

Castor oil derived poly(urethane urea) networks with reprocessability and enhanced mechanical properties

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ABSTRACT

Castor oil (CO) derived polyurethane networks exhibit poor mechanical properties and non-reprocessibility due to flexible, highly and permanently cross-linked network structures. To overcome these defects, we designed and fabricated a series of poly(urethane urea) (PUU) networks by reacting CO-based polyurethane precursor with different amounts of 4-aminophenyl disulfide (APD). The equilibrium swelling behavior, mechanical properties, stress relaxation and reprocessibility of the COPUU networks in detail in this study. The swelling ratio increased with increasing APD content due to the reduced crosslink density. The mechanical properties of the COPUU networks are tunable over a broad range (either as elastomers or as plastics) depending on the APD component inputs. The tensile strength, Young's modulus and elongation at break for COPUU composed of CO/APD (W/W, 7:3) were improved by 11.7, 2.7 and 5.2 times, respectively, compared to the control CO-based polyurethane without APD. The COPUU can be reprocessed though thermal compression molding and the mechanical properties recovered completely after reprocessing at 180 °C for several cycles. The stress relaxation of COPUU accelerated with increasing APD content due to the increasing concentration of exchangeable disulfide linkage.

Keywords: *Covalent adaptable network; Stress relaxation; Mechanical property*

1. Introduction

Covalent adaptable networks (CANs) combine the advantages of both thermoplastics and thermosets [1-4]. They are composed of a dynamically cross-linked network that is stable at service temperature and is able to rearrange its network topology via covalent bonds exchange reaction at elevated temperature [5]. Therefore, CANs behave as permanently cross-linked thermoset at service temperatures but are still able to flow like thermoplastic at high temperatures when exchange reaction occurs actively [3-5]. CANs have attracted ever-increasingly attentions and have been widely fabricated via various chemical techniques such as addition-fragmentation chain transfer chemistry [6,7], reversible Diels-Alder (D-A) reaction [8,9], disulfide exchange chemistry [10-12], and transesterification [2,13,14].

Meanwhile, renewable resources have attracted progressively interests in materials science due to aggravated global warming and threat of environmental pollution with respect to fossil-based resources, and stringent governmental rules and regulations [15-17]. Plant oils have attracted attentions in synthesis of biopolymers, due to their renewability, ease of availability, and environmental benignity [18,19]. Among the various plant oils, castor oil (CO), containing ~90% ricinoleic acid, is one of best choices to synthesize various biopolymers such as polyamide, polyester, and polyurethanes [20-22]. Especially, it has played a very important role in the early stage of polyurethane industry before the invention of synthetic polyols [23]. Polyurethane coatings, elastomers, adhesives, foams, and interpenetrating polymer networks can be prepared from castor oil directly [24-29]. CO-based polyurethane networks show some appealing properties such as flexibility and water resistance, however, they are not

suitable for structural applications due to the poor mechanical properties [23,30-32]. In addition, CO-based polyurethanes are usually thermosets with permanent crosslinking structure thus cannot be reshaped/reprocessed [33-35]. These defects account for the lowered interest of CO in polyurethane industry after the availability of synthetic polyols. Regardless of these drawbacks, the continuously increased concerns on the environment protection and the resource sustainability have led to more interests in fabrication of polyurethanes from the castor oil, and a series of progresses have been attained on high-performance modification of CO-based polyurethanes in recent years [15,23,31,36-40]. However, these advanced CO-based polyurethanes are still not reprocessable.

As mentioned, incorporation of dynamic crosslinks to form CO-based CANs may make CO-based polyurethanes reprocessable. Disulfide linkages have attracted much attention in the design of a series of CANs [41]. The exchange of the disulfides occurs under several conditions, such as in the presence of catalysts, at moderate temperatures or under UV radiation, which enables the design of self-healing or processible networks under various conditions [10,42,43]. Aromatic disulfides are versatile and easy to be incorporated into polymer networks and some aromatic disulfides such as 4-aminophenyl disulfide (APD) are commercially available [41]. APD, containing two amino groups that are able to react with various functional groups, has been successfully incorporated into some petroleum-based poly(urethane urea) (PUU) and epoxy thermosets to fabricate self-healing or reprocessable networks [11,12,44,45].

