

Solvent-Free Synthesis of Self-Healable and Recyclable Crosslinked Polyurethane Based on Dynamic Oxime-Urethane Bonds

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Electronic Supplementary Information

Abstract Polyurethane is widely used for its versatility in design and range of performance. Self-healing and recyclable dynamic polyurethane networks have attracted extensive attention due to their potential to extend service life and ensure safety in use, as well as to promote sustainable use of resources. Developing green and environment-friendly methods to obtain this material is an interesting and challenging task, as the majority of current dynamic polyurethane networks utilize the solution polymerization method. The use of solvents makes the processes complicated, harmful to environment, and increase the cost. Poly(oxime-urethanes) (POUs) are emerging dynamic polyurethanes and show great potential in diverse fields, such as biomaterials, hot melt adhesives, and flexible electronics. In this study, we utilized the solubility properties of dimethylglyoxime in raw material poly(ethylene glycol) to prepare POUs through bulk polymerization for the first time. This method is simple, convenient and cost-efficient. Simultaneously, copper ion coordination improves POUs strength and dynamic properties, with mechanical strength up from 0.54 MPa to 1.03 MPa and self-healing recovery rate up from 85.5% to 91.8%, and activation energy down from 119.6 kJ/mol to 95.4 kJ/mol. To demonstrate the application of this technology, self-healing and stretchable circuits are constructed from this dynamic polyurethane network.

Keywords Polyurethane; Dynamic covalent bonds; Oxime-urethane bonds; Self-healing; Recycle

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INTRODUCTION

Polyurethane is a versatile and widely utilized material with an annual output of nearly 30 million tons, accounting for 7.9% of the total plastic production.^[1,2] Furthermore, polyurethane is the dominant class of cross-linked polymers, representing 31% of the total thermoset materials market.^[3] Thermoset polyurethane, with its cross-linked structure, offers superior solvent resistance, thermal stability, and mechanical properties, making it a preferred choice in demanding applications such as aerospace.^[4] Despite its benefits, traditional thermoset polyurethane is not recyclable or reusable after molding, resulting in waste of resources and environmental pollution.^[5] Hence, there is a need to develop polyurethanes that combine the stability of cross-linked thermoset polyurethane with the processability of linear thermoplastic polyurethane.

The introduction of dynamic covalent bonds into cross-linked polyurethanes can break down the strict boundary between thermoplastic and thermoset polyurethanes.^[6,7] These bonds can be broken and re-formed spontaneously or

through external stimuli such as light,^[8,9] heat,^[10] pH,^[11,12] and catalysts.^[13] The application of a stimulus can disrupt the dynamic covalent bonds in the cross-linked polyurethane, leading to its processability.^[14,15] Upon removal of the stimulus, the cross-linked polyurethane with dynamic chemical bonds retains the same stability as traditional thermoset polyurethanes. In addition, this type of polyurethane also exhibits unique features such as self-healing,^[6] stimulus response,^[11] controllable degradation,^[16] etc. The introduction of dynamic covalent bonds endows cross-linked polyurethane with excellent comprehensive properties. However, the crosslinked network restricts the mobility of chains, hindering the exchange capacity of dynamic covalent bonds. Balancing the demands for stability and dynamic performance remains a significant challenge in the development of dynamic covalent polyurethane networks.^[17,18] Furthermore, due to the poor solubility between monomers, the method of solution polymerization is often utilized in the production of dynamic polyurethanes.^[19] This method is more complex and costly compared to the bulk polymerization method commonly used in the industrial production of polyurethane, limiting its further advancement. Besides, during production, the release of these solvents into the air can lead to pollution, while the existence of residual organic solvents in the final product can create

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safety hazards for consumers. Efforts towards reducing the use of organic solvents, simplifying the preparation process, and lowering the cost of synthetic monomers are crucial for overcoming these challenges.^[19]

