Journal of Renewable Materials
DOI:10.32604/jrm.2020.08165
Research Article

Tech Science Press

Thermally Reversible, Self-Healing Polyurethane Based on Propyl Gallate and Polyurethane Prepolymers with Varied Isocyanate Content

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Received: 7 August 2019; Accepted: 21 October 2019

Abstract: Thermosetting polyurethanes are widely used in various fields owing to their excellent elasticity, strength and solvent resistance. Three environmental friendly propyl gallate-based self-healing polyurethanes were prepared from polyurethane prepolymers with varying isocyanate content. The thermal stabilities of the polyurethanes were tested using thermogravimetric analysis. Their self-healing and mechanical properties were analyzed using a universal testing machine and dynamic thermomechanical analysis. The polyurethanes were found with high self-healing ability and excellent mechanical properties due to the absence of phenolic carbamate. These qualities improved with increased isocyanate content and the prolonged self-healing time. We found, therefore, that the propyl gallate-based polyurethane has potential for use in industrial applications as self-healing materials.

Keywords: Propyl gallate; thermosetting polyurethane; self-healing ability; mechanical property

1 Introduction

The thermosetting polymers are three-dimensional compounds with infinite molecular weights and have good physical and mechanical properties owing to their cross-linked network structure. They are widely used in industries such as aerospace, electronics, and machinery [1].

Thermosetting polymers can be damaged by external forces such as light and heat. Such vulnerability seriously decreases the safety and usage lifetime of these polymers. Damaged thermosetting polymers can hardly self-heal and to produce large amounts of solid waste. At present, damaged thermosetting polymers are disposed through landfills, chemical degradation, and pyrolysis incineration [2-3].

All of the above methods have shortcomings (non-biodegradability, organic pollution, wastewater pollution, waste gas pollution, high energy consumption). While thermosetting polymers can be repaired using self-healing technology, a safe, environmentally friendly disposal method for these polymers is urgently needed. Development of active self-healing thermosetting polymers have become a hot research topic. Intrinsic self-healing is the reversible reaction of the molecular structure or macromolecular diffusion to complete polymer self-healing. This reaction needs to be carried out using light, heat, humidity, or electromagnetics. The reversible reaction mainly include dynamic covalent bonds (e.g., S–S, Diels–Alder) and dynamic non-covalent bonds (e.g., hydrogen bonds, metal ligands, electrostatic interactions), The energy of covalent bond is stronger than that of non-covalent bonds and can stabilize the mesh structure of the thermosetting polymer. Thermal reversible self-healing has been widely investigated due to its simple operation and easy implementation [4-6].

Polyurethane (PU) is one of the most important thermosetting polymers, and can not be reproduced. It is obtained by curing (cross-linking) with polyol and isocyanate [7]. Better circular utilization of thermosetting polyurethanes, can be achieved through self-healing polyurethanes with dynamic covalent bonds and has been agreat research topic in recent years [8-9]. Yang et al. [10] prepared self-healing polyurethanes from an isocyanate-terminated polyurethane prepolymer with furfuryl amine and bismaleimide via Diels–Alder/Retro Diels–Alder reactions. The polyurethanes had good mechanical properties and a self-healing efficiency up to 80~95%. Lu et al. [11] prepared a self-healing polyurethane from an isocyanate-terminated prepolymer, a tri-functional homopolymer of hexamethylene diisocyanates (tri-HDI), and an aromatic disulfide diamine. The resulting product had a self-healing efficiency up to 97.4% and a tensile strength of 7.7 MPa. Bahram Ramezanzadeh et al. [12] synthesized a self-healing polyurethane with hydroxyl-terminated polybutadiene, three functional amino alcohols, and 4-Aminophenyl disulfide. These chain extenders and healing agents improved the mechanical and healing properties of the polyurethane coatings. However, most self-healing polyurethanes are prepared by introducing reversible special functional groups from petrochemical-based raw materials. It is imperative to study self-healing polyurethanes from renewable resources as well as bulk structures with self-healing groups [13-15]. Propyl gallate is the esterification product of gallic acid (hydrolysis product of gallnut tannin extracted from Chinese Galls) and contains three active phenolic hydroxyl groups.