In order to impart CO-based polyurethane with reprocessibility and improve its

mechanical properties simultaneously, we plan to incorporate APD into CO-based polyurethane to synthesize a novel poly(urethane urea) network via reacting APD with CO-based polyurethane precursors in this study. We believe that APD with disulfide linkage, benzene rings, and amino groups can work as a multifunctional modifier for CO-based polyurethane. Firstly, the APD with benzene rings could increase the structural stiffness thus reinforce the strength and the modulus of the networks. Secondly, incorporation of APD would reduce the crosslink density of the networks by increasing the chain length between crosslinking sites, which then can improve the ductility of the networks. At last, the networks with disulfide bonds can rearrange their topologies through disulfides exchange reaction at elevated temperatures, which imparts the networks with reprocessability.

2. Experimental section

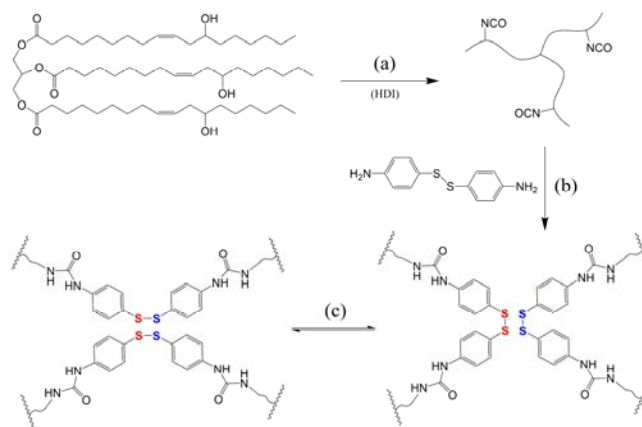
2.1. Materials

Castor oil (CO, AR grade) and 4-aminophenyl disulfide (APD, AR grade) were purchased from Adamas Reagent, Ltd (Shanghai, China) and were used as received. Hexamethylene diisocyanate (HDI, 99%) was procured from Aladdin Industrial Corporation and was used without any purification. Chloroform was purchased from Chuandong Chemical Co., LTD (Chongqing, China).

2.2. Synthesis of poly(urethane urea)s

Poly(urethane urea) (PUU) was synthesized by a two-step bulk polymerization procedure, as shown in Scheme (1a and b). In the first step, CO-based polyurethane

precursor was prepared by reacting CO with HDI at 90 °C under N₂ atmosphere for an hour. In the second step, PUU was generated reacting of the precursor with APD at the same condition for 0.5 hour.



Scheme 1. Synthesis of COPUU via a two-step catalyst free method (a and b) and exchange reaction of aromatic disulfides during thermal processing (c).

The molar ratio of –NCO from HDI to –OH from CO plus –NH₂ from APD was fixed at 1:1. Four PUUs were synthesized by varying weight ratio of CO/APD from 9:1, to 8:2, 7:3 and 6:4. They were abbreviated to COPUU-1, COPUU-2, COPUU-3, and COPUU-4, respectively. The sample sheets with dimension of 100×100×0.5 mm³ of these COPUUs were prepared by compression molding at 180 °C under 10 MPa for 5 min. For property comparison, a control CO-based polyurethane (COPU) sample sheet was prepared by cure of polyurethane precursor obtained by reacting of CO and HDI with –NCO/-OH molar ratio of 1:1 at 90 °C for an hour. The feeding compositions of the samples are listed in Table 1.

Table 1. Feeding compositions of COPU and COPUUs.

Sample	CO (wt %)	APD (wt %)	HDI (wt %)
COPU	80.50	0	19.50
COPUU-1	70.03	7.78	22.19
COPUU-2	60.08	15.02	24.9
COPUU-3	50.97	21.84	27.19
COPUU-4	42.39	28.26	29.35

2.3. Tensile tests

The tensile tests were performed on a MTS E44 universal testing machine at room temperature with crosshead speed of 10 mm/min with standard dumbbell-shaped samples bars with neck width of 4 mm and thickness of 0.5 mm. The length between the two pneumatic grips was 25 mm. Five measurements were carried out for each sample and the averaged result was reported.

2.4. Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR spectra were recorded on a RF-5301PC spectrophotometer (Shimadzu, Japan) under reflective mode in the wavenumber ranging from 400 cm⁻¹ to 4000cm⁻¹ with the resolution and number of scans as 4 cm⁻¹ and 32 times, respectively.

2.5. Gel fraction and swelling measurements

The gel fraction was measured by solvent extraction. About 1 g (w_0) sample was immersed in 25 mL chloroform at room temperature for 3 days to dissolve the un-crosslinking part and reach equilibrium swelling. The weight of the swollen sample was measured as w_1 after removing the surface solvent with filter paper. The insoluble residue was isolated from the solution by filter and weighed (w_2) after drying at 80 °C for 24 h. The gel fraction (G_f) was calculated by

$$G_f = \frac{w_2}{w_0} \times 100\% \quad (1)$$

The equilibrium swelling volume fraction (φ) can be calculated by

$$\varphi = \frac{w_0 / \rho_2}{w_1 / \rho_1 + w_0 (1 / \rho_2 - 1 / \rho_1)} \times 100\% \quad (2)$$

where ρ_1 and ρ_2 are the densities of solvent and the sample, respectively.

