5.05 ppm) was assigned to the resonance of tertiary hydrogen in the lactide unit (O–CO–CH(CH₃)–O) in polymer chains. Signal g (δ : 4.37–4.34 ppm) was assigned to the resonance of tertiary hydrogen of the lactide unit at the end of the polymer chains. Signals d (δ : 4.20–4.00 ppm), a (δ : 2.40–2.29 ppm), b (δ : 1.66–1.62 ppm), and c (δ : 1.45–1.35 ppm) were ascribed to the resonance of methylene hydrogens related to (O–CH₂–(CH₂)₄–CO), (O–(CH₂)₄–CH₂–CO), (O–CH₂–CH₂–CH₂–CH₂–CO), and (O–CH₂–CH₂–CH₂–CH₂–CO), respectively. After comparing the integral area of signal e and signal g, the average number of lactide units in a polymer chain was calculated as x . The ratio of integral of signal d to 2 times of integral of signal g was the average number of caprolactone units in a polymer chain as y . The number-average molecular weight (M_n) of PCLA was $144.13x + 114.14y$. According to Fig. 1, M_n of the obtained PCLA was about 30000 g·mol⁻¹. The ratio of x to y

was about 9:1 which was consistent with the feed ratio of LA to CL.

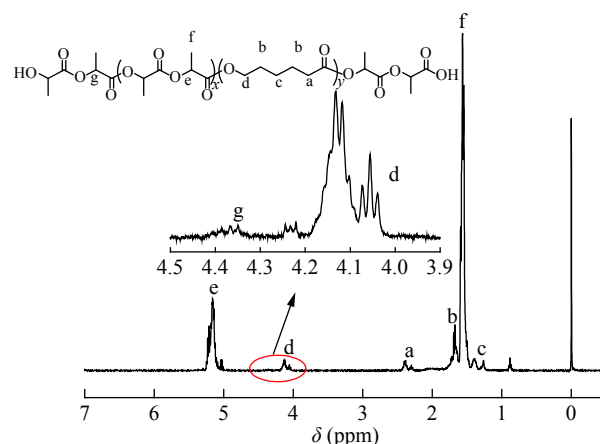


Fig. 1 ¹H-NMR spectra of random copolymer PCLA

The synthesis procedures of PU0 and PU1 are presented in Scheme 1. FTIR spectra as shown in Fig. 2 confirmed the successful synthesis of PU1. The characteristic absorption band of –NCO groups at 2336 cm⁻¹ completely disappeared for PU1, indicating that all the –NCO groups were expended after the introduction of 4,4'-aminophenyl disulfide.^[25,26] At the same time, the band at 1600 cm⁻¹ in the form of a shoulder corresponding to –NH–CO–NH– appeared.^[17] The vibration in the range of 3500–3200 cm⁻¹ was due to the –NH stretching. The weight-average molecular weights of PU0 and PU1 were 4.63×10^4 and 9.34×10^4 g·mol⁻¹ with the polydispersity of 2.12 and 2.35, respectively.

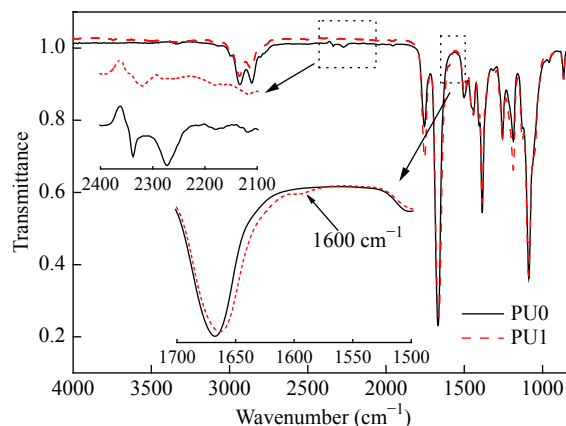


Fig. 2 FTIR spectra of PU0 and PU1

Thermal Properties and Structures

DSC curves of PCLA, PTMEG, PU0, and PU1 during cooling and re-heating cycles are presented in Fig. 3. During the cooling scan (Fig. 3a), PTMEG exhibited an exothermic peak (crystallization) around 11 °C with crystallization enthalpy about 117.7 J·g⁻¹. PCLA showed a glass transition phenomenon around 39 °C. With the incorporation of PTMEG, HDI, and 4,4'-aminophenyl disulfide, no significant difference in glass transition temperatures of PU0 or PU1 was observed.