The the present work was aimed to acquire thermoset polyurethanes with high self-healing ability and environmental friendliness. Propyl gallate was selected as the raw material. We synthesized three environmental friendlyand self-healing polyurethanes using propyl gallate and polyurethane prepolymers with variying isocyanate contents. The thermal stability, mechanical properties, and self-healing properties of the three polyurethanes were analyzed and compared. We explored the effect of prepolymer isocyanate content on self-healing properties. The three polyurethanes containing phenolic carbamate exhibited high self-healing ability.

2 Experiment

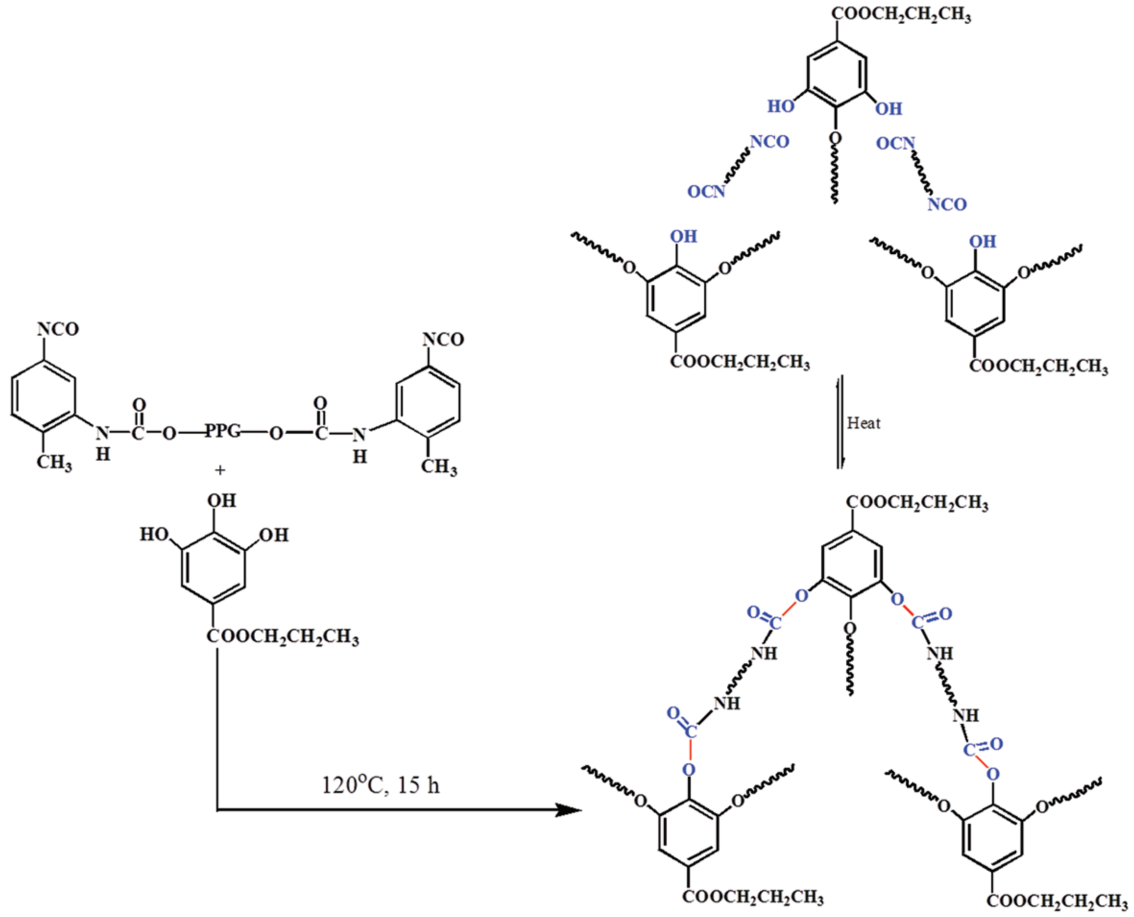
2.1 Materials

Propyl gallate was obtained from Shandong Kangqin Biological Technology Co., Ltd. (Shandong, China). The isocyanate-terminated polyurethane prepolymers (NCO% = 4.5, 5.5 and 6.2%) were prepared by 2, 4-tolylene diisocyanate and polypropylene glycol (PPG) and obtained from Shandong INOV Polyurethanes Corporation (Shandong, China). Dibutyltin dilaurate (DBTDL) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).

