

SELF-HEALING BIODEGRADABLE POLY(UREA-URETHANE) ELASTOMERS BASED ON HYDROGEN BONDING INTERACTIONS*

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Abstract Self-healing poly(urea-urethane)s (PUUs) showing a tolerance to mechanical damage are particularly desirable for high-performance elastomeric biomaterials. In this study a kind of biodegradable PUUs was synthesized from poly(ϵ -caprolactone) diol with L-lysine ethyl ester diisocyanate (LDI) extended with L-lysine ethyl ester dihydrochloride (LEED) in DMF and characterized by using ^1H -NMR, FTIR, DSC, XRD, SEM and tensile tests. Interestingly, they exhibited a self-healing characteristic upon exposure to 37°C for as short as 30 min with the tensile strength keeping at 4.23 MPa and the elongation at break reaching to 627%. It is revealed that increasing the hard segment content in PUUs benefits the self-healing performance, and on the opposite increasing the soft segment content contributes to the biodegradability.

Keywords: L-lysine ethyl ester diisocyanate; Poly(ϵ -caprolactone) diol; Poly(urea-urethane); Self-healing; Biodegradable.

INTRODUCTION

When our body suffers an injury, the damage heals autonomously, and the materials properties can recover fully. Based on the autonomic healing performance of biological systems, self-healing polymers, featured with the intrinsic ability of self-repair in response to cracks arising from physical and chemical stresses within their use environment have attracted tremendous attention in recent years^[1, 2]. To date, self-healing polymers used in the field of biomedical materials have seldom been reported^[3–7]. These biomedical materials are inevitable to experience mechanical and chemical breakdown when they are subjected to loading and degradation effects *in vivo*, so that they are difficult to be repaired. The significance of the self-healing property of the biodegradable biomaterials is that it can not only avoid failures initiated by accumulated microcracks produced inevitably in the process of implantation in the human body for various surgery manipulations, but also prevent the acceleration of biodegradation where the cracks play remarked roles. Ratner^[8] raised the concept of “biomaterials that heal” to describe biomaterials that can actively promote wound healing except self-healing. To design and prepare synthetic biomaterials with the intrinsic ability to autonomously heal mechanical damage would be highly preferable for implants that not only replace tissues, but also self-heal themselves.

Several approaches for introducing the self-healing event in synthetic materials have been explored. They begin with irreversible systems, such as microcapsule based systems^[9–12], microvascular systems^[13], carbon nanotubes^[14], *etc.* However, those irreversible systems have a potential drawback, as they can only heal one time. Therefore, there is an increasing interest in reversible systems, which can break and heal repeatedly upon external stimuli^[15–17]. These reversible systems are constructed by either covalent interactions, such as

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Diels-Alder (DA) processes^[18–20] and disulfide links^[21], or non-covalent interactions, such as hydrogen bonding^[22–24], π - π stacking^[25] and hydrophobic interactions^[26–30]. Leibler *et al.* had created a series of self-healing polyurethane (PU) elastomers crosslinked *via* hydrogen bonds instead of chemical crosslinker^[31]. When the polymer was broken or cut, it can be simply healed by bringing together the fractured ends for as little as few minutes to self-heal autonomously at ambient temperature. This process was reproducible, and the healed materials displayed reasonably conserved mechanical properties after several repetitions.

Nowadays segmented polyurethane (PU) and poly(urethane-urea) (PUU) elastomers have received much attention for the development of biodegradable polymers due to their mechanical properties, surface chemistry and morphology, as well as a variety of promising medical applications, for example, nontoxic implants as temporary scaffolds for tissue regeneration or replacement^[32]. They are usually synthesized by introducing some labile moieties susceptible to hydrolysis in the polymer structure, such as polylactide (PLA) and poly(ϵ -caprolactone) (PCL) diols. Moreover, to eliminate the toxic by-products when they are degraded, such diisocyanates derived from amino acids, especially L-lysine are usually used^[33–36]. To our knowledge, however, there are a few reports on the self-healing biodegradable polyurethanes in literature.

PUU elastomers are copolymers that possess alternating hard and soft segment sequences, in which the hard segments are blocks formed by the reaction of a diisocyanate with a low molecular weight diamine, whereas the soft segments are blocks of a high molecular weight polyester diol. Immiscibility between the soft and hard segments induces microphase separation, which is a key factor that highly influences the mechanical properties of these multiblock copolymers. As compared to PU elastomers, by adding diamine chain extender rather than diol, urea groups are included in the hard segment, resulting in much more hydrogen bonds formed between two kinds of proton donors (urethane N—H and urea N—H groups) and three kinds of proton acceptors (urethane C=O, urea C=O and ester C=O groups) in the copolymers^[37–41]. The strength of the hydrogen bonds between urea groups is stronger than that between urethane groups, as the polarity of urea groups is stronger than that of urethane groups, and one urea group is constructed of one carbonyl group and two N—H groups while one urethane group, only contains one carbonyl group and one N—H group. As the hydrogen bonding interactions are additive and reversible, incorporating urea groups would endow the PUUs not only the preferred mechanical strength, but also the reversible self-healing character. To this end, a kind of biodegradable self-healing PUUs was designed and synthesized with poly(ϵ -caprolactone) (PCL) diol and ethyl 2,6-diisocyanatohexanoate (LDI) extended with L-lysine ethyl ester dihydrochloride (LEED) in DMF. The structure of the resulting PUUs was characterized by means of ¹H-NMR, FTIR, DSC, XRD, SEM and tensile tests. The efficacy of self-healing performance based on hydrogen bonding interactions as well as the biodegradability was demonstrated in this study.

