



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-reprocessability 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 reprocessability of the COPUU networks were investigated 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 through 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.

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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

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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 reprocessibility.

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 h.

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.

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-5301 PC spectrophotometer (Shimadzu, Japan) under reflective mode in the wavenumber ranging from 400 cm⁻¹ to 4000 cm⁻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.

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