2.2 Preparation of Propyl Gallate-based Polyurethane

The following materials were introduced into a four-neck flask with a mechanical stirrer and a thermometer: 2.12 g propyl gallate, 29.40 g isocyanate-terminated polyurethane prepolymer (NCO% = 4.5%), 0.16 g (0.5 wt. % of propyl gallate and isocyanate-terminated polyurethane prepolymer) dibutyltin dilaurate. The mixture was heated to 100°C, stirred, and evacuated to eliminate bubbles. After the bubbles were completely removed, the reaction mixture was poured onto a tetrafluoroethylene plastic substrate and cured at 120°C for 15 h to obtain the propyl gallate-based polyurethane resin (PU1, Scheme 1).

The PU2 (propyl gallate and isocyanate-terminated polyurethane prepolymer, NCO% = 5.5%), and PU3 (propyl gallate and isocyanate-terminated polyurethane prepolymer, NCO% = 6.2%) were prepared according to the same synthetic route.



Scheme 1: Synthesis route and structure of propyl gallate based polyurethane resin and the self-healing process

2.3 Structure Characterization

The chemical structure of the propyl gallate-based self-healing polyurethanes was characterized using an IS10 Fourier transform infrared spectrometer (Thermo Fisher Nicolet, USA).

2.4 Isocyanate Content

The isocyanate content of the prepolymers was determined according to ISO14896-2009.

2.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analyses was performed using a TGA Q500 (TA Instruments) instrument. About 4 mg of each sample were scanned from 30 to 600°C at a heating rate of 10°C min^{-1} under nitrogen gas at a flow rate of 100 mL min^{-1}.

2.6 Dynamic Thermomechanical Analysis

The dynamic thermomechanical analysis was done using a TA DMA-Q 800 dynamic thermomechanical analyzer (NETZSCH Instrument Manufacturing Co., Ltd. Germany). The dynamic thermomechanical analysis conditions were −80~150°C (temperature range), 3°C/min (heating rate), and 1 Hz (testing frequency).

2.7 Measurement of Mechanical Properties

The tensile strength and elongation at break were examined using an MCT4303 universal testing machine (Shenzhen Xinsansi Material Testing Co., Ltd., China), according to GB/T528-1998. Five parallel sample data sets were tested and averaged. The test conditions were room temperature (test temperature), 500 mm/min (stretching speed), and 20 mm × 4 mm × 5 mm (sample specification).

2.8 Self-healing Properties

The self-healing properties of the propyl gallate-based polyurethanes were investigated by measuring tensile strength and elongation at break at different time points. The self-healing efficiency of PU was calculated as follows:

$$\begin{aligned}\text{Healing efficiency} =& \text{tensile strength and elongation at break after healing}/\\ & \text{tensile strength and elongation at break original} \times 100\%\end{aligned}$$

3 Results and Discussions

3.1 Characterization of Propyl Gallate-based Polyurethane

Figure 1 shows the Fourier transform infrared analyses of the three PUs. The peak at 3200-3500 cm^{-1} and 2265 cm^{-1} corresponded to the phenolic hydroxyl bending vibration in propyl gallate and the –NCO stretching vibration in the polyurethane prepolymer respectively. When propyl gallate reacted with the polyurethane prepolymer, a new absorption peak appeared at 3292 cm^{-1}; which was assigned to the characteristic absorption peaks of N–H. The characteristic absorption peaks of C=O and C–N were observed at 1721 cm^{-1} and 1224 cm^{-1}.

