Preparation and Properties of Self-Healing Polyurethane Elastomer Derived from Tung-Oil-Based Polyphenol

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ABSTRACT: A tung-oil-based polyphenol (ATOM), containing the phenolic hydroxyl group, was synthesized from tung oil and 4-maleimidophenol by the Diels–Alder addition reaction. Then self-healing thermostetting polyurethanes were prepared from ATOM and the polyurethane prepolymer. The chemical structure and cross-link network were confirmed by Fourier transform infrared spectroscopy (FTIR) and swelling tests. The products partially dissolved in trichlorobenzene when the temperature rose to 110 °C. Temperature-variable FTIR confirmed that the phenolic urethane starts to partially dissolve at 100 °C, which can be explained by the experimental phenomenon in swelling tests. Tensile property analysis showed that the broken and healed thermosets maintained about 46–64% of their original tensile strengths and 81–88% of their original elongations at break, respectively.

1. INTRODUCTION

Thermosetting polyurethanes are extensively used in coatings and adhesives because of their thermal stability and solvent resistance. However, the annually increasing industrial demand of polyurethanes has led to the dump of abundant polyurethane materials.1–5 The stable cross-linking network of thermosetting polyurethanes accounts for their implicity and unrecoverability, which lead to resource waste and environmental pollution. For this reason, self-healing polyurethanes become a new development trend due to the internal ability to restore physical failures and microcracks.6 Self-healable polyurethanes can be produced through dynamic covalent bonding (e.g., Diels–Alder (DA) or retro-DA reaction7–10 esterification11, disulfide bonds,12–15 acylhydrazone bond,16 alkoxyamine chemistry,17 transcarbamoylation,18,19 nitroxides20,21) or noncovalent bonding (e.g., H2 bonding,22 π–π stacking,23 metal-ion binding24). The noncovalent method based on hydrogen bonding or metal–ligand linking can heal a polymer repeatedly but largely weakens the noncovalent connection. In comparison, covalent bonds particularly strengthen the restoring performance of polymers.

Among the dynamic covalent bonds, the disulfide or acylhydrazone bond and the DA reaction are of high significance for self-healable polyurethanes. The intrinsic self-repair of the disulfide bond is based on its instability. Under certain conditions (e.g., temperature, pH, illumination), the covalent bonds easily break and recombine with other sulfur atoms to achieve self-repair as well as redox reaction between the disulfide bond and sulfhydryl groups.12–15 The formation and fracture of acylhydrazone bonds are reversible under acidic conditions, which underlie the preparation of hydrogels with a reversible gel–sol conversion property.25 However, this reversible reaction only occurs in acidic solutions and does not apply to general polymer materials. Unlike other essential self-healing approaches, the DA reaction is suitable for production of self-healing polymers owing to its gentle conditions, less side reactions, and heat reversibility. However, the reverse reaction temperature of most DA reactions is very high, and many reverse reactions can only produce stable aromatic compounds instead of dienes or dienophiles.7–10 This is why self-healable polyurethane research on DA reactions is mostly limited to the reversible DA reactions between maleimide and furan.7–10 The self-repair capability of polymers is particularly attributed to these reversible covalent bonds, which must be incorporated to polymers in the above self-

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healing systems. Enthetic groups are essentially important in such a complicated process.

Here, we aimed to clarify the possibility of producing self-healing thermosetting polyurethanes. The urethane bonds in common polyurethanes consisting of isocyanate and alcoholic hydroxyl groups are stable and undergradable. Similarly, phenolic hydroxyl reacts with isocyanate, and phenolic urethane can reversibly degrade into phenol and isocyanate. Thus, self-repairing thermosetting polyurethanes can be produced without introducing other special functional groups. As reported, with urushiol, propyl gallate, catechol, and tert-butylhydroquinone instead of polyol as polyphenols, Cao et al. prepared a cross-linked self-healing polyurethane under heating.27,28

Plant oils are valuable eco-friendly feedstock of industrial materials. The dry tung oil fatty acids (TOFAs) consist of ~80% eleostearic acid with three conjugated double bonds. Noticeably, the DA reaction between TOFAs and dienophile is very easy.29 The efficient, versatile, and selective DA reaction can also be conducted to prepare thermosetting polymers. Ideally, the preparation routes should be efficient and convenient in which industrial bio-feedstock is often used in accordance with sustainability plans.30,31 Inspired by the reversible reaction between phenolic hydroxyl and isocyanate, here, we planned to prepare a self-healing and recyclable thermoset polyurethane via the cross-linked reversible reaction between tung-oil-based polyphenol (ATOM) and isocyanate. The ATOM was prepared from natural tung oil in a facile and universal way. This study presents this bio-friendly substance with a phenolic hydroxyl group and long-chain structure, which offers high compatibility and thermal self-healing ability to phenolic polyurethanes.