The oxime-urethane bonds (DOU bonds) are cutting-edge dynamic covalent bonds that have gained attention in recent times.^[20] Polyurethanes incorporating this type of bond are referred to as poly(oxime-urethanes) (POUs).^[21] POUs exhibit unique characteristics like self-healing and recyclability,^[22] making them a popular choice for various applications including biomaterials,^[23] hot-melt adhesives,^[24] flexible electronics,^[25] and other fields.^[26] However, their preparation method is limited to solution polymerization.^[21] In this work, after a number of trials, we discovered that dimethylglyoxime (DMG) can be dissolved in raw material poly(ethylene glycol) (PEG), which enabled the successful preparation of the POUs (DOU-PU) by solvent-free bulk polymerization. To address the challenge of balancing both the mechanical and dynamic properties of polyurethane, which are often in conflict due to different requirements for the molecular network, we utilized the strategy of incorporating copper ion coordination with DMG to synthesize Cu-DOU-PU (Fig. 1). The coordination leads to dynamic crosslinking, greatly improving the material's mechanical properties.^[27] Furthermore, the coordination between CuCl₂ and DOU bonds can lower the free energy barrier of the urethane bonds, resulting in better dynamic properties of polymer network.^[17,28] The resulting Cu-

DOU-PU, which contains hydrogen bonds, coordination bonds, and DOU bonds, was found to possess excellent comprehensive properties.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (PEG, $M_n \sim 1000 \text{ g mol}^{-1}$) and isophorone diisocyanate (IPDI, 99%) were purchased from Aladdin. Dimethylglyoxime (DMG, 98%) and copper (II) chloride (CuCl₂, 99%) were purchased from Sinopharm Chemical Reagent. Hexamethylene diisocyanate trimer (3HDI) was purchased from Wanhua Chemical (China). All reagents were used as received without further purification unless otherwise noted.

Synthesis Routes to DOU-PU and Cu-DOU-PU

DOU-PU

PEG (100 g) was added to a glass reactor equipped with a mechanical stirrer and dried at 80 °C for 2 h under vacuum. DMG (11.6 g) and IPDI (36.21 g) were added to the reactor and heated to 80 °C for 3 h under a nitrogen atmosphere. 3HDI (12.43 g) was added and the reaction was continued for 5 h. Then, the reaction mixture was poured into a polytetrafluoroethylene mold and reacted at 100 °C for 23 h to produce DOU-PU.

Cu-DOU-PU

PEG (100 g) was added to a glass reactor equipped with a mechanical stirrer and dried at 80 °C for 2 h under vacuum. DMG (11.6 g), IPDI (36.21g) and CuCl₂ (0.166 g) were added to the