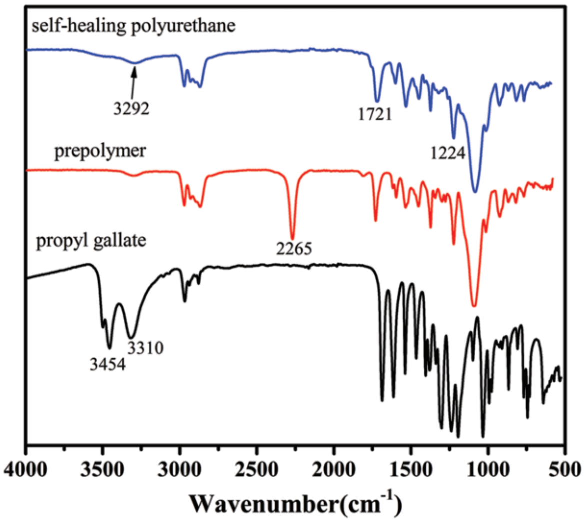


Figure 1: FTIR spectra of PU

3.2 TGA

The thermal decomposition behaviors of the PUs were examined by TGA under a nitrogen atmosphere. The TGA curves of PU1, PU2, and PU3 are shown in Fig. 2. $T_{5wt\%}$ and $T_{10wt\%}$ (Tintial based on 5% and 10% mass loss) are summarized in Tab. 1.

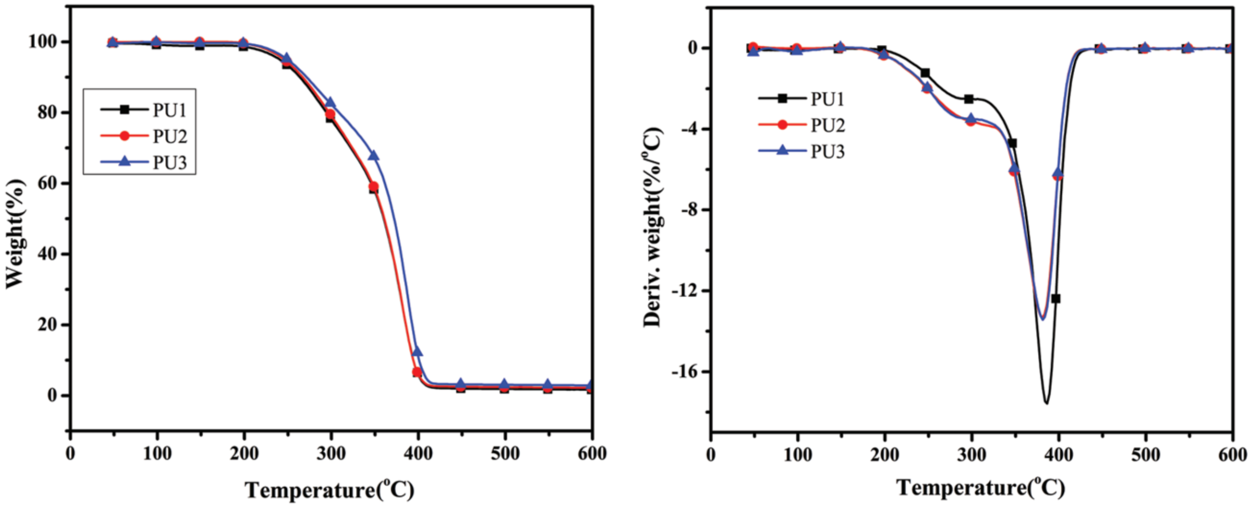


Figure 2: TG/DTG curves of PU1, PU2 and PU3

Table 1: TGA data of PU1, PU2 and PU3

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)
PU1	254.7	279.2
PU2	246.4	266.7
PU3	240.9	261.4

Each of the PU samples displayed similar TGA curves. Samples decomposed occurred in two stages. The first stage was the thermal evaporation of small molecules formed by the cleavage of the phenolic urethane at high temperature. The second stage was the thermal decomposition of the polyurethane polymer matrix.