2.6. Stress relaxation

Stress relaxation was performed on a TA DHR-1 rotational rheometer. The disk sheet with thickness of 1 mm and diameter of 25 mm was prepared by compression molding and used for the measurement. The sample sheet between the two plates was first equilibrated at the chosen temperature for 5 min and then a 1% strain step was employed. The development of the storage modulus versus time was recorded for stress relaxation analysis.

2.7. Dynamic Mechanical Analysis (DMA)

Thermo-mechanical properties were measured on a TA Instruments DMA Q800 under a tensile resonant mode at a heating rate of 3 °C/min from -60 °C to 80 °C and with a frequency of 1 Hz. The samples with dimension of 35 mm (length) × 6 mm (width) × 0.5 mm (thickness) were used for the measurement.

3. Results and discussions

3.1. Characterization of COPUU networks

Fig.1 shows a digital photos of COPUU sample particles (with COPUUs as an example) and of the sample sheets of COPU and COPUUs. The control COPU sheet showed transparent and colorless appearance. Integrated sheets of COPUUs were obtained by compression molding from their particles, indicating that COPUUs are processible, which is due to the presence of aromatic disulfides that can undergo exchange reaction to rearrange the network structure. With aromatic disulfides, COPUUs showed transparent and slightly yellow appearance [12, 44].



Fig. 1. Digital photo of prepared COPUU particles with COPUU-3 as an example (a); digital photo of COPU sheet prepared by pre-curing in flask followed by curing in hot mold under pressure (b); and digital photos of COPUUs sheets prepared by compression molding of their particles: COPUU-1 (c), COPUU-2 (d), COPUU-3 (e) and COPUU-4 (f).

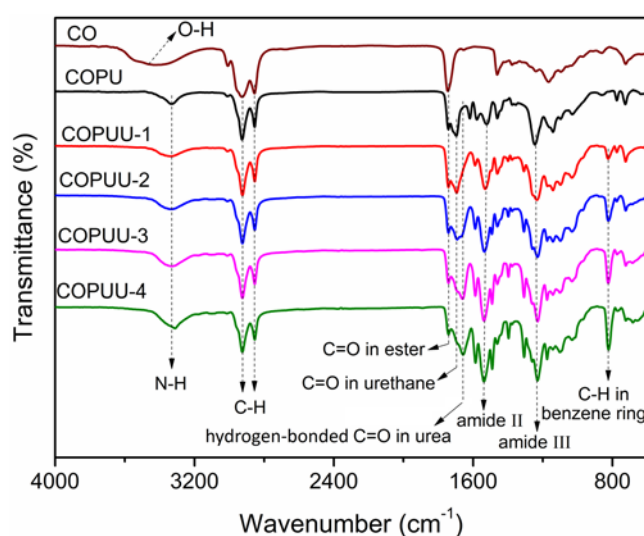


Fig. 2. FT-IR spectra of CO, COPU and COPUUs.

The structures of COPU and COPUUs were characterized by FT-IR and gel fraction measurement. Fig. 2 shows the FT-IR spectra of CO, COPU, and the COPUUs. The stretching vibration of O-H for CO at 3430 cm^{-1} disappeared on the spectra of both COPU and COPUUs. Instead, a new absorption band appeared at $\sim 3320\text{ cm}^{-1}$ which is attributed to the stretching vibration of N-H of urethane/urea group formed by the chemical reaction of -OH or -NH₂ with -NCO. The characteristic absorption of -NCO group was not found at $\sim 2270\text{ cm}^{-1}$ for both COPU and COPUUs [46]. These phenomena indicate that both -OH and -NCO were consumed completely during the reactions. The stretching vibration of C=O in ester group of CO appeared at $\sim 1745\text{ cm}^{-1}$ [23], which was also observed for both COPU and COPUUs. Apart from the C=O in ester group, absorption of C=O in urethane group was observed for COPU at $\sim 1695\text{ cm}^{-1}$ [47]. For COPUUs, a new absorption occurred at $\sim 1660\text{ cm}^{-1}$ with the absorption intensity increased gradually with increase in the content of APD, which is due to hydrogen-bonded C=O stretching. Luo et al [47] has attributed a urea carbonyl stretch at 1666 cm^{-1} hydrogen bonding in disordered regions. For the stronger hydrogen bonds in ordered or crystalline regions, stretching occurs at an even lower frequency ranging from 1628 to 1643 cm^{-1} . The ordered hydrogen-bonded carbonyl stretching is absent in this work, which indicates the amorphous structure of these COPUUs [48]. The combinations of -N-H out-of-plane bending and -C-N stretching were observed for COPU and COPUUs at ~ 1540 and $\sim 1234\text{ cm}^{-1}$, corresponding to amide II and III regions, respectively [47]. The gradually enhanced absorption at $\sim 800\text{ cm}^{-1}$ with increasing APD content in COPUUs was due to the out-of-plane bending vibration of