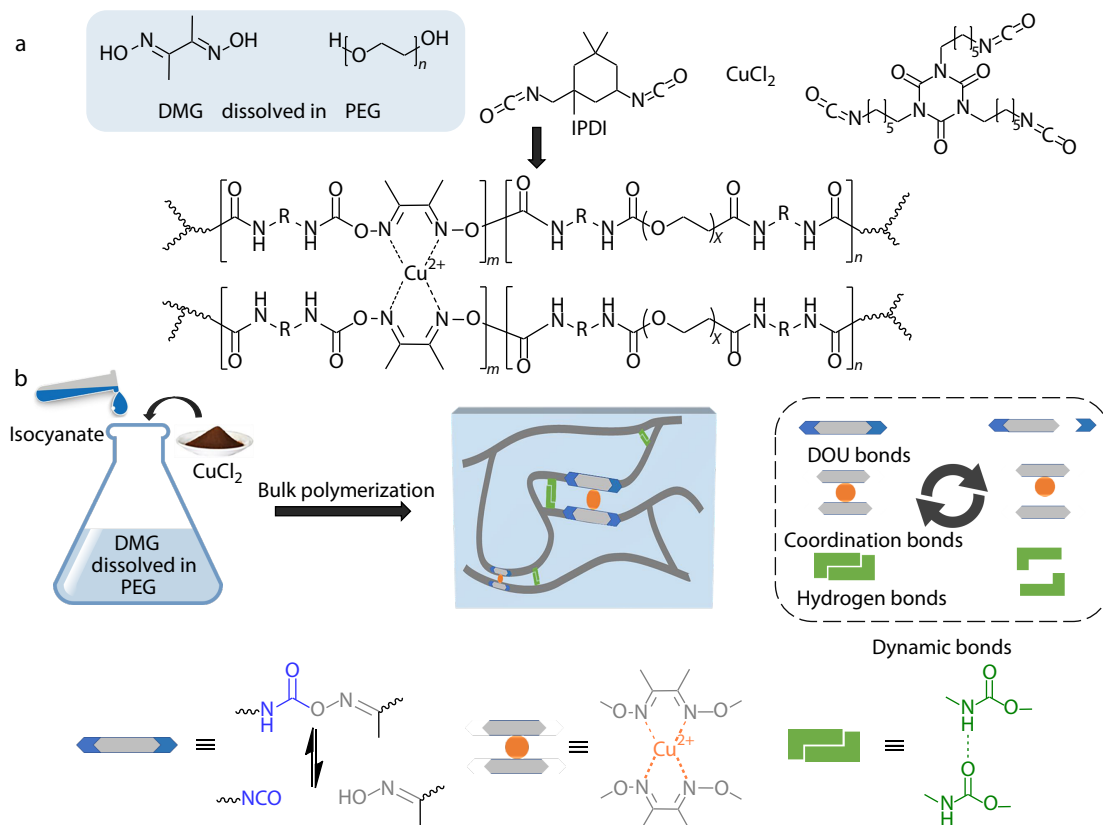


Fig. 1 Design of Cu-DOU-PU elastomer based on triple dynamic bonds. (a) Molecular structure of Cu-DOU-PU elastomer; (b) Schematic diagram of synthesis and structure of Cu-DOU-PU elastomer. Triple dynamic bonds including DOU bonds (blue arc and gray stick), metal coordination bonds (gray stick and orange circle), and hydrogen bonds (green polygons) constructed Cu-DOU-PU.

reactor and heated to 80 °C for 3 h under a nitrogen atmosphere. 3HDI (12.43 g) was added and the reaction was continued for 5 h. Then, the reaction mixture was poured into a polytetrafluoroethylene mold and reacted at 100 °C for 23 h to produce Cu-DOU-PU.

Characterization

All tests were performed at room temperature unless otherwise noted. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 8700 spectrometer with ATR accessory and thermal controller (Thermo Electron Corporation). The spectra were collected through 64 scans with a spectral resolution of 4 cm^{-1} over a wavenumber range of 4000–500 cm^{-1} . Uniaxial tensile tests were performed on an electronic universal testing machine (Changchun Kexin Test Instrument Co., Ltd., WDW3020) at a tensile rate of 50 $\text{mm}\cdot\text{min}^{-1}$. Glass transition temperatures were obtained by differential scanning calorimeter (DSC, NETZSCH, DSC 204F1, China) at a heating rate of 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$ under a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was performed on a DMA1 (Mettler-Toledo) dynamic mechanical analyzer. Rectangular samples were tested at a strain of 0.1%, a frequency of 1 Hz, and a heating rate of 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$. Thermogravimetric analysis (TGA) was performed on a NETZSCH Libra/209F1 instrument under a nitrogen atmosphere at a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$. The transmittance of these sample with a thickness of 0.20 mm was measured by a UV-Vis spectrophotometer (TU-1901/TU-1901), and the wavelength range was 200–800 nm. Then, the stress relaxation test and temperature sweep test were carried out in Anton Paar's high-temperature rotational rheometer. The sample was a disc structure with a diameter of 25 mm and a thickness of about 1 mm. Heating during the temperature sweep from 40 °C to 160

°C at a rate of 3 $^{\circ}\text{C}\cdot\text{min}^{-1}$, with a set strain of 0.5% and a frequency of 1 Hz. A strain of 5% is applied at a constant gap during stress relaxation.

RESULTS AND DISCUSSION

The DOU-PU was synthesized utilizing commercially available raw materials including PEG, isophorone diisocyanate (IPDI), hexamethylene diisocyanate trimer (3HDI), and DMG through a solvent-free one-pot polycondensation method. To improve its properties, copper ions were added and coordinated with DMG to produce the Cu-DOU-PU (Fig. 1). The selection of IPDI with a large bulky structure, which inhibited crystallization and formed loosely packed hard domains that favor chain mobility,^[29,30] was made as the hard segment in order to enhance chain mobility and improve the dynamic properties of the POUs. The 3HDI provides the formation of a crosslinked network to achieve the stability of the POUs. Since the reaction between DMG and isocyanate is slow, it is necessary to check whether the isocyanate reacts completely under the experimental conditions. The structure of the POUs were characterized by FTIR spectroscopy in the attenuated total reflection (ATR) mode. As shown in the FTIR spectra of DOU-PU and Cu-DOU-PU in Fig. 2(a), the absorption band at 2270 cm^{-1} indicating the stretching vibration of isocyanate completely disappeared, indicating the completion of the reaction between DMG and isocyanate. FTIR spectra also indicated the presence of hydrogen bonds (N—H) and C=O bonds (3325 and 1720 cm^{-1} , respectively), which are characteristic groups of polyurethane. The FTIR spectrum of Cu-DOU-PU is found to be similar to that of DOU-PU, indicating that the polymer structure remained