The $T_{5wt\%}$ of PU1, PU2, and PU3 was 254.7°C, 246.4°C and 240.9°C, respectively and the the $T_{10wt\%}$ were 279.2°C, 266.7°C, and 261.4°C, respectively. Thus, as the isocyanate content increased, the initial thermal decomposition temperature of the polyurethane gradually decreased. This may be because, as the isocyanate content of polyurethane prepolymer increased, the esterification reaction of propyl gallate increased, which had lots of electron-with drawing groups of propyl esters on the phenyl ring. The electron-with drawing group and the steric effect reduced the negative charge density of the phenolic hydroxyl group on the benzene ring and reduced the thermal stability of the phenolic urethane in PU [16-18].

3.3 Mechanical and Self-healing Properties

3.3.1 Mechanical Properties

Mechanical properties, particularly tensile strength and elongation at break, determine the application scope of polyurethane materials. A universal testing machine was used to determine the tensile strength and elongation at break of PU1, PU2, and PU3. Fig. 3 shows the stress-strain curves of the samples. As shown in Fig. 3, as isocyanate content increased, tensile strength and elongation at break both were enhanced in all three samples. The PU3 had the highest tensile strength and elongation at break (2.21 MPa, 716.0%). This was likely due to enhancement of the crosslink density and rigid groups in PU3 with the increased propyl gallate content [19-20].

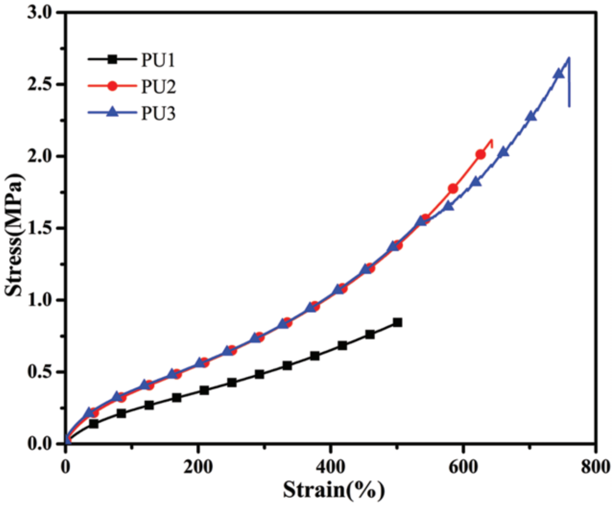


Figure 3: Stress-strain curves of PU1, PU2 and PU3

3.3.2 Self-healing Properties

To study the self-healing ability of gallic acid-based polyurethane, the tensile strength and elongation at break of PU1, PU2, and PU3 were tested before and after healing. Self-healing efficiency was calculated as follows (1) and (2), with the corresponding data summarized in Tab. 2.

$$\text{Self}-\text{healing efficiency stress} = \text{Tensile strength after healing}/\text{Tensile strength original} \times 100 \tag{1}$$

$$\text{Self}-\text{healing efficiency strain} = \text{Elongation at break after healing}/\text{Elongation at break original} \times 100 \tag{2}$$

Table 2: The self-healing efficiencies of PU1, PU2 and PU3

Sample	Tensile strength Healing (%)	Elongation at break Healing (%)
PU1	50.5	73.4
PU2	65.2	79.6
PU3	73.9	97.3

The stress-strain curves of PU3 for varying self-healing time duration are shown in Fig. 4. At the healing time of 10 and 15 h, the mechanical properties of the sample were partially recovered and exhibited good self-healing ability. After healing for 15 h, the stress was 1.19 MPa, with strain of 742.0%. The self-healing efficiency of tensile strength and elongation at break were 63.1% and 97.3%, respectively. The mechanical property was almost recovered and the sample was unbroken at the crack surfaces during the

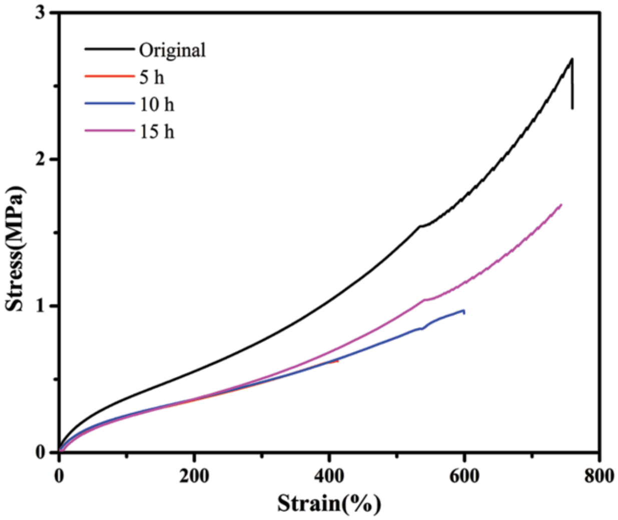


Figure 4: Stress-strain curve of self-healing PU3 at 130°C for various self-healing times