2. MATERIALS AND METHODS

2.1. Materials. The tung oil used in this study was purchased from the Luodian County Anling Vegetable Oil Plant, China. 4-Maleimidophenol (98%, Tianjin Heowns Biochem LLC, China) and ethyl acetate (AR, ≥99.5 wt %, Nanjing Chemical Reagent Co., Ltd., China) were used as received. Dibutyltin dilaurate (95%) was obtained from Aladdin Industrial Corporation. Prepolymer (PTHFTDI) with an NCO content of 6.2%, which compounded from polytetrahydrofuran and toluene diisocyanate and has a relative molecular weight of 1350, was obtained from Shanghai Jiren International Trading Co., Ltd., China.

2.2. Synthesis. Tung oil can be used to prepare eleostearic acids, which mainly include the α-isomer (cis-9,trans-11,trans-13-octadecatrienoic acid) and β-isomer (trans-9,trans-11,trans-13-octadecatrienoic acid).32 However, the DA reaction only occurs with the trans–trans conjugated bi-bonds.33,34 To check the content of tung oil eleostearic acids, we obtained methyl esters of TOFAs via alcoholysis. Figure 1 shows the total ionization gas chromatograph (GC) and composition of methyl esters of TOFAs. The methyl esters consisted of 83.77% methyl eleostearates. Thus, tung oil contained 83.77% methyl esters of TOFAs. The methyl esters consisted of 83.77% eleostearic acids in glyceride.

Figure 2 illustrates the generation path of the adduct of tung oil and 4-maleimidophenol (ATOM). According to the eleostearic acid contents in glyceride, the molar ratio of 4-maleimidophenol to eleostearic acid was 1:1. Tung oil (100 g) and 4-maleimidophenol (53.74 g) were loaded into a 500 mL four-neck flask for 2.5 h of reaction at 140 °C, forming the brownish red ATOM.

2.3. Preparation of Tung-Oil-Based Polyurethanes. At a phenolic hydroxyl to isocyanate molar ratio of 1:1, 0.5% dibutyltin dilaurate as the catalyst was added to the total mass of polyphenol and PTHFTDI. After ATOM, PTHFTDI and dibutyltin dilaurate were all dispersed in ethyl acetate, and the mixed solutions were heated to 50 °C and vacuumed to remove the bubbles (0.098 MPa). The resulting solutions were poured onto four tetrafluoroethylene plates and cured at 50 °C/2 h + 80 °C/8 h and 50 °C/2 h + 80 °C/4 h + 120 °C/8 h. The products were labeled PTHFTDI-ATOM-80 and PTHFTDI-ATOM-120, respectively (abbreviated as PU-80, and PU-120, respectively). Figure 3 illustrates the reversible cross-linked reactions between phenol hydroxyls and isocyanates. Figure 4 shows the thermoset polyurethane network from phenol urethanes.

2.4. Characterization. 2.4.1. Gas Chromatogram Analysis (GC). The METOFA concentration was detected via an Agilent 7890A GC under the N2 condition, with acetone as the solvent, and equipped with an Agilent HP-5 capillary column (Agilent, USA). The oven started at 100 °C for 1 min, then heated at 10 °C/min to 280 °C, and held there for 10 min.

2.4.2. Fourier Transform Infrared Spectroscopy (FTIR). The chemical structures of tung oil, 4-maleimidophenol, ATOM, PTHFT, the prepolymer, and the self-healing polyurethane were determined by an FTIR device (Nicolet IS10 Instrument, USA) within 4000–400 cm−1 in the total reflection mode.

The temperature-variable FTIR was conducted on an IS10 FTIR device (Nicolet, Waltham, MA, USA). The samples smeared on a NaCl window plate were cured at 80 or 120 °C for 8 h and then tested from 4000 to 400 cm−1 under the transmission mode. The temperature program was as follows: 30 °C for 3 min, ramping to 190 °C, and cooling to 120 °C with holding for 3 min per 10 °C.

2.4.3. Nuclear Magnetic Resonance (NMR). The 1H-NMR spectra of tung oil, 4-maleimidophenol, and ATOM in deuterated chloroform were recorded on an AVANCE III HD 400 MHz spectrometer at ambient temperature.