However, the crystallization of PTMEG was significantly suppressed due to the incorporation of hard segment of polyurethane.^[14,27] The crystallization of PTMEG was completely suppressed in PU0 while partly suppressed in PU1. According to the crystallization enthalpy of PU1 ($6.1 \text{ J} \cdot \text{g}^{-1}$) and the content of PTMEG in PU1 (20 wt%), the crystallinity of PTMEG segments in PU1 was about 25.9% ($= 6.1/(20\% \times 117.7)$) of the raw PTMEG used. The residual crystallized segments of PTMEG endowed PU1 with two transitions during heating and cooling scans, which would introduce triple shape memory properties to PU1 (will be discussed later). The suppressed crystallization could be further confirmed by the DSC curves of the re-heating cycle as shown in Fig. 3(b). PCLA, PU0, and PU1 showed glass transitions at around 44°C . PTMEG and PU1 exhibited endothermic peaks at around 27°C and 29°C with melting enthalpy of 123.8 and $5.2 \text{ J} \cdot \text{g}^{-1}$, respectively.

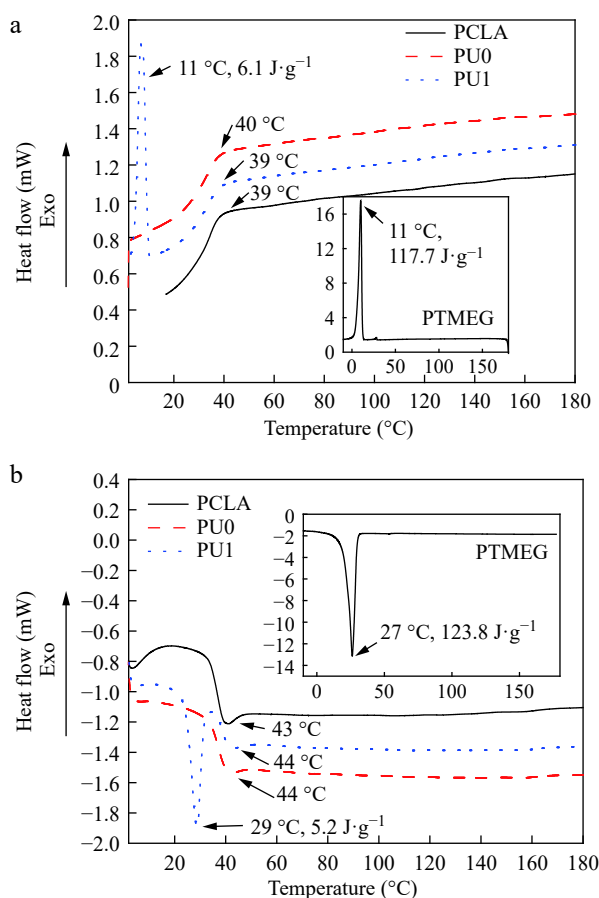


Fig. 3 DSC curves of PCLA, PTMEG, PU0, and PU1 during (a) cooling and (b) re-heating scans

To confirm the structure of PU0 and PU1, XRD patterns were obtained as shown in Fig. 4. Neat PTMEG had high crystallinity according to the results of DSC. As shown in Fig. 4, peaks at 20° and 24° were ascribed to the typical triclinic structure (α -form) of PTMEG.^[28] PCLA synthesized from D,L-LA and ϵ -CL showed no crystalline peaks of PLLA ($2\theta = 16.7^\circ$ and 19.1°) or peak of PCL ($2\theta = 21.4^\circ$).^[29] No crystalline peaks were found in the XRD pattern of PU0 while two sharp peaks with lower intensity

originated from PTMEG appeared on PU1 pattern. The results showed that PTMEG segments in PU1 were partly crystallized and were consistent with the results from DSC.

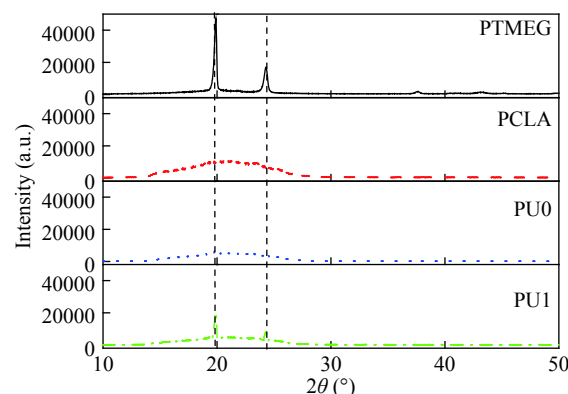


Fig. 4 XRD patterns of PTMEG, PCLA, PU0, and PU1

The stress relaxation curves of PU0 and PU1 at a strain of 50% and 50°C are shown in Fig. 5. The stress relaxation curves consist of a fast relaxation zone and a plateau zone afterwards directly. Stress decreased fast in the first 10 min (fast relaxation zone) and then much slower after 20 min (the plateau zone). The stress decreased nearly to zero in 60 min for PU0 and PU1, indicating that PU0 and PU1 had linear structures. The incorporation of disulfide bonds was accompanied by an increasing amount of hard segments in polyurethane, which acted as physical crosslinks and reinforcing element.^[19] Therefore, the relaxation of PU1 was slower than that of PU0 as shown in Fig. 5. The calculated relaxation time (τ) of PU0 and PU1 was 7.81 and 15.28 min, respectively.