EXPERIMENTAL

Materials

Poly(ϵ -caprolactone) diol (PCL, $M_n = 1250$) (Sigma, USA) was placed in a vacuum at 80°C for at least 24 h to remove residual water prior to reaction. Ethyl 2,6-diisocyanatohexanoate (L-lysine ethyl ester diisocyanate, LDI, 99%) (Dahong Chemical Reagents Company, Jiangsu Province, China) and L-lysine ethyl ester dihydrochloride (LEED, 99%) (Alfa Aesar, USA) were used without further treatment. Stannous octoate (Sigma Aldrich, USA) was used as a catalyst for the prepolymer synthesis without purification. Tetrahydrofuran (THF) was refluxed with Na to move water and distilled before use. Triethylamine (TEA) (VAS Chemical Reagents Company, Tianjin, China) was refluxed with *p*-toluenesulfonylchloride and distilled under vacuum. *N,N*-dimethylformamide (DMF) was stirred with CaH₂ and distilled under reduced pressure. Lipase AK (Amano, Japan) was stored at 2–10°C before use. All other solvents and reagents were of analytical grade.

Synthesis and Film Casting of Poly(urea-urethane)s

PUUs were synthesized *via* a solution polymerization, two-step reaction procedure. First, LDI was reacted with PCL with variable feed molar ratios of LEED to LDI (the diisocyanate/(macrodiol and diamine) molar ratio kept

at 1.05:1) in anhydrous DMF at 80°C under magnetic stirring and nitrogen flow. The prepolymer content in the reactor was controlled at 250–300 g/L. The reaction was catalyzed using stannous octoate (0.1% weight with regard to the monomer weight to toluene) and allowed to proceed at 80°C for 180 min. The temperature was lowered to 25°C, and then a preset amount of chain extender LEED was added and stirred for about 30 min. The temperature again rose to 60°C, and allowed to react for approximately another 48 h. The polymers were precipitated in freezing distilled water, stood for 24 h, filtered, washed several times to remove the residual DMF and unreacted reagents, and finally dried at 60°C under vacuum for 48 h. The three segmented copolymers obtained were designed as PUUx-1250 in Table 1, where x indicates the feed molar ratio of LEED to LDI, and 1250 stands for the number average molecular weight of PCL diol used.

Solid films were prepared by solution casting. The resulting PUUs were dissolved in chloroform at a concentration of 50 g/L. The solutions were poured into a level 5 cm Teflon casting dish at room temperature. The dishes were covered to prevent dust from contaminating the film and excessively fast casting, which can result in surface defects. The cast films were removed from the casting dishes and dried at 60°C under vacuum for 48 h to remove residual solvent and stored in a desiccator until use.

Characterization of Poly(urea-urethane)s

¹H-NMR (400 MHz) spectra were recorded on a Bruker ARX 400 spectrometer at room temperature using CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard.

Molecular weight (M_n and M_w) and polydispersity index (PDI) were determined using a Waters 2410 gel permeation chromatography (GPC) instrument. THF was used as a mobile phase at a flow rate of 1 mL/min. A sample concentration was approximately 5–10 mg/mL in freshly distilled THF, with an injection volume of 20 μ L.

FTIR spectra were measured using Shimadzu IR Prestige-21 FTIR spectrometer at room temperature in the range between 4500 cm^{-1} and 500 cm^{-1} with a resolution of 2 cm^{-1} and 20 scans. The 10 mg/mL PUU copolymer solution in CHCl₃ was directly coated onto a piece of KBr plate. A thin film of the sample was formed on the KBr plate after rapid evaporation of the CHCl₃ under vacuum, and then measured at room temperature.

The wide-angle X-ray diffraction (WXR) measurements were carried out with powder samples using a Philips X'Pert Pro diffractometer with an X'celerator detector in a reflection mode. The radiation source used was Ni-filtered, Cu K α radiation with a wavelength of 0.154 nm. The voltage was set to 40 kV and the current 20 mA. Samples were mounted on a sample holder and scanned from 4.5° to 60° in 2θ at a speed of 5 deg/min.

Differential scanning calorimetry (DSC) experiments were carried out with a Netzsch PC-200 instrument. Samples were heated in a nitrogen atmosphere from room temperature to 200°C at 10 K min⁻¹ heating rate. They were held at 200°C for 5 min before a quenching step to -90°C at 10 K min⁻¹. Once more, the sample was held at -90°C for 5 min, before a second heating step was performed. The second heating step was performed over the range of -90°C to 200°C at 10 K min⁻¹. The reported values represent the mid-point temperature for the T_g and T_m of the second heating cycle.

Mechanical tensile stress measurements were conducted using an Instron 6022 electronic universal testing machine. Dog bone shaped specimens (width 4 mm, length 20 mm) were prepared. Three samples from each PU were measured. The strain rate for the PUs experiments was 100 mm/min.

Scanning electron microscopy (SEM) experiments were carried out with a Hitachi S-4800 Scanning Electron Microscope. The samples were gold-sprayed before measurements.

Degradation Experiments

For *in vitro* degradation, PUUs were investigated by exposing to PBS and lipase solutions. The sample degradation behavior was monitored by gravimetry.

Hydrolytic degradability

Films cast as described above were cut into samples (1 cm × 1 cm), weighed and placed in 25 mL conical flasks respectively (multiple samples for each time point analysis). PBS (pH = 7.4, 12.0 mL) was added to each flask. The flasks were placed in a shaking water bath at 37°C. PBS was replaced every 7 days. Samples were removed in the preset time, washed three times with distilled, deionized water, exhaustively dried under vacuum at 35°C for 24 h, and weighed.