2.4.4. Thermal Gravimetric Analysis (TGA). TGA was tested on a NETZSCH STA 409 PC (Netzsch, Germany) from 25 to 600 °C (10 °C/min) and under a nitrogen condition.
2.4.5. Dynamic Mechanical Analysis (DMA). DMA was performed on a Q800 DMA device (TA Instruments, USA) with a film tension configuration and oscillation at 1 Hz and from −80 to 180 °C at 3 °C/min. The sample dimensions were about 40 mm (L) × 7 mm (W) × 0.6 mm (T).

2.4.6. Mechanical Properties. Tensile strength, Young’s modulus, and elongation at break were detected on a CMT4303 universal test instrument (SANS, China) as per GB/T 13022-1991 type II at a speed of 100 mm/min and region of 20.0 mm (L) × 4.0 mm (W) × 0.6 mm (T). To ensure accuracy, all samples were detected at 25 °C in quintuplicate.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. Figure 5 shows the FTIR spectra of tung oil, 4-maleimidophenol, and the adduct of tung oil and maleimidophenol (ATOM). The characteristic peaks at 3401 and 3477, 3032 and 3112, and 2924 and 2853 cm⁻¹ corresponded to the stretching vibrations of phenol hydroxyl, olefin C–H, and methyl and methylene groups, respectively. The peaks at 1742 and 991 cm⁻¹ were ascribed to the ester group and conjugate double bond, respectively. The strong peaks of the conjugate double bonds at 991 and 1063 cm⁻¹ almost disappeared in the spectra of ATOM compared with those of tung oil and 4-maleimidophenol, respectively. The FTIR spectra imply the occurrence of a DA reaction in the double bonds.

The ¹H-NMR spectra of tung oil, 4-maleimidophenol, and ATOM are shown in Figure 6 in which the attribution of the major ingredient is shown below:
proton chemical shift is labeled. Tung oil and ATOM are both in single isomeric structures (Figure 6). The chemical shifts of the conjugated triene protons in tung oil are 5.69–6.72, 6.38–6.45, and 6.08–6.20 ppm. Clearly, the peaks at 7.14–7.23 ppm correspond to the double bond of the ester in the maleimide ring of 4-maleimidophenol. Compared with tung oil and 4-maleimidophenol, the peaks at 6.38–6.45 and 6.08–6.20 ppm ascribed to the conjugated triene protons were nearly not found in the spectra of ATOM. Nevertheless, the new peaks at 3.2–3.4 ppm imply the presence of a six-atom ring in ATOM. The FTIR and \(^1\)H-NMR spectra validate the successful preparation of ATOM.

3.2. Polymerization and Characterizations of the Self-Healing Network. Figure 3 illustrates the reversible cross-linked reactions between ATOM and PTHFT. Infrared spectra of PTHFT, ATOM, PTHFT-ATOM (0 min), PU-80, and PU-120 verified the polymerization (Figure 7). PTHFT-ATOM (0 min) means that the PTHFT and ATOM are first mixed and PU-80 and PU-120 heated in nitrogen at 10 °C/min, and Table 1 lists the temperature at 5% weight loss (T\(_{5\%}\)), the maximum weight losses in the first and second stages (T\(_{max,1}\), T\(_{max,2}\)) and char yields at 300, 400, and 600 °C (W\(_{res,300}\), W\(_{res,400}\), W\(_{res,600}\)). Compared with PU-80, the above five indices of PU-120 are all slightly larger, suggesting that the thermal stability of PU-120 is higher than that of PU-80.

Glass transition temperature (T\(_g\)) refers to the temperature at the peak on the tan δ versus temperature curve. Viscoelastic characteristics, including tan δ variation with temperature, are usually detected via DMA. Figure 9 shows the storage modulus (E') and loss factor (tan δ) of PU-80 and PU-120. The T\(_g\)s of PU-80 and PU-120 are 0.10 and −2.42 °C, respectively, indicating that the two samples both have one T\(_g\) and these polymer systems are uniform and congenial. The storage modulus profiles in Figure 5 show that the storage modulus of PU-120 is higher than that of PU-80 between −80 and −20 °C. The difference of E' was primarily attributed to the self-structure of the polymer. According to thermogravimetric analysis, it can be found that the thermal stability of PU-120 is higher than that of PU-80. This may be due to the fact that PTHFT and ATOM were cross-linked more fully at higher temperatures. PU-120 had the higher cross-link density and then exhibited the higher storage modulus than PU-80 between −80 and −20 °C. Cross-linking density (ν\(_c\)) can be calculated by the rubber elasticity theory with storage modulus (E') in the rubber state\(^{28,59}\)

\[
E' = 3\nu_cRT
\]

where T is the temperature in kelvin (K) and R is the ideal gas constant (8.314 J/mol-K). In this study, E' at T\(_g\) + 30 K was selected for calculation of \(\nu_c\) which ensured that the copolymerized systems were in the rubber state. The \(\nu_c\) of each copolymerized system is shown in Table 2.