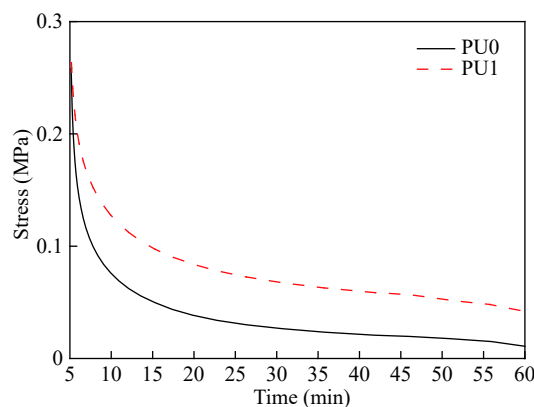


Fig. 5 Stress relaxation curves of PU0 and PU1 at 50°C

Self-healing Properties

To quantitatively evaluate the self-healing properties of the polyurethane, tensile tests were performed on the original strips and strips healed at various temperatures for different healing time. The typical stress-strain curves of the original, scratched, and healed strips of PU1 are presented in Fig. 6. To highlight the effect of disulfide bonds on the healing of polyurethane, PU0 strips without disulfide bonds were scratched and healed at 80°C for different healing time. The healing efficiencies at various temperatures for different hea-

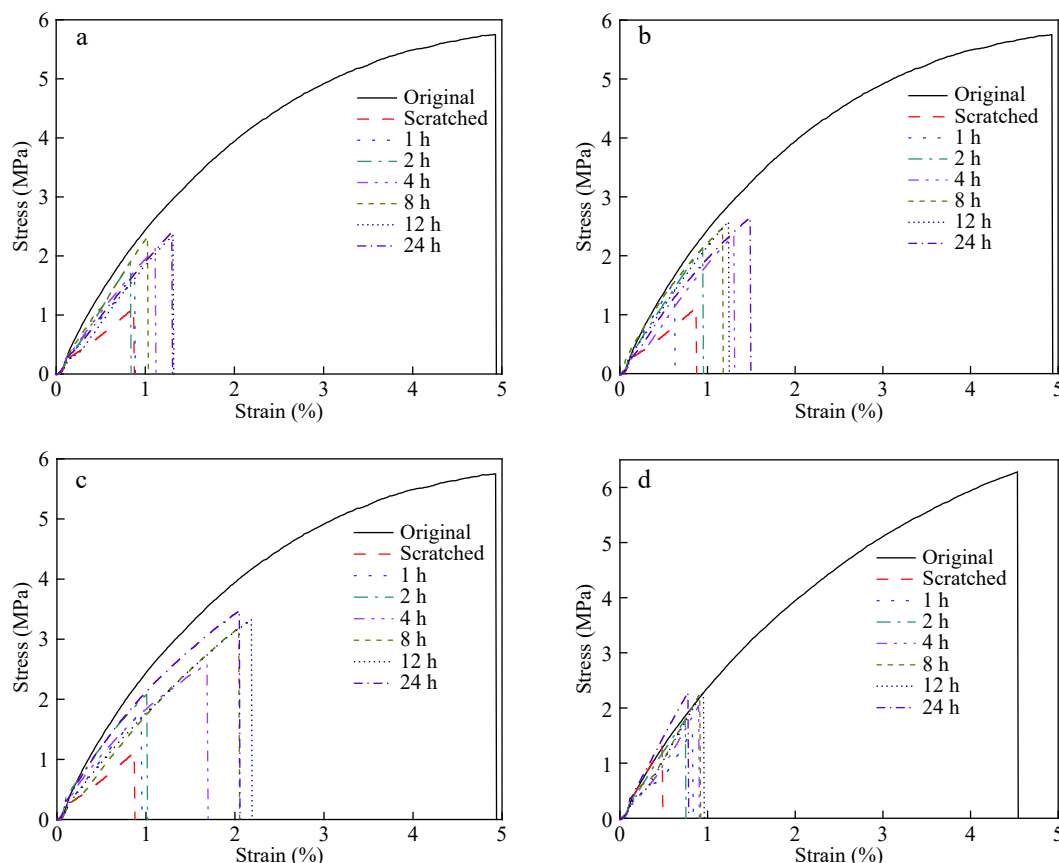


Fig. 6 Typical stress-strain curves of the original, scratched, and healed specimens of PU1 at (a) 60 °C, (b) 70 °C, and (c) 80 °C, and (d) PU0 healed at 80 °C