Enzymatic degradability

Films cast as described above were cut into samples (1 cm × 1 cm), weighed and placed in 25 mL conical flasks respectively (multiple samples for each time point analysis). Lipase AK solution (10 mg/mL, 2.0 mL), MgCl₂ solution (0.1%, 2.0 mL) and PBS (pH = 7.4, 8.0 mL) were added to each flask. The flasks were placed in a shaking water bath at 37°C. The Lipase AK solutions were replaced every 3 days to compensate for loss of enzyme activity with incubation time. Samples were removed after 1, 2, 3, 6, 9, 12, 15, 18, 21 and 24 days, and each was placed in 15 mL methanol to remove reversibly bound enzyme. The samples were then rinsed three times with distilled, deionized water, exhaustively dried at 35°C under vacuum for 24 h, and weighed. Weight loss was gravimetrically monitored at various time intervals. In all the experiments, a minimum of three samples was measured and averaged.

The weight loss percentage was calculated from the following relation:

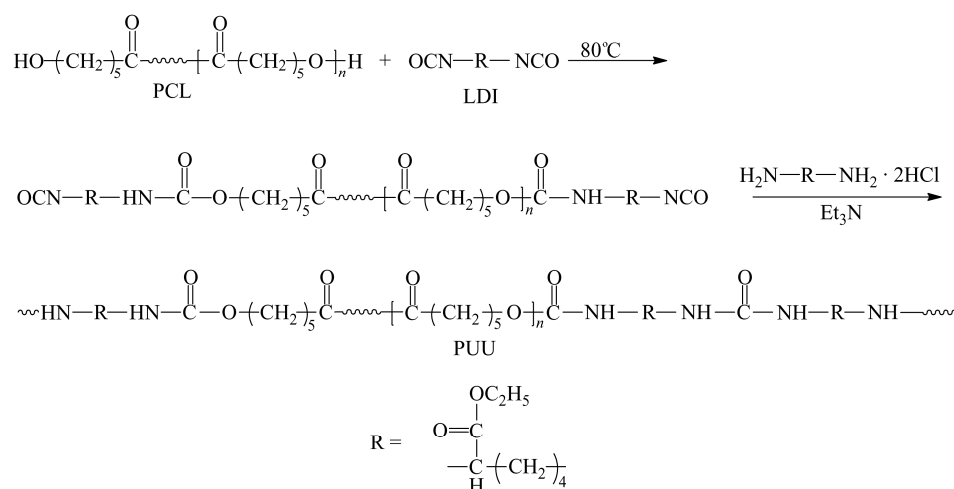
$$\text{Weight loss (\%)} = [(W_0 - W_t) / W_0] \times 100 \quad (1)$$

where W_0 and W_t are the weight of dried specimen at time 0 and t , respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization of LDI-based PUUs

As previously reported, the biodegradable PUUs were synthesized from PCL diol of $M_n = 2000$ with LDI and LEED in DMF and electrospun into tubular scaffolds for vascular tissue engineering^[39,40]. The L-929 cells and HUVECs were used to assess their cytotoxicity and cell adhesion and proliferation ability, exhibiting both the cells attached well to and remained viable on these scaffolds. In this study, when the PCL diol of $M_n = 2000$ was substituted by that of $M_n = 1250$, the resulting PUUs presented not only the excellent mechanical properties, but also the self-healing attribute due to a higher density of hydrogen bondings. The synthetic pathway of these PUUs is shown in Scheme 1. Their compositions and mechanical/thermal data are summarized in Table 1. The yield of PUUs was in a range of 79%–85%.



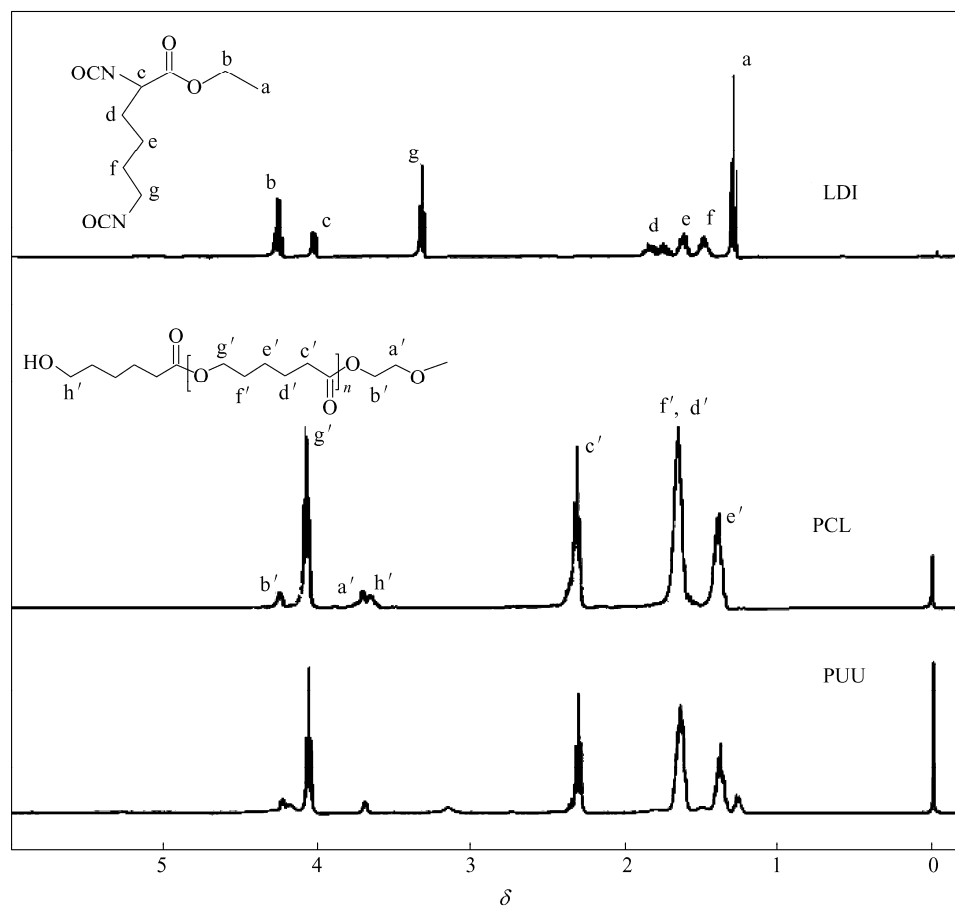
Scheme 1 Synthetic pathway of poly(urea-urethane)s based on PCL diol and LDI extended with LEED