C-H of benzene ring. This absorption did not occur for COPU due to the absence of the benzene ring. The results indicated that polyurethane and poly(urethane urea)s were successfully synthesized through the reaction of CO with HDI or with HDI and APD.

To confirm the cross-linking structure of COPU and COPUUs, we measured the gel fraction of the samples by immersion in chloroform for 3 days. The gel fraction of all the samples were around 97%, which affirmed the network structures of both COPU and COPUUs. The equilibrium swelling was measured to semi-quantitatively evaluate the crosslink density of the samples since they showed very similar gel fractions. The equilibrium swelling volume fraction was 54.3% for COPU and the value increased gradually to 55.8%, 56.6%, 58.0% and 60.0% for COPUU-1, COPUU-2, COPUU-3 and COPUU-4, respectively, indicating a reduction in crosslink density with increasing the APD content. The results are reasonable because APD is a bi-functional compound. Thus, the reaction between APD and HDI leads to a linear segment, which locates between crosslink sites of the sample. Therefore, the segment length between crosslink sites increased, and the crosslink density decreased with the increase in the APD content.

3.2. Mechanical properties

The static mechanical properties of the samples were studied by tensile testing. Fig. 3 shows the stress-strain curves of COPU and COPUUs. COPU with flexible and highly crosslinking network structure behaved as very soft and weak, where both the tensile strength (σ) and the elongation at break (ϵ) were very small with the values of 0.80 ± 0.07 MPa and $36 \pm 4\%$, respectively. The material also showed very low Young's modulus (E) with 4.88 ± 0.26 MPa. Those parameters are in a good agreement with the results

reported by Hablot et al [49]. COPUUs showed enhanced mechanical properties compared with COPU, where both σ and E showed uptrends with increasing APD content, while ϵ first increased and then decreased. COPUU-1, COPUU-2 and COPUU-3 showed the typical tensile behavior of the elastomers. Due to the small content of APD, the improvement in the mechanical properties of COPUU-1 was limited. The values of σ , E and ϵ were 0.81 ± 0.02 MPa, 5.31 ± 0.35 MPa and $44 \pm 3\%$, respectively. With increasing APD content, σ and ϵ increased to 2.60 ± 0.41 MPa and $158 \pm 10\%$ for COPUU-2 and further to 9.37 ± 0.49 MPa and $188 \pm 15\%$ for COPUU-3. The E values of COPUU-2 and COPUU-3 increased to 7.36 ± 0.38 and 13.16 ± 1.23 MPa. The σ , E and ϵ of COPUU-3 were 11.7, 2.7 and 5.2 times higher than those of COPU, respectively. With further increasing APD content, COPUU-4 exhibited plastic-like tensile behaviors with the σ , E and ϵ of 11.82 ± 1.37 MPa, 249.14 ± 39.28 MPa and $20 \pm 5\%$, respectively.

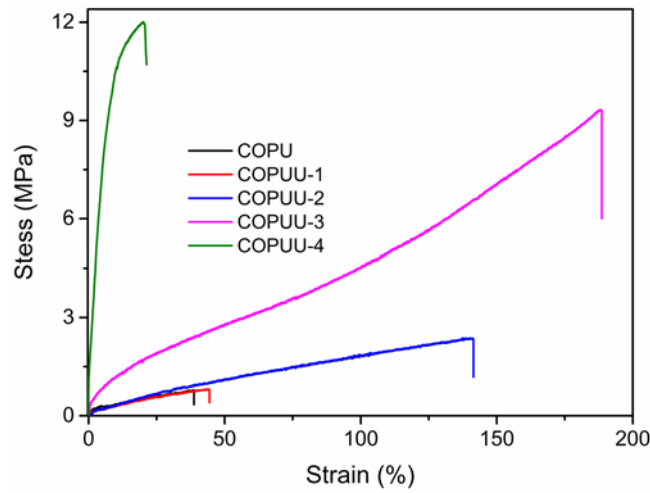


Fig. 3. Stress-strain curves of COPU and COPUUs.