ling time are summarized in Table 1. As shown in Fig. 6 and Table 1, the tensile strength of original PU1 and PU0 was 5.75 and 6.28 MPa, respectively. After the strips were scratched, the tensile strength decreased to 1.13 and 1.30 MPa, respectively. Considering the effects of the healing time, the healing efficiencies of all samples increased with the healing time. For example, the healing efficiency of tensile strength of PU1 (healed at 80 °C) increased from 31.4% to 60.5% when the healing time was prolonged from 1 h to 24 h.

Sarma *et al.* and Belenguer *et al.* reported that the dynamic exchange of aromatic disulfides could occur at room temperature both in solution and in solid state using a tertiary amine as the catalyst,^[30,31] but this reaction has not been exploited for the preparation of self-healing polymers.

Rekondo *et al.* reported self-healing poly(urea-urethane) elastomers showing high healing efficiency at room temperature without the need of any catalyst or external intervention.^[17] Recently, the mechanism of disulfide exchange *via* radicals has been well-proven by Nevejans *et al.*, who investigated the underlying mechanisms for self-healing of poly(disulfide)s. The self-healing event of disulfide bonds derived from the radical-mediated reaction involving the cleavage of disulfide bonds followed by the subsequent radical transfer of sulfur-based radicals.^[32] In our system, the disulfide bonds could undergo dynamic exchange reaction through the cleavage and re-bonding of disulfide bonds upon exposure to heat as shown in Fig. 7. The exchange reaction of disulfide bonds could be triggered when the system was

Table 1 Healing efficiencies (%) of tensile strength and elongation at break at various temperatures for different healing time*

Sample	Healing temperature (°C)	Items	Healing time (h)					
			1	2	4	8	12	24
PU1	60	Tensile strength	28.1	32.5	37.0	40.5	41.0	41.8
		Elongation at break	17.8	16.8	22.5	20.1	26.6	26.3
	70	Tensile strength	27.1	37.1	41.0	43.1	44.9	46.1
		Elongation at break	12.6	19.2	26.4	23.7	25.1	30
	80	Tensile strength	31.4	36.2	45.1	55.4	57.8	60.5
		Elongation at break	19.2	20.5	34.2	41.4	44.2	41.6
PU0	80	Tensile strength	25.3	28.3	32.5	35.7	36.7	36.4
		Elongation at break	18.3	16.5	19.8	20.1	21.0	17.1

* The tensile strength and elongation at break of the original (non-damaged) samples of PU1 and PU0 were 5.75 MPa, 4.93% and 6.28 MPa, 4.54%, respectively. The tensile strength and elongation at break of the damaged (scratched) samples of PU1 and PU0 were 1.13 MPa, 0.87% and 1.30 MPa, 0.48%, respectively.