Table 1. Compositions and mechanical/thermal data of poly(urea-urethane)s based on PCL diol and LDI extended with LEED

Entry	PCL/LEED/LDI (mol/mol/mol)	σ_m (MPa)	ε_m (%)	T_g (°C)	T_c (°C)	T_m (°C)
PUU0.1-1250	0.9/0.1/1.05	1.30 ± 0.05	16.9 ± 0.02	-53.5	-11.6	37.2
PUU0.3-1250	0.7/0.3/1.05	15.74 ± 0.32	1584.5 ± 125.4	-51.1	—	—
PUU0.5-1250	0.5/0.5/1.05	16.95 ± 0.27	1620.3 ± 87.5	-50.7	—	—

The sample PUU0.3-1250 was selected to carry out a GPC analysis. Its GPC trace showed a nearly symmetrical and unimodal peak with a relatively low PDI of 1.21. The M_w was determined to be 11.87×10^4 and M_n to be 9.8×10^4 , respectively. It is reasonable that the relatively high molecular weights imparted the high mechanical properties of both PUU0.3-1250 and PUU0.5-1250 samples.

The $^1\text{H-NMR}$ spectra of the LDI, PCL diol and a selected PUU sample are depicted in Fig. 1. Compared with LDI and PCL diol, the $\text{OCN}-\text{CH}_2-$ signal (g) as triplet at $\delta = 3.34$ and $\text{OCN}-\text{CH}-\text{CO}(\text{O})$ signal (c) as triplet at $\delta = 4.04$ in LDI, and the $\text{HO}-\text{CH}_2$ end-group signal (h') of PCL diol appearing as a triplet at $\delta = 3.65$ totally disappeared in the $^1\text{H-NMR}$ spectrum of PUU, because the $-\text{NCO}$ had reacted with the end-group ($-\text{OH}$) of PCL diol, leading to the signal of methylene in LDI shifted to $\delta = 3.16$. In addition, the signal at $\delta = 1.25$ in the PUU spectrum was assigned to the $-\text{CH}_3$ in the ethoxycarbonyl of LDI. At the same time, all the methylene signals in PCL diol were also well identified here. It suggested that the target PUUs were successfully synthesized from PCL diol of $M_n = 1250$ and LDI extended by LEED in DMF.

**Fig. 1** $^1\text{H-NMR}$ spectra of LDI, PCL and PUU in CDCl_3

The FTIR spectra of LDI, PCL and PUU are outlined in Fig. 2. As seen, the broad peaks at 2950 and 2870 cm^{-1} correspond to symmetric and asymmetric stretching vibration modes of C—H bonds. The polycondensation resulted in the formation of PUUs, as evidenced by the strong absorption band of N—H stretching vibration modes at around 3370 cm^{-1} . This absorption was attributed to the formation of —NHCOO— and —NHCOHN— groups with concomitant quantitative disappearance of the isocyanate group (—NCO) at 2260 cm^{-1} and the —OH located at 3300–3550 cm^{-1} range in the pure LDI and PCL spectra during the reaction. The peak at approximately 1645 cm^{-1} is consistent with the C=O stretching of urea carbonyl group as reported^[42] at 1645–35 cm^{-1} , and the C=O stretching of the ester carbonyl peak at 1719 cm^{-1} is also in agreement with that previously reported at 1720 cm^{-1} . All these results provided direct evidence confirming that the PUUs were successfully synthesized from PCL diol and LDI extended by LEED in DMF.

IR spectroscopy has been extensively utilized to get insight into hydrogen bondings in poly(urea-urethane)s^[43, 44]. The hydrogen bondings are evidenced by a frequency shift to a wave number higher or lower than that observed when these groups are free (not hydrogen bonded). The vibration absorption peak in the regions at 3380–3370 cm^{-1} (N—H stretching mode), consistent with the stretching vibration of hydrogen-bonded and non-hydrogen-bonded N—H groups, became broader and stronger, and shifted to a lower frequency with increasing the content of the hard segments as shown in Fig. 2, clearly indicating the increase of the density of hydrogen bonding. Although only the peak at 1645 cm^{-1} of PUU0.5-1250 (C=O stretching mode of urea carbonyl groups) was visible, and the others were weak or absent, the changes can be seen obviously in the range at 1560–1490 cm^{-1} (amide II and III regions) in PUU0.1-1250, PUU0.3-1250 and PUU0.5-1250 at 1525, 1535 and 1550 cm^{-1} , respectively, implying that the frequency of N-H deformation vibration mode shifted to a higher location due to the enhance of hydrogen bondings. Above all, the hydrogen bondings became increasingly stronger with the increase of the hard segment content.