CO contains flexible chains with low molecular weight; the flexible structure results in the low strength of the material and the highly cross-linked structure results in low break strain, which accounts for the poor mechanical properties of COPU. Similar

mechanical properties were also reported for some other plant oil derived networks such as epoxidized soybean oil thermosets [20,50,51]. Incorporation of APD with stiff benzene rings played three roles in varying the mechanical properties of the COPUUs. Firstly, the stiff benzene rings could enhance the stiffness of the network. Secondly, the formation of urea hydrogen bonding is helpful to improve the strength of the polymer network. Thirdly, the chain lengths between the crosslinking sites increased thus the crosslink density of the network decreased with increasing APD content, which accounts for the drastically improved break strain of COPUU-2 and COPUU-3 [18,20]. For COPUU-4, the content of hard segment, consisting of APD and HDI, is higher than that of soft segment (CO), thus it becomes hard and brittle with high modulus and low elongation at break. COPUUs with tailored mechanical properties from elastomer to plastic-like materials could be fabricated by changing their compositions. COPUU-3 with suitable composition showed the highest break strain with balanced strength and modulus. It will be used as the typical COPUU in the following discussion.

The dynamic mechanical properties of COPU and COPUUs were studied by DMA. Fig. 4 shows the variation of storage modulus (E') and $\tan \delta$ as a function of the temperature. From the E' plots (Fig. 4a), it is obvious that the COPPUs showed higher storage moduli than the control COPU, the E' value increased with the increasing APD content at any given temperature, and the drastic loss in storage modulus shifted to a higher temperature with increasing APD content. The reinforced storage moduli were ascribed to the increased stiffness of the networks, due to the increased fraction of stiff benzene rings with increasing APD content. In addition, the high E' value maintains to

higher temperatures for the COPUU with high APD content, indicating a better heat resistance with higher APD content. Corresponding to the drop of E' on storage modulus plots, loss peak appears on $\tan \delta$ plots of all samples (Fig. 4b), relating to the α -relaxation (i.e., glass transition) of the samples. It is reasonable that the glass transition temperature (T_g) increased gradually with increasing APD content due to the improved stiffness of the network structure. The damping peak height of the COPU and COPUUs reduces gradually with increasing APD content, again relating to the enhanced stiffness of the network, which restricts the chain movement thus lowers the damping in transition [52].

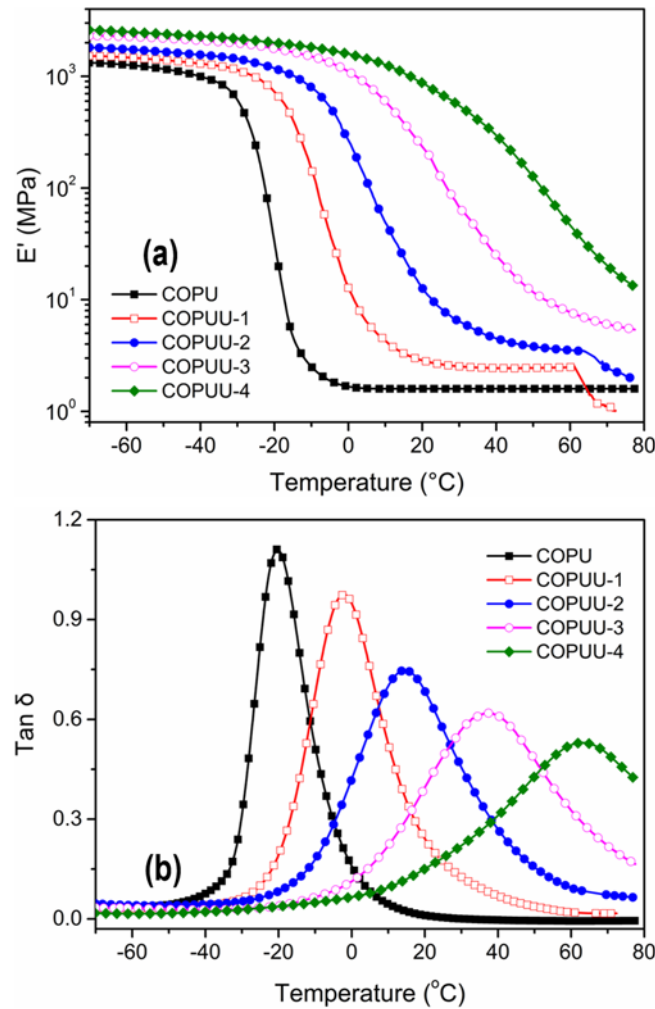


Fig. 4. Storage modulus and $\tan \delta$ as a function of temperature for COPU and COPUUs.