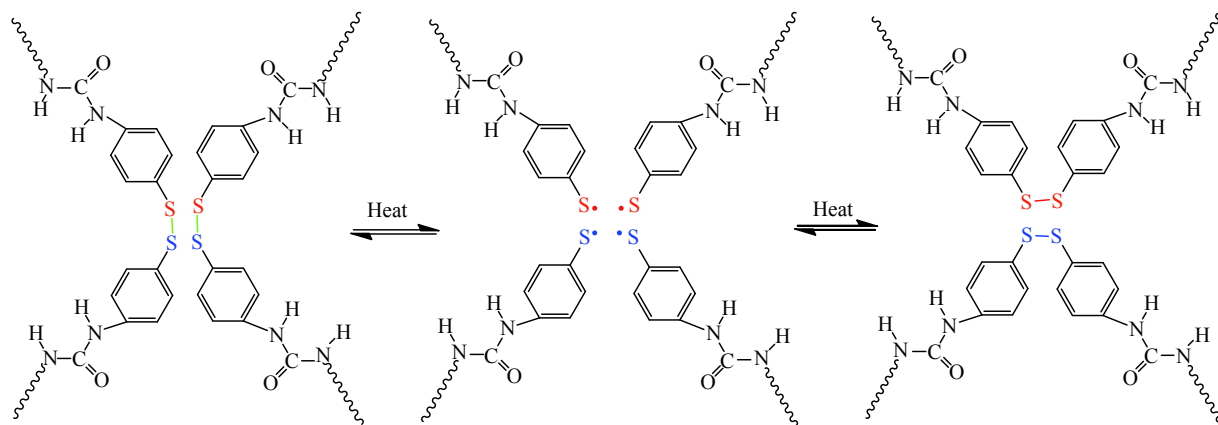


Fig. 7 The cleavage and re-bonding of the disulfide bonds under heat

heated above 60 °C and the damage of polymers containing disulfide bonds could be healed.^[3] According to the theory of Wool and O'Connor, the healing process of a crack could be divided into several stages, including rearrangement, surface approaching, wetting, diffusion, and randomization.^[33] Therefore, surface approaching or closure of the crack was the prerequisite of healing. The diffusion rate of polymer chains controlled the healing speed. As discussed in the above section, the glass transition temperatures of amorphous PU1 and PU0 were around 39 °C. At the healed temperatures investigated in this work, the polymer segments had enough mobility and the polymers exhibited good shape memory properties which would be discussed in the next section. After being heated to the healing temperatures, the scratched and deformed surfaces could recover to their original positions and bring the separated surfaces into contact. The disulfide exchange reaction accelerated the chain interdiffusion between crack surfaces after closure and the crack healing was achieved.^[20]

Higher healing temperatures led to higher healing efficiencies. According to the underlying mechanisms for self-healing of poly(disulfide)s proposed by Nevejans *et al.*, the dynamic exchange of disulfide bonds was a radical-mediated reaction.^[32] Therefore, the increase of radical concentration and activity with increasing temperature resulted in higher healing efficiencies at higher healing temperatures as shown in Fig. 6 and Table 1. At lower healing temperatures, such as 60 and 70 °C, the concentration and activity of the radicals were lower, leading to lower healing efficiencies less than 50%. The healing efficiency of PU1 reached 60.5% after being healed at 80 °C for 24 h. The value is much lower than the healing efficiency (93.43%) of PEG-PTMEG-based disulfide polyurethane (with 3.3 wt% S–S bonds) in our previous work.^[14] As reported by Lai *et al.*, PTMEG-based polyurethane containing 3.75 wt%–8.83 wt% disulfide bonds (S–S bonds) had self-healing efficiencies in the range of 85%–90%.^[19] The lower healing efficiency in this work might be due to the lower density of S–S bonds in the polymer chains. The molecular weight of PCLA segments in PU1 chains was about 30000 g·mol^{−1}, resulting in a lower S–S content of PU1 (only 0.7 wt%). Canadell *et al.* also reported that the self-healing efficiencies increased with the increase of S–S content.^[3] Therefore, the self-healing efficiency of

PCLA-based disulfide polyurethane might be increased by reducing the molecular weight of PCLA segments, which would be investigated in our future work.

Besides, hydrogen bonds in the hard segments or soft segments of polyurethane could also be activated when the temperature was above the glass transition temperature or melting temperature of the crystallized domains. The dynamic exchange of hydrogen bonds on the crack surfaces might also make a contribution to the healing procedure.^[17] Therefore, PU0 had healing efficiencies of less than 40% after being healed at 80 °C for 24 h. The result confirmed further that the higher healing efficiencies of PU1 were due to the dynamic exchange of disulfide bonds, which was consistent with the results in our previous work.^[14]

Healing repeatability is a critical factor for service reliability of the self-healing polymers.^[34] Scratching and healing cycling tests of PU1 were carried out at 80 °C for 24 h to investigate the repeatability of healing behavior. The stress-strain curves are presented in Fig. 8. The healing efficiencies after 1, 2, 3, 4, and 5 cycles were 60.5%, 53.1%, 41.0%, 35.2%, and 32.3%, respectively. The healing repeatability decreased significantly with the cycle times. The dissatisfactory healing repeatability might be improved by increasing the density of disulfide bonds in the polyurethane chains.

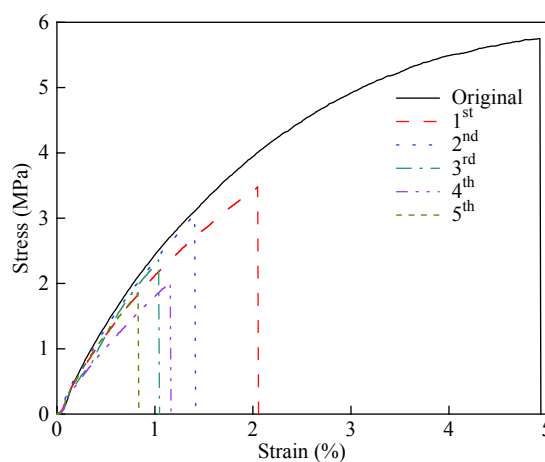


Fig. 8 Stress-strain curves of PU1 (the original strip and strips after 1, 2, 3, 4, and 5 scratching and healing cycles at 80 °C for 24 h)