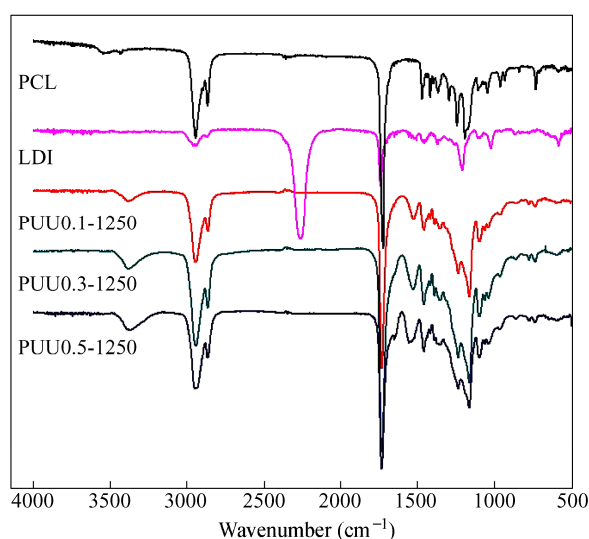


Fig. 2 FTIR spectra of LDI, PCL and PUUs with different hard segment contents

The DSC curves are shown in Fig. 3 and data are summarized in Table 1. As can be seen, PUU0.1-1250 displayed a strong endothermal melting trace and an exothermal crystallizing trace. The peak at 37.2°C (T_m) corresponded to the melting of the PCL soft segment, and the crystallization exotherm was observed at −11.6°C (T_c), pointing out that this segmented poly(urea-urethane) was microphase separated. However, both of the peaks of PUU0.3-1250 and PUU0.5-1250 were very low or absent, indicating that the degree of crystallinity was either very low or absent. Thus, the increase of the content of the hard segment tended to non-crystallization, in the other words, the degree of microphase separation was decreased, clearly implying the increase of the hydrogen

bonding density. Furthermore, the T_g of all the poly(urea-urethane)s changed very little, suggesting the inconspicuous microphase separation to increase the hydrogen bonding density.

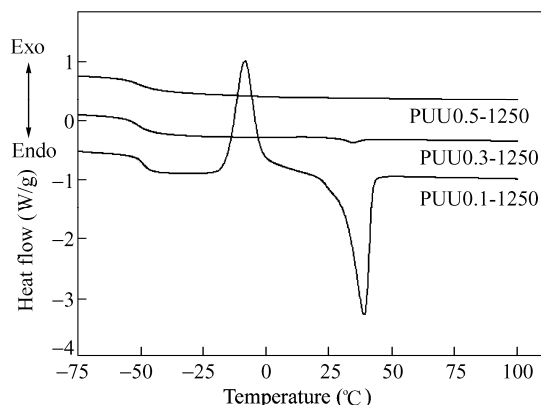


Fig. 3 DSC curves of poly(urea-urethane)s

As mentioned above, the crystallizability of PCL segments was significantly affected by the hard segments due to the hard segments of the LDI-based PUUs with asymmetric short-chain branches^[45] arising from the asymmetric structure of LDI and LEED. Evidently the increase of the hydrogen bonding density with increasing the content of the hard segment would be beneficial to the self-healing performance of the resulting PUUs.

X-ray measurements toward the crystallization of PCL are presented in Fig. 4. It was clear from the X-ray spectra that the PCL ability to crystallize was reduced when it was reacted with LDI. Furthermore, only PUU0.1-1250 was able to crystallize at a high PCL content, while the crystallization peaks of the other two samples were widened. Crystallinity was decreased with increasing the hard-segment content, in accordance with DSC results, further indicating that the microphase separation was depressed due to the high hard-segment content and asymmetric chemical structure of LDI and LEED, making a contribution to the increase of the hydrogen bonds density.