Table 2 shows the \(\nu_c\)'s of PU-80 and PU-120 of different cured systems. From Table 2, PU-80 and PU-120 had nearly the same cross-linking density, and the \(\nu_c\) of PU-120 was slightly higher than that of PU-80. In PU-120, higher cured temperature might be more helpful to overcome the effect of steric hindrance in copolymerized system. Thus, PU-120 had higher cross-linking density than PU-80.

3.4. Depolymerization of the Self-Healing Network of Phenolic Polyurethanes. 3.4.1. Dissolution of Phenolic Polyurethanes. Thermoset polymers with the dimensional network hardly dissolve and only swell in organic solvents, even at high temperature. The polyurethanes were put into trichlorobenzene at 25 °C and then heated to 80, 100, or 110 °C.
to test the volume variation (Figure 10). The initial volumes of PU-80 and PU-120 at 25 °C were both 1 cm\(^2\). After soaking at 80 and 100 °C for 5 h, both samples swelled and the volumes were enlarged to 2.9 and 4 cm\(^2\) (PU-80) and to 2.59 and 4 cm\(^2\) (PU-120), respectively. When at 100 °C, PU-80 and PU-120 were still insoluble, but after 5 h of immersion at 110 °C, both samples were partially trichlorobenzene-soluble. The underlying reason was that the polyurethane networks became unstable and were partially destroyed by the temperature rise in the solvent. After further soaking in the solvent at 120 °C, the samples were nearly all dissolved, suggesting that the networks were fully destroyed after the temperature rise. The dissolution tests confirm that the covalent bonds were partially cut off from the network, so the network dissolved at 120 °C.

3.4.2. Temperature-Variable FTIR. The separation and rebound of the reversible urethane bonds and the decomposition temperatures of PTHFTDI-ATOM were dynamically tracked by temperature-variable FTIR, which clarified the variation of covalent bonds. The PTHFT-ATOM was dissolved, bubble-removed, uniformly mixed, cast on the NaCl window, and healed at 80 °C for 8 h. The samples were scanned from 25 to 190 °C and then cooled to 110 °C (Figure 11). The cleavage initial temperature \(T_c\) of phenolic urethane generally corresponds to the peak of \(-\text{NCO} (2273 \text{ cm}^{-1})\) that starts to appear in the temperature-variable FTIR spectra. Herein, the peak of \(-\text{NCO}\) was not found from 25 to 90 °C but appeared above 100 °C. This result is highly consistent with the dissolution tests. Moreover, the peak of \(-\text{NCO}\) was not strengthened at above 150 °C, implying the new balance in reversible reaction between phenolic hydroxyl and \(-\text{NCO}\). The peak of NCO vanished again after cooling down to 110 °C in 0.5 h. The isocyanate and phenolic hydroxyl groups

![Figure 8. TG and TGA curves of different specimens.](image)

### Table 1. Thermal Properties of Different Specimens at a Constant Heating Rate

| Sample | \(T_{5\%}\) \(^{a}(\degree C)\) | \(T_{max}^{b}(\degree C)\) | \(T_{max}^{c}(\degree C)\) | \(W_{res}^{300}(\%)\) | \(W_{res}^{400}(\%)\) | \(W_{res}^{600}(\%)\) |
|--------|-----------------|-----------------|-----------------|----------------|----------------|----------------|
| PU-80  | 256.2           | 292.2           | 421.7           | 89.29          | 67.52          | 7.39           |
| PU-120 | 261.9           | 293.9           | 423.7           | 90.04          | 68.56          | 7.56           |

\(^{a}\)T\(_{5\%}\) is the temperature at which 5% weight loss is incurred. \(^{b}\)T\(_{max}^{a}\) and T\(_{max}^{b}\) are the maximum weight losses in the first and second stages, respectively. \(^{c}\)W\(_{res}^{300}\), W\(_{res}^{400}\), and W\(_{res}^{600}\) are the residue yields at 300, 400, and 600 °C, respectively.