tensile testing. The bonding force and the movement of molecular chains between the interfaces were enhanced with time, and were quite remarkable for a thermoset elastomeric material [21-23].

As shown in Fig. 5 and Tab. 2, the self-healing efficiency of tensile strength for PU1, PU2, and PU3 were 50.5%, 65.2%, 73.9%, respectively. The self-healing efficiencies of the elongation at break were 74.3%, 79.6%, 97.3%, respectively. As the isocyanate content increased, self-healing efficiency was strengthen. The damaged polyurethane achieves self-healing by breaking and recombining phenolic carbamate bonds at a specific temperature. As the isocyanate content increased, the rate at which phenolic urethane bonds broke and recombined increased [24].

The self-healing mechanism of polyurethane with phenolic urethane bonds can be attributed to two reasons: Firstly, the phenolic urethane can decompose into phenol and isocyanate through a reversible reaction at high temperature, and then re-form at another temperature. Secondly, the hydrogen bonds between urethanes can promote contact between the fracture surfaces.

3.4 Dynamic Thermomechanical Analysis

The samples (PU1, PU2, and PU3) were examined using dynamic thermomechanical analysis (Fig. 6). The trends of the three storage modulus curves were similar. The storage modulus gradually declined with the temperature rise within the range of −80 to 10°C. The storage modulus was stable above 10°C. The highest storage modulus of the three samples was seen in PU3. As the isocyanate content increased, the storage modulus of the PU gradually increased due to the cross-linking density and the hydrogen bonding between the urethane groups.

Glass transition temperature (Tg) is the main indicator of the low-temperature resistance of polyurethane materials. The temperature corresponding to the tanδ maximum was taken as the Tg of the PUs. With greater isocyanate content, the Tg gradually increased. This is likely because, wthe PU polar groups increased at higher propyl gallate content, while the intermolecular forces and hydrogen bonds were strengthened, enhancing Tg [25-28].

3.5 Macro- and Micro-structural Analysis

The self-healing behavior of PU3 was studied with a camera and an anoptical microscope (Fig. 7). The self-healing process of PU3 consists of three parts. The PU3 was first cut into two sections,which then