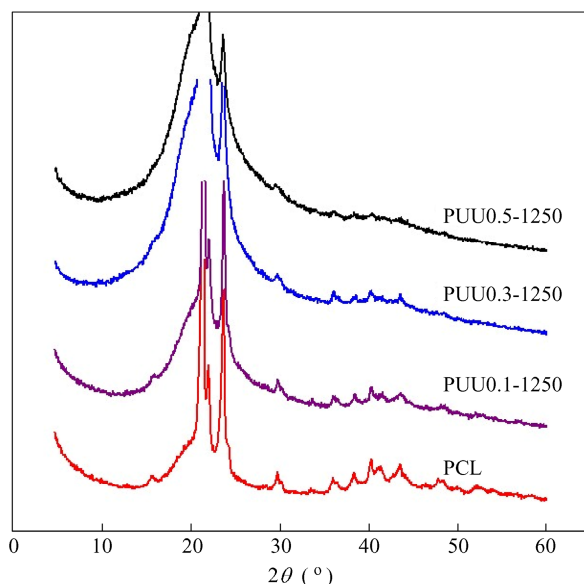


Fig. 4 X-ray diffraction patterns of PCL and poly(urea-urethane)s

Observation of Self-healing PUUs by SEM

Before the scanning electron microscope (SEM) images were taken, the film samples were cut into two pieces by gently tapping a fresh razor blade into a machined starter notch respectively, and brought the fractured ends together as closely as possible immediately to ensure sufficient self-healing. As the hydrogen bonding units may react with the closest ones in their section, the samples were treated at 37°C for about 30 min, and then cooled to room temperature. SEM images of the broken samples PUU0.1-1250, PUU0.3-1250 and PUU0.5-1250 cut without bringing together the fractured ends are shown in Figs. 5(A), 5(B) and 5(C). The cracks were obviously visible. Figures 5(D), 5(E) and 5(F) are the surface images of the healed interfaces, corresponding to A, B and C samples. Images (E, F) reveal that the fracture ends were self-healed almost completely leading to a homogeneous material with only a slight mismatch interface, suggesting a remarkable mending efficiency. Sample D corresponding to PUU0.5-1250 failed to heal with obvious crack. Because the two pieces that need to mend could not be matched perfectly when held together, the scar on the healed surface was clearly visible as a white line. Figures 5(G) and 5(H) are the longitudinal section images of the healed location of samples E and F, respectively, showing a homogeneous material at the healed place consistent with the unbroken place. They gave a clearer, more dramatic view of the healing effect. However, due to the weakness of healing effect, the cross-section image of PUU0.1-1250 was not obtained. Evidently, the self-healing is improved by the increasing of the hard segment content, directly arising from the higher hydrogen bonding density as previously mentioned. In the other words, the stronger the hydrogen bonding, the better is the self-healing effectiveness.

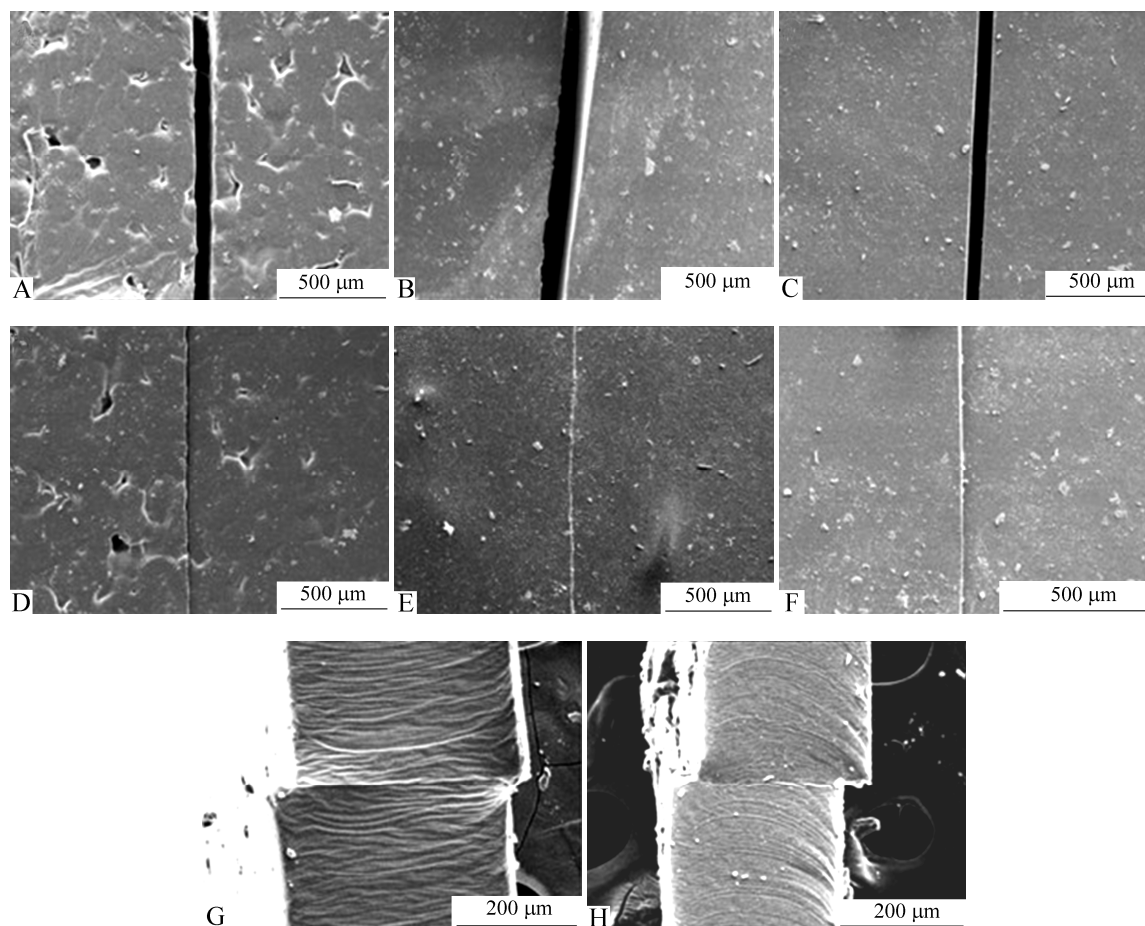


Fig. 5 Healing efficiency of polymers: (A), (B) and (C) images of the surface of broken specimens before healing; (D), (E) and (F) images of the surface of healed specimens after bringing together the fractured ends at 37°C for 30 min, corresponding to PUU0.1-1250, PUU0.3-1250 and PUU0.5-1250, respectively; (G) and (H) longitudinal section images of healed specimens, corresponding to PUU0.3-1250 (E) and PUU0.5-1250 (F)

As shown in Fig. 3, only PUU0.1-1250 displayed T_m at 37.2°C and T_c at -11.6°C, while both of PUU0.3-1250 and PUU0.5-1250 gave nearly no any endothermal melting trace and exothermal crystallizing trace. Taking into account the very low self-healing ability of PUU0.1-1250 as mentioned above, the high self-healing performance of the PUU samples appeared not to be contributed from the melting and crystallizing processes of the soft segments in this study.