3.3. Stress relaxation and reprocessability

The stress relaxation of the materials was measured on rotational rheometer by monitoring the evolution of shear storage modulus with time. Fig. 5 shows the stress relaxation curves of COPU and COPUUs at 180 °C. The network structure of the control COPU cannot be rearranged, as it does not contain aromatic disulfide. It showed no relaxation in the early stage. The followed slight relaxation may be resulted from the break of covalent bonds due to thermal degradation by placed in a high temperature environment for long time. Significant stress relaxations are shown for COPUUs and the relaxation accelerated with increasing amount of APD due to the increasing concentration of disulfide bonds, as shown in Scheme 1c. Based on the Maxwell model for describing the viscoelasticity of the materials, the time needed to relax 63% of the initial stress can be used to designate the relaxation time [53, 54]. Then the relaxation time for COPUU-1 at 180 °C was 63.4s, and the time decreased significantly to 16.6, 7.0 and 3.3 s for COPUU-2, COPUU-3 and COPUU-4, respectively. The stress relaxation of such transient polymer network, can be described in the form of stretched exponential decay in theories [55], as $G \sim e^{(\beta t)^\alpha}$, where β is the breakage rate of the crosslinks and α is the stretched factor. By fitting the curves in Fig. 4, we can obtain the parameters for these samples as listed in Table 2.

Table 2 fitted parameters for the stress relaxation of COPU and COPUUs at 180 °C.

Sample	COPU-0	COPUU-1	COPUU-2	COPUU-3	COPUU-4
Parameter					
β (s ⁻¹)	5.69364E-6	0.03315	0.27914	3.39689	253.8938
α	0.19793	0.32754	0.31489	0.26243	0.20664

From Table 2, it is clearly shown that the inverse of the stress relaxation time or the

breakage rate of the crosslinks increases significantly from COPU-0 to COPUU-4. Meanwhile, the stretched factor is 0.26 ± 0.07 . For a transient polymer network with monodispersed mesh size and single energy barrier to break the crosslinks, the stretched factor should be equal to 1, while a smaller stretched factor can be induced by a broad distribution in the breakage energy barrier or in the mesh size [55-57].

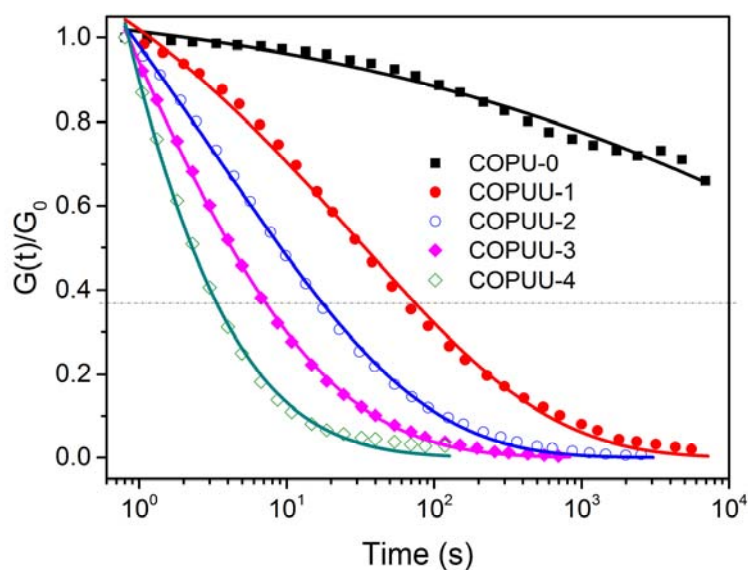


Fig. 5. Stress relaxation of COPU and COPUUs at 180 °C, with both experimental data and theoretically fitted lines.

With such short relaxation time, all the COPUUs are easy to be reprocessed at elevated temperatures. We reprocessed the sample through compression molding of the small chips, which were cut from their sheets. Taking COPUU-3 as a typical example, an integrated sheet (Fig. 6b) was achieved after compression molding of its chips (Fig. 6a). In contrast, compression molding of COPU chips (Fig. 6c) did not lead to an integrated sheet (Fig. 6d).