Surface Analysis

To illustrate of the self-healing behaviors of PU0 and PU1 visually, POM was used to observe the scratches before and after being healed for different time at various temperatures, as shown in Fig. 9. It is obvious that the scratches on PU1 films showed obvious change even after 2 h of healing (Figs. 9a–9c). The scratches nearly disappeared and only closed trace lines of the scratch were found on PU1 surfaces after 24 h of healing at 60 and 70 °C (Figs. 9a and 9b). More than that, the scratch even disappeared with no trace line on PU1 surface after being heated for 24 h at 80 °C as shown in Fig. 9(c). However, the scratch on PU0 surface only became narrow and was still visible (Fig. 9d).

Optical profiler was also employed to confirm the healing procedure further as shown in Fig. 10. PU0 and PU1 strips all achieved certain degree of crack surface approaching after being healed at various temperatures. The crack surfaces came closer as the healing time or healing temperature increased. However, detailed images of the area near the cracks revealed certain differences. After being healed at 80 °C for 24 h, the scratch on PU1 surface almost disappeared (Fig. 10c) while the scratch on PU0 surface was still visible (Fig. 10d).

Shape Memory Properties

The healing of polymer materials included crack closure and crack healing. Closure of the crack was critical for the subsequent healing reaction.^[35] The destruction of a material was often accompanied by a large deformation or crack difficult to repair. In order to address this challenge, the shape memory property was introduced into self-healing materials to help close the crack. According to results from DSC, PU1 had a melting point of crystallized PTMEG segments around 30 °C and a glass transition of amorphous PCLA segments

around 40 °C. The melt-crystallization and glass transition of PU1 would bring about triple shape memory properties. 35 and 50 °C could be chosen as the deformation and triggering temperatures, while 0 and 35 °C could be chosen as the fixation temperatures. Compared with conventional dual-SMPs, triple SMPs could memory at least two temporary shapes, enabling more flexible applications such as intelligent medical devices, assembling systems, and minimally invasive surgery.^[24,36] The triple shape memory behaviors of PU1 were evaluated and the stress-strain-temperature diagram is presented in Fig. 11(a). The fixation ratios and recovery ratios were calculated according to Eqs. (5)–(8). PU1 had excellent shape fixity at 35 and 0 °C with fixation ratios of 94.3% and 98.3%, respectively. The shape recovery ratios at 35 and 50 °C were 76.6% and 85.1%, respectively. PU1 chains had a block structure including the micro-phase separation of crystallized PTMEG segments, amorphous PTMEG segments, amorphous PCLA segments, and hydrogen bonded urethane linkages. When deformation occurred at higher temperature, the chains were stretched and oriented. In our system, the orientation of the stretched chains at 0 °C was preserved by the hydrogen bonded urethane linkages as well as the entanglements of amorphous PCLA segments and crystallized PTMEG segments. However, a certain fraction of the chains and chain segments were still ‘unlocked’ and preserved mobility. When the tensile load was removed, the ‘unlocked’ chains generated an instantaneous retractive force, resulting in a fixation ratio of 98.3% (less than 100%). At 35 °C, the orientation of the stretched chains was preserved by the hydrogen bonded urethane linkages and the entanglements of amorphous PCLA segments. The temperature was very close to the glass transition temperature of amorphous PCLA segments (39 °C during the cooling cycle). The PCLA segments