Tensile Test of LDI-based PUUs

The tensile testing results of original PUU samples are summarized in Table 1 and the stress-strain curves are displayed in Figs. 6(a) and 6(b). It was clear that the mechanical properties are strongly influenced by the hard segment content. Tensile strength and the breaking elongation ratio were increased with increasing the hard segment content. All the curves showed the samples were typical thermoplastic elastomers.

To quantify the self-healing efficiency, the tensile testing experiments were carried out to quantify the recovery of the mechanical strength^[23]. At the middle of the dog bone samples, a crack was created by gently tapping a fresh razor blade, separating the samples into two pieces. After the structural failure, the two pieces were matched as closely as possible immediately, held together with a clamp, treated at 37°C for about 30 min, and cooled to room temperature. Representative stress-strain curves for the healed materials are plotted in Figs. 6(c) and 6(d). As expected, even when the contact time for the two broken parts was as short as 30 min, the self-healed samples still showed the tensile strength of (2.59 ± 0.28) MPa and the elongation at break of $(516 \pm 75)\%$ for PUU0.3-1250, and (4.23 ± 0.42) MPa and $(623 \pm 101)\%$ for PUU0.5-1250, respectively. However, the self-healed PUU0.1-1250 sample was too weak to give reliable values. In addition, the stress-strain trends behaved similar to the original materials. In order to more intuitively describe the tensile tests of the self-healed

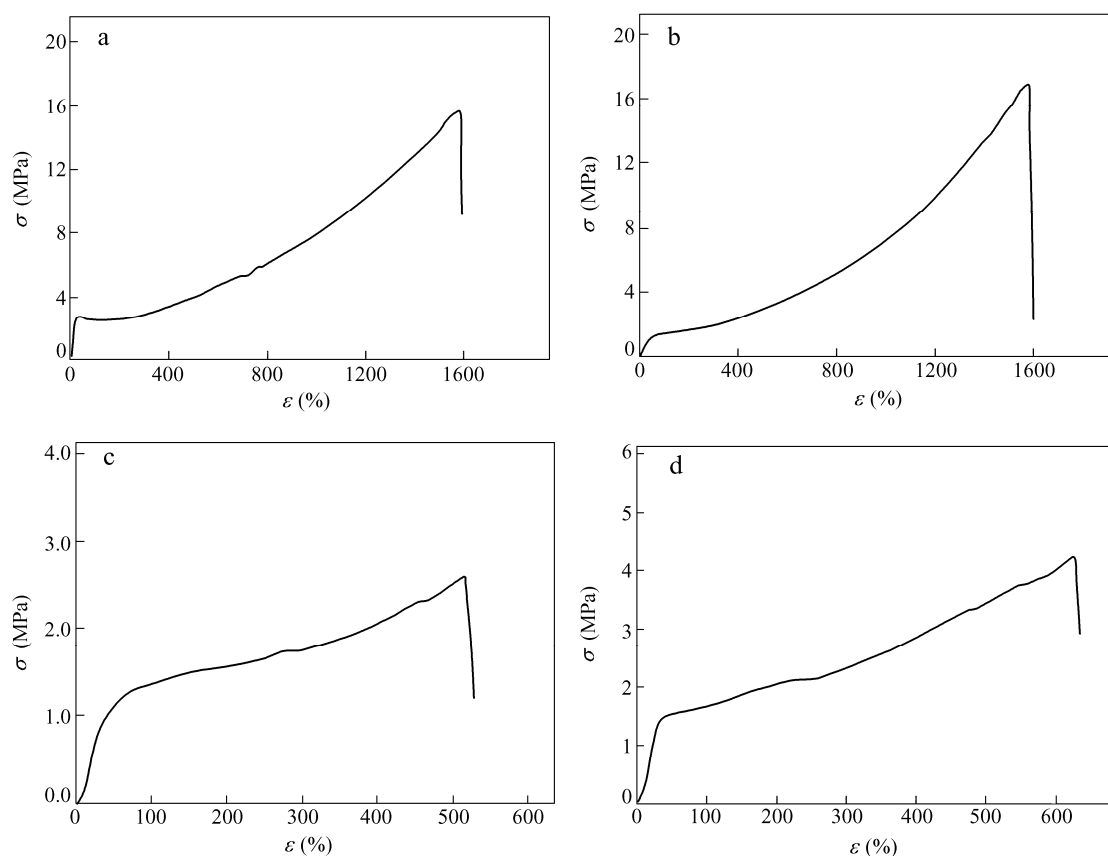


Fig. 6 Stress-strain curves of self-healed samples: (a) original sample of PUU0.3-1250, (b) original sample of PUU0.5-1250, (c) self-healed PUU0.3-1250 and (d) self-healed PUU0.5-1250