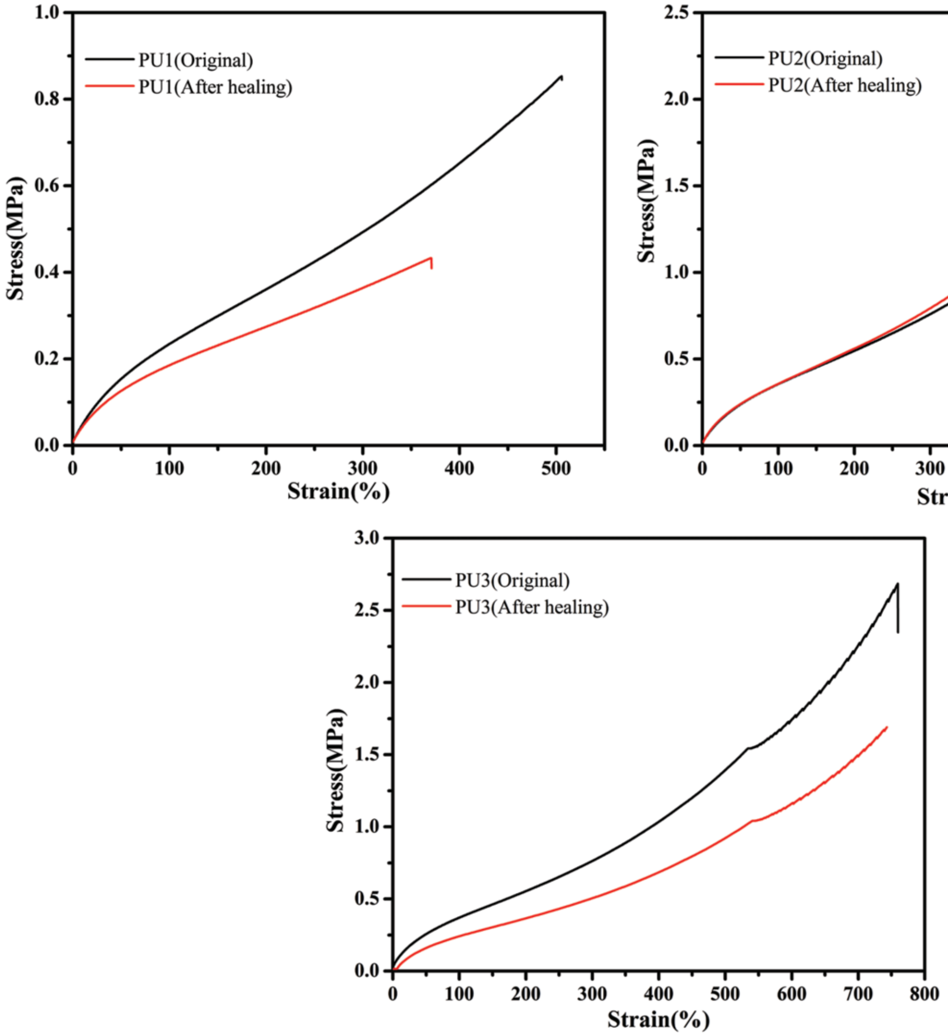


Figure 5: Strain-stress curves for the original and healed PU1, PU2 and PU3

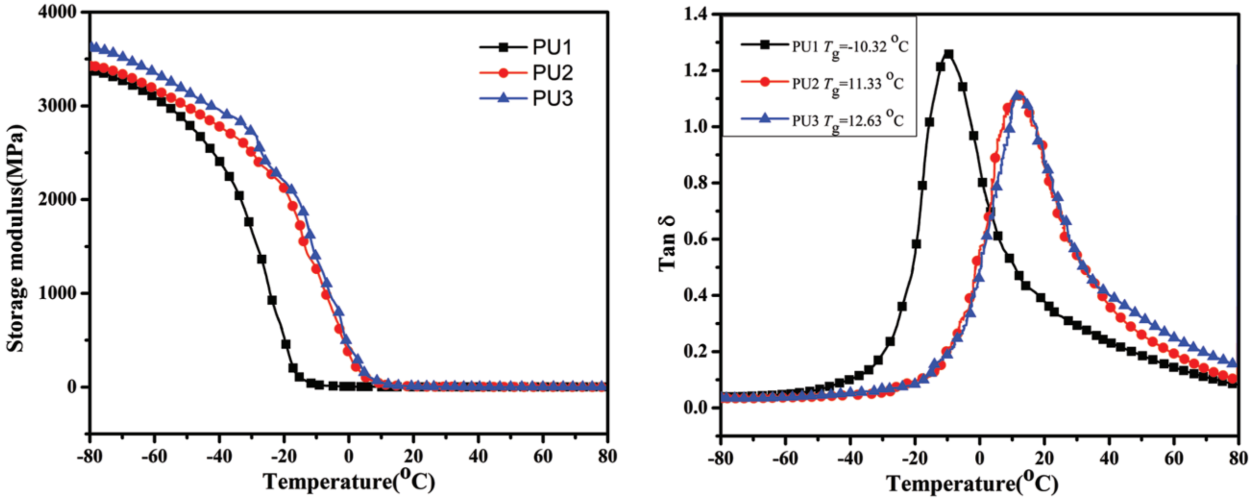


Figure 6: DMA curves of the different PU samples

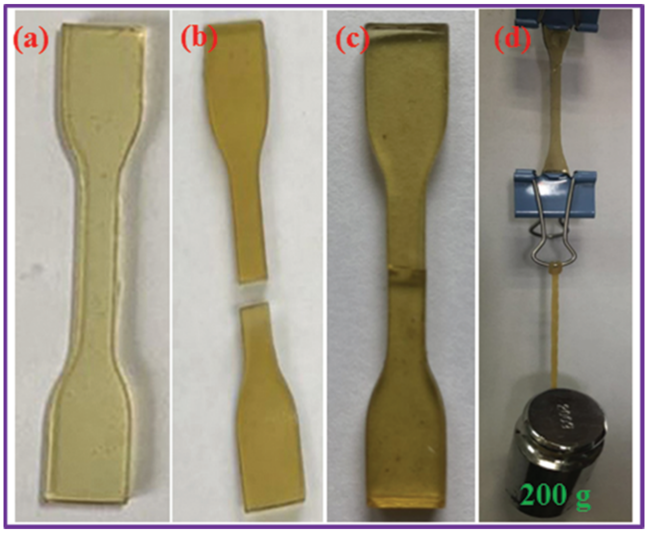


Figure 7: Digital images of PU3 after self-healing at 130°C for 15 h

seamlessly contacted and heated at 130°C for 15 h. Finally, the two sections were reconnected to form a whole. The self-healed PU was able to bear at least 200 g. The PU with phenolic urethane successfully self-healed and demonstrated high thermal reversibility [29].

Figure 8 shows the microstructure of PU3 after self-healing at 130°C for 0, 10, and 15 hours. We observed that the scratches gradually decreased with time. After 15 h, the scratches nearly disappeared. These microscopic results agree well with our stress-strain results [30].

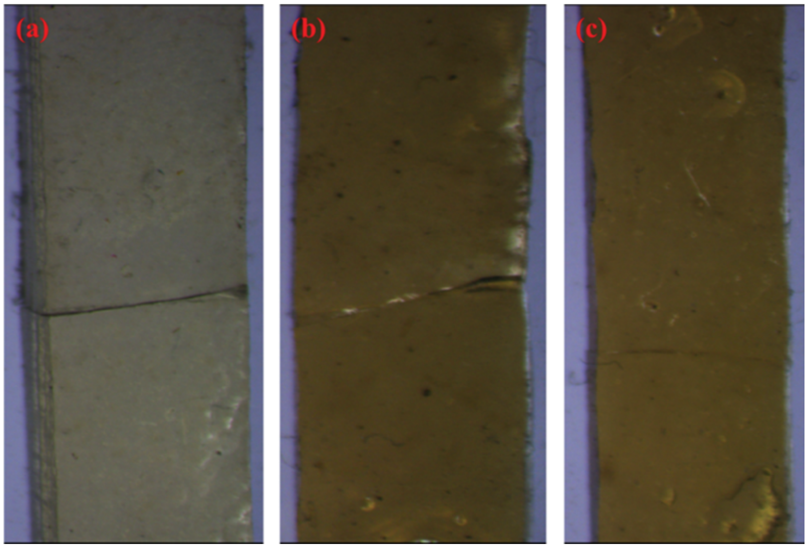


Figure 8: Optical microscope images of PU3 after self-healing at 130°C for (a) 0 h, (b) 10 h, (c) 15 h

4 Conclusions

Three environmental friendly and self-healing propyl gallate-based polyurethanes were prepared using polyurethane prepolymers with varying isocyanate contents. The thermal self-healing of thermosetting polyurethane can be achieved through the introduction of phenolic urethane and its dynamic covalent bonds. As the isocyanate content of the polyurethane prepolymer increased, the initial thermal decomposition temperatures of the PU gradually decreased. Furthermore, the tensile strength, elongation at break, storage modulus, and glass transition temperatures of the PU increased. Finally, the PU samples had excellent thermal self-healing properties with a self-healing efficiency above 50%.

Acknowledgement: This project was supported by the National Natural Science Foundation of China. (Grand No. 31570563), Jiangsu Province Biomass Energy and Materials Laboratory, China (Grant No. JSBEM-S-201807), Fundamental Research Funds of Chinese academy of forestry (CAFYBB2017MB017).

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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