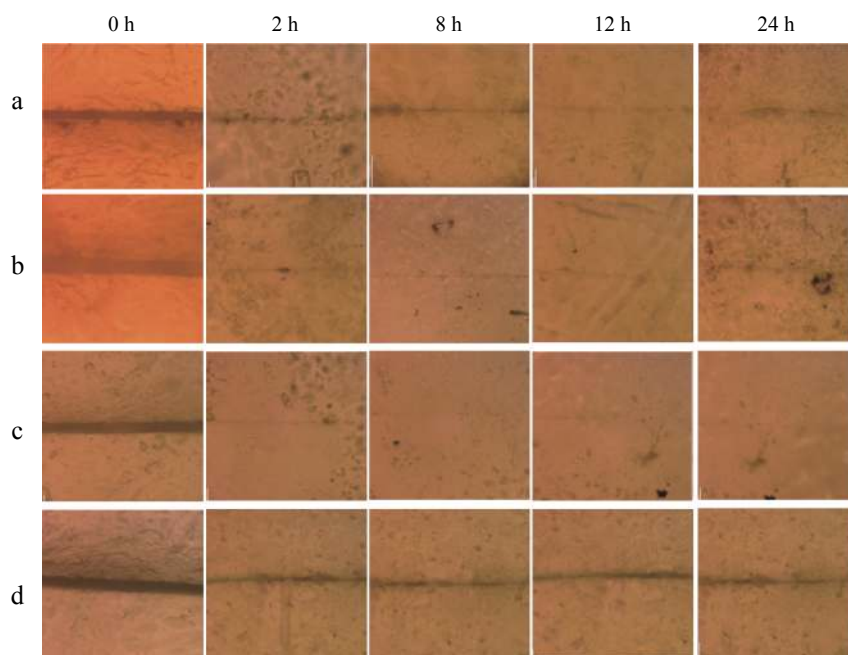


Fig. 9 Optical images of scratches on PU0 and PU1 surfaces before and after being healed for different time at various temperatures: (a) 60 °C (PU1); (b) 70 °C (PU1); (c) 80 °C (PU1); (d) 80 °C (PU0) (400×)

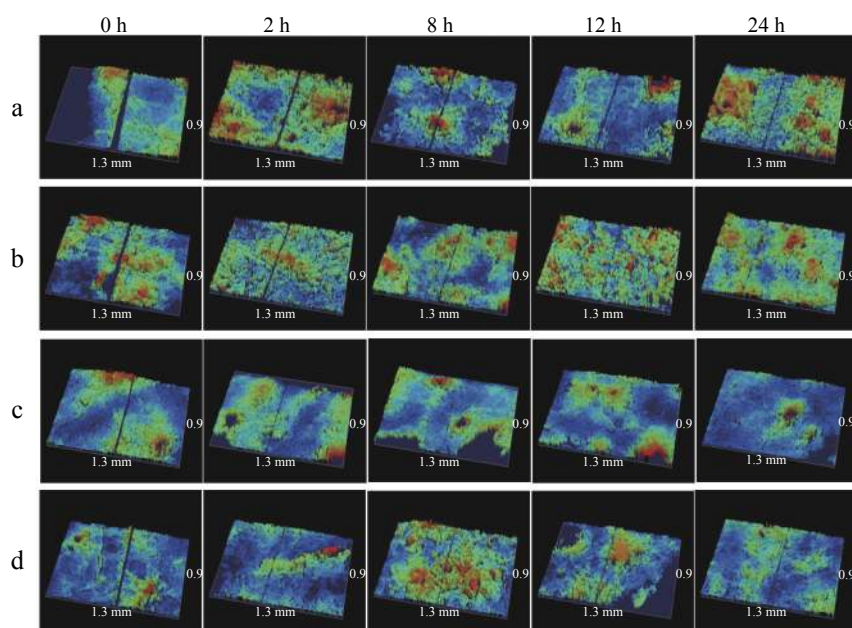


Fig. 10 Images of scratches on PU0 and PU1 surfaces before and after being healed for different time at various temperatures: (a) 60 °C (PU1); (b) 70 °C (PU1); (c) 80 °C (PU1); (d) 80 °C (PU0) (100×)

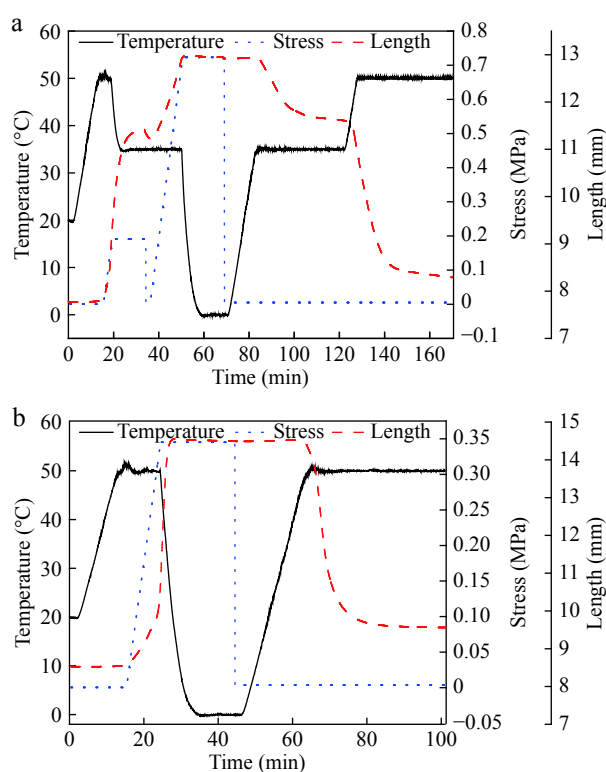


Fig. 11 Typical cyclic thermomechanical tensile cycles for (a) triple shape memory behavior of PU1 and (b) shape memory behavior of PU0

was not frozen sufficiently, leading to lower shape fixity of 94.3%.