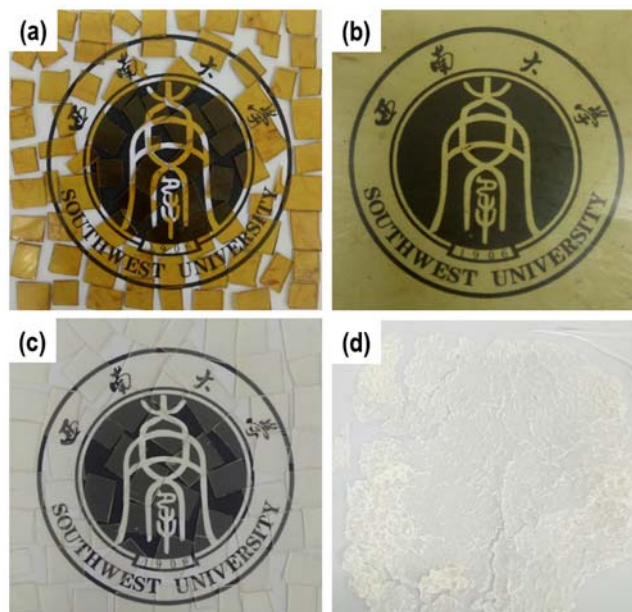


Fig. 6. Digital photos of COPUU-3 chips (a), reprocessed COPUU-3 (b), COPU chips (c) and reprocessed COPU (d).

The effect of the temperature on the stress relaxation of COPUUs was studied by using COPUU-3 as the example. Fig. 7 shows the stress relaxation curves of COPUU-3 at different temperatures. As shown in Fig. 7, the relaxation is particularly slow at 100 °C due to the low exchange reactivity at low temperatures, which indicates that the network structure almost froze and the dimension stability could remain at temperature below 100 °C. It is obvious that the relaxation process accelerated at elevated temperatures, which is reasonable because the reactivity of disulfide exchange reaction is enhanced at high temperatures. The fitted breakage rate and the stretched factor are shown in Table 3, where the breakage rate increased extensively with increasing temperatures. Meanwhile, if we take the breakage rate as $\beta \sim e^{-w_b/k_B T}$, then we can obtain the value of the energy barrier to break the crosslinks, approximately as $82k_B T_r$ ($T_r=27$ °C), by assuming an identical energy barrier for all crosslinks for simplicity.

Table 3 fitted parameters for the stress relaxation of COPUU-3 at various temperatures.

Temperature	100°C	120°C	140°C	160°C	180°C
Parameter					
β (s ⁻¹)	1.17324E-5	5.56132E-4	0.00253	0.03207	3.39683
α	0.14392	0.33324	0.36909	0.44219	0.26243

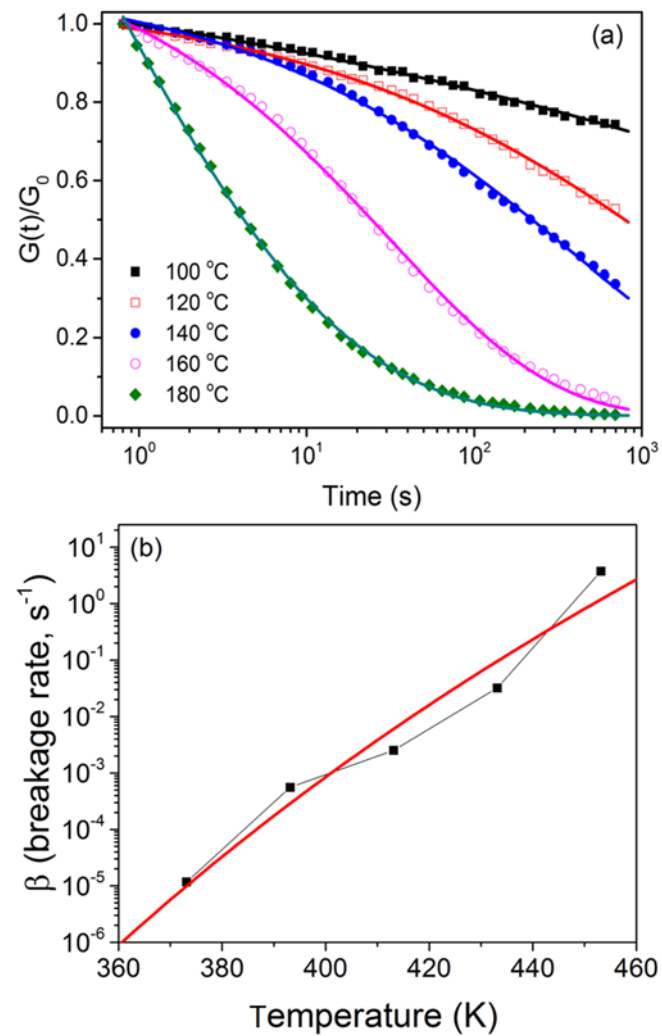


Fig. 7. (a) Stress relaxation of COPUU-3 at different temperatures, with both experiment data and theoretically fitted lines. (b) Breakage rate of the crosslinks as a function of temperature, with squares from experiments and red line of theoretical fitting.