![Figure 9. DMA curves of PU-80 and PU-120.](image)

### Table 2. \(T_g+30\), \(E'\) at \(T_g+30\), and \(\nu_e\) values of PU-80 and PU-120

| Sample | \(T_g+30\) \(^{a}(\degree K)\) | \(E'\) at \(T_g+30\) \(^{b}(\text{MPa})\) | \(\nu_e\) \(^{c}(\text{mol/m}^3)\) |
|--------|-----------------|-----------------|----------------|
| PU-80  | 328.25          | 1.83            | 223.52         |
| PU-120 | 325.73          | 2.06            | 253.56         |

\(^{a}\)T\(_g+30\) is the temperature at which 5% weight loss is incurred. \(^{b}\)E' at \(T_g+30\) is the storage modulus at \(T_g+30\). \(^{c}\)\(\nu_e\) is the mass density.
bonded again in this slow cooling process, which facilitated the reversible polyurethane connection.

3.5. Self-Healing Behavior of Phenolic Polyurethanes. Considering the self-repairing ability, we aimed to test the possibility of mechanical recovery after failure and self-curing. The self-repair is essentially ascribed to the “separation and reconnection” between the phenolic hydroxyl and NCO groups. The dissolution tests and temperature-variable FTIR both suggest that the occurring temperature of the reversible reaction between phenolic hydroxyl and isocyanate is about 100−110 °C. Thus, we set the self-healing temperature at 110 °C. A dumbbell-like sample was scissored in the middle, and the two cut surfaces were immediately put tightly with no pressure applied (Figure 12). After heating to 110 °C in a convection oven, the two pieces self-healed after 10 h. The two pieces resisted severe deformation despite a crack scare (Figure 12).

The self-curing behaviors of PU-80 and PU-120 were compared via tensile analysis. Self-curing ability is defined as the ratio of tensile properties before and after the curing (Table 3). The tensile strength and elongation at break of PU-80 decreased from 1.46 to 0.68 MPa and from 1093.50 to 963.89% after healing, respectively, indicating that the self-cured PU-80 maintained about 46.57 and 88.15% of the initial tensile properties, respectively. In comparison, the self-healed PU-120 maintained about 64.20 and 81.25% of the initial tensile properties, respectively. Our previous work used the same prepolymer (abbreviated to PTHFT or PTHFTDI) with an NCO content of 6.2%, which compounded from polytetrahydrofuran and toluene diisocyanate. Propyl gallate, catechol, and tert-butylhydroquinone were chosen for preparation of three phenolic polyurethanes.27 According to the tensile property analysis, it could be learned that the self-healing abilities of the initial elongation at break of these three kinds of polyurethanes were in the following order: PTHFTDI-propyl gallate (93.67%) > PTHFTDI-urushiol (72.01%) > PTHFTDI-catechol (68.63%).27 This study presents another bio-friendly substance with a phenolic
hydroxyl group and long-chain structure, which offers high compatibility and thermal self-healing ability to phenolic polyurethanes. The temperature-variable FTIR suggests the partial dissociation of phenolic urethane. Thus, when the cracked surfaces of the broken samples were interlinked, the destroyed tensile properties cannot be completely repaired. When the cracked surfaces were put in air, the isocyanate reacted with atmospheric water to form covalent urea bonds, which were irreversible under the tested conditions. Thus, the cracked surfaces can be passivated by water, so the self-healing ability of the broken samples was weakened. However, the healed samples were efficiently cured and recovered the mechanical properties to the original levels.

4. CONCLUSIONS

The adduct of tung oil and 4-maleimidophenol (ATOM) was successfully prepared from the Diels–Alder reaction of tung oil. Self-curing thermoset polyurethanes were synthesized from ATOM and the polyurethane prepolymer. The polymerization of the self-healing network was tested via FTIR, temperature-variable FTIR, TGA, and DMA. Specifically, reversible urethane bonds were formed from phenol hydroxyls and isocyanates that can separate under heating and rebind upon cooling. These urethane bonds contributed to the self-repair of the thermoset polyurethane network via temperature regulation. The products were elastomers and did not dissolve in organics below 110 °C. The self-healing thermosets achieved about 81–88% and 46–64% of the initial elongation at break and tensile strength, respectively, and thus are applicable to self-curing coatings or adhesives.

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The authors declare no competing financial interest.

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