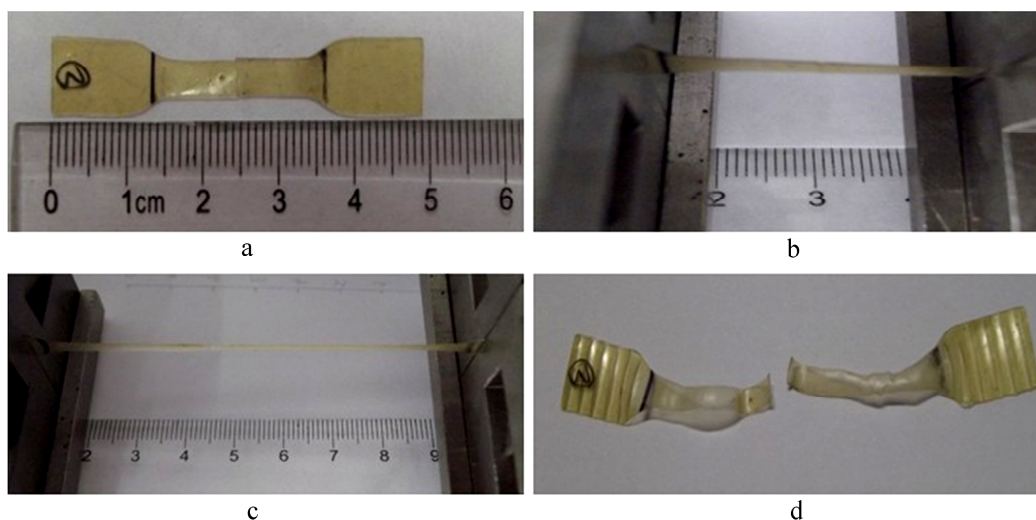


Fig. 7 Photographs before (a) and after stretching (b), (c) and (d) of a healed sample in the process of tensile test

samples, we took photographs of the stretching process (Fig. 7). The fracture was again located at the healed position, and the self-healed samples were stretched well indicating a good healing efficiency. All these pictures revealed that the PUU materials obtained were indeed self-healed, and held the better self-healing performance with the higher hard segment content. In the other words, the high hard segment content can enhance the hydrogen bonding density due to the increase of urea groups giving rise to a good self-healing efficiency.

Biodegradation Experiments of LDI-based PUUs

The mass loss curves of PUU samples in PBS and lipase solutions are showed in Fig. 8. As can be seen, the weight loss values were increased with decreasing the hard segment content in both solutions, and a much lower mass loss was observed in PBS compared to lipase solution, indicating a lesser tendency for non-enzymatic hydrolysis of PUUs.

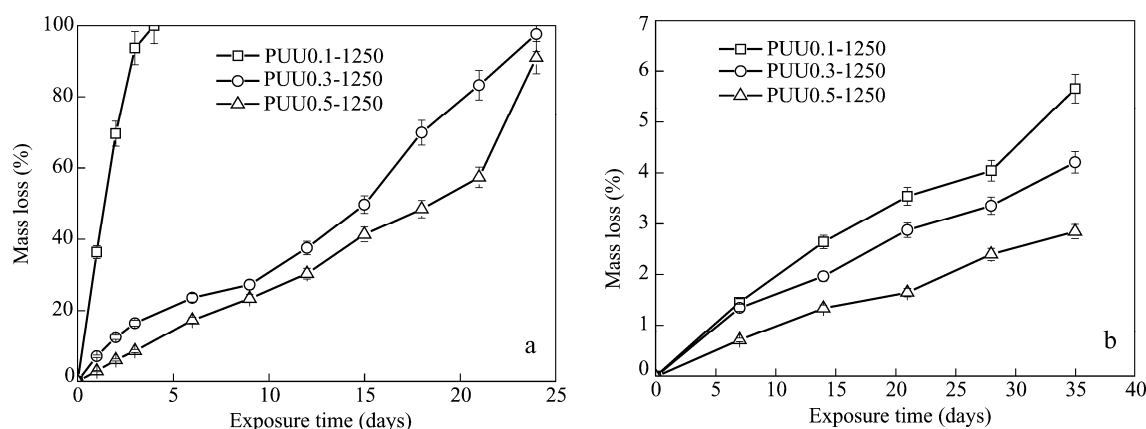


Fig. 8 Mass loss profiles for PUU0.1-1250, PUU0.3-1250 and PUU0.5-1250: (a) lipase exposure and (b) PBS exposure (Error bars represent 5% of data.)

As for the hydrolytic degradation in PBS, a maximum mass loss of 5.65% was noted in PUU0.1-1250 after 35 days, indicating a very slow hydrolytic biodegradation rate for these PUU samples due to the strong hydrophobicity of PCL. However, being exposed to lipase solution, they experienced a higher mass loss, implying that the resulting PUUs are more susceptible to enzymatic degradation. PUU0.1-1250 degraded

completely even after three days, whereas PUU0.3-1250 and PUU0.5-1250 degraded slowly, showing an approximately 97.66% and 91.02% weight loss after 24 days, respectively. These results suggested that the biodegradation rate, mechanical property and self-healing efficiency of PUU elastomers can be properly adjusted by changing the hard segment content.

CONCLUSIONS

In this study a kind of self-healing biodegradable poly(urea-urethane) was prepared. The hydrogen bonding mainly stemmed from the urea groups is responsible for the observed self-healing properties. It is crucial to bring the fractured ends together as quickly as possible to obtain sufficient self-healing, as the hydrogen bonding units may react with the closest ones in their section. What is noticeable is that the self-healing process can take place at 37°C, close to the human body temperature, and moreover, these PUUs are biodegradable, holding the great potential for significantly extending biomaterial lifetimes, especially for the implants, by avoiding failures initiated by accumulated microcracks. Further work is needed to determine the effect of the molecular weight of soft segment, healing time as well as humidity on the self-healing efficiency.

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