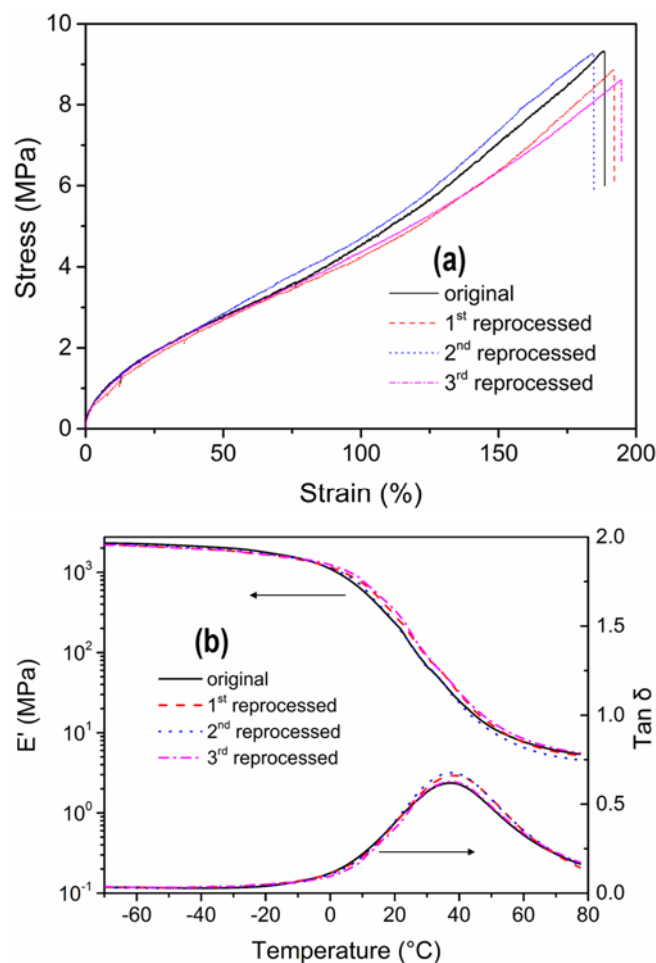


Fig. 8. (a) Stress-strain curves in tensile tests and (b) DMA curves of the original and the reprocessed COPUU-3 samples.

To study the reprocessibility of the material, we reprocessed a COPUU-3 sample by compression molding at 180 °C for three times. The reprocessed sheet was subject to gel fraction measurement, tensile testing and dynamic mechanical analysis. The gel fractions were all around ~97% regardless of the repeated times, which indicates that the network structure of COPUU maintained after thermal reprocessing. The stress-strain curves in Fig. 8a demonstrated that the mechanical properties were almost fully recovered after being reprocessed by compression molding at 180 °C for several cycles. The tensile strengths were around 9.0 MPa and the elongations at break were around 185%, regardless of the reprocessing cycles. DMA curves in Fig. 7b also confirmed a

satisfactory recovery of the mechanical properties since both storage modulus (E') and $\tan \delta$ only changed slightly between the original and reprocessed samples. All these results indicated that COPUUs have excellent reprocessibility without breakdown of network structures and obvious change in the mechanical properties after reprocessing.

4. Conclusions

To endow castor oil-based polyurethane network with enhanced mechanical properties and reprocessibility simultaneously, castor oil-based poly(urethane urea) (COPUU) was prepared by chemical reaction between 4-aminophenyl disulfide (APD) and castor oil-based polyurethane precursor. The tensile strength and Young's modulus of COPUU increased gradually and its elongation at break first increased and then decreased with increasing APD content. COPUU-3 with feed CO/APD ratio of 7/3 showed the excellent balanced mechanical properties with tensile strength, Young's modulus and elongation at break improved by 11.7, 2.7 and 5.2 times, respectively, compared to the control COPU. COPU show almost no stress relaxation due to the absence of exchange reaction. Stress relaxation of COPUU occurred at high temperatures and the relaxation time reduced with increasing APD content due to the increasing concentration of exchangeable covalent bonds. The COPUU showed excellent reprocessibility as evidenced by the fully recovered mechanical properties after thermal processing for several times.

Acknowledgements

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