The driving force for shape recovery of polymers was of entropic origin from the elasticity of polymer chains. Shape memory polymers possess structures similar to elastomeric networks including fixed (or hard) phases and reversible (or

soft) phases.^[37,38] In our case, the hydrogen bonded urethane linkages and entanglements of macromolecules served as the fixed phases (hard segments) while the PCLA and PTMEG chains and chain segments served as the reversible phases at 50 °C. The hard segments played an important role in providing sufficient physical interaction to sustain the original shape. Moreover, the soft segments acted as the switching components to fulfil external response and memorize temporary shape after the deforming progress. PU1 had a recovery property with a recovery ratio of 85.1% at 50 °C. PU0 (Fig. 11b) had shape recovery properties with a fixation ratio of 99.83% at 0 °C and a recovery ratio of 83.00% at 50 °C. Upon heating, PU1 strips could remember their original shapes and brought the crack surfaces in contact. When the exchange reaction of disulfide bonds was triggered, the scratches were healed, resulting in self-healing of the polyurethane. For samples without disulfide bonds (PU0), shape memory behaviors led to crack closure (as shown in Fig. 9d and Fig. 10d), but no intrinsic self-healing component through dynamic disulfide bond exchange occurred, resulting in low self-healing efficiency as shown in Table 1.

To observe the triple shape memory property of PU1 intuitively, a physical shape fixing and recovery test was also conducted as illustrated in Fig. 12. A strip of PU1 (original shape A) was folded at one end in a 50 °C hot water bath and fixed by being cooled quickly to the first temporary shape B in a 35 °C water bath with the stress loaded. Then the marked end of the strip was folded and fixed in iced-water bath (0 °C). After the release of the load, the second temporary shape C was obtained. For the recovering procedure, the temporary shape C recovered to the temporary shape B' in a 35 °C water bath and then further recovered to the original shape A' in a 50 °C water bath. It could be seen that the recovering of both the first temporary shape and the original shape was nearly complete. PU1 had good triple-shape me-

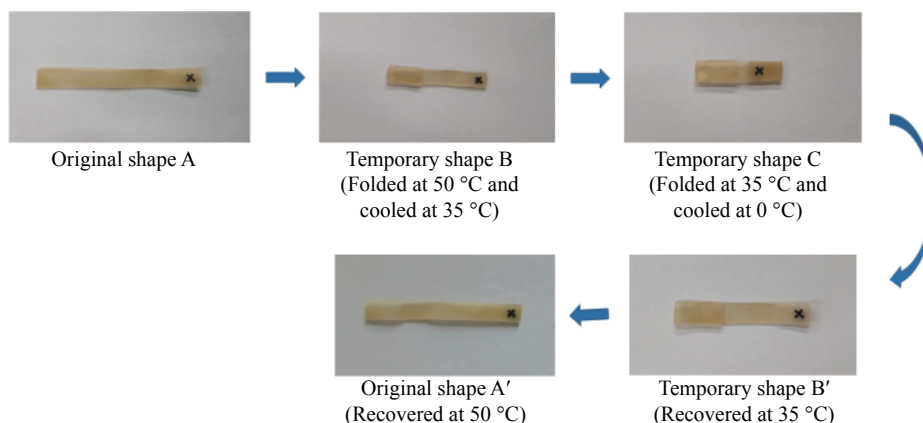


Fig. 12 The triple-shape memory recovering procedure of PU1

mory properties. Combining the self-healing properties and the triple shape memory properties, PU1 might have wide applications in multi-shape coatings, films, and step-by-step deploying structures.

CONCLUSIONS

In conclusion, a reversible disulfide bond-based self-healing polyurethane with triple shape memory property was prepared by chain extending of random copolymer poly(lactide-co-caprolactone) (PCLA) with hexamethylene diisocyanate (HDI), polytetrahydrofuran (PTMEG), and 4,4'-aminophenyl disulfide. The reversible disulfide bonds were incorporated into polymer chains by the introduction of 4,4'-aminophenyl disulfide. The structures, shape memory properties, self-healing properties, and self-healing mechanism of the polyurethane were investigated. The results showed that as-prepared self-healing polyurethane exhibited self-healing properties up to 60% and triple shape memory properties around 35 and 50 °C with shape fixation ratios of 94.3% and 98.3%, shape recovery ratios of 76.6% and 85.1%, respectively. The work presented here could provide some basic information for PCLA-based self-healing polyurethanes. Further attentions could be paid to the effects of disulfide bond density on the self-healing efficiencies and the applications in multi-shape coatings, films and, step-by-step deploying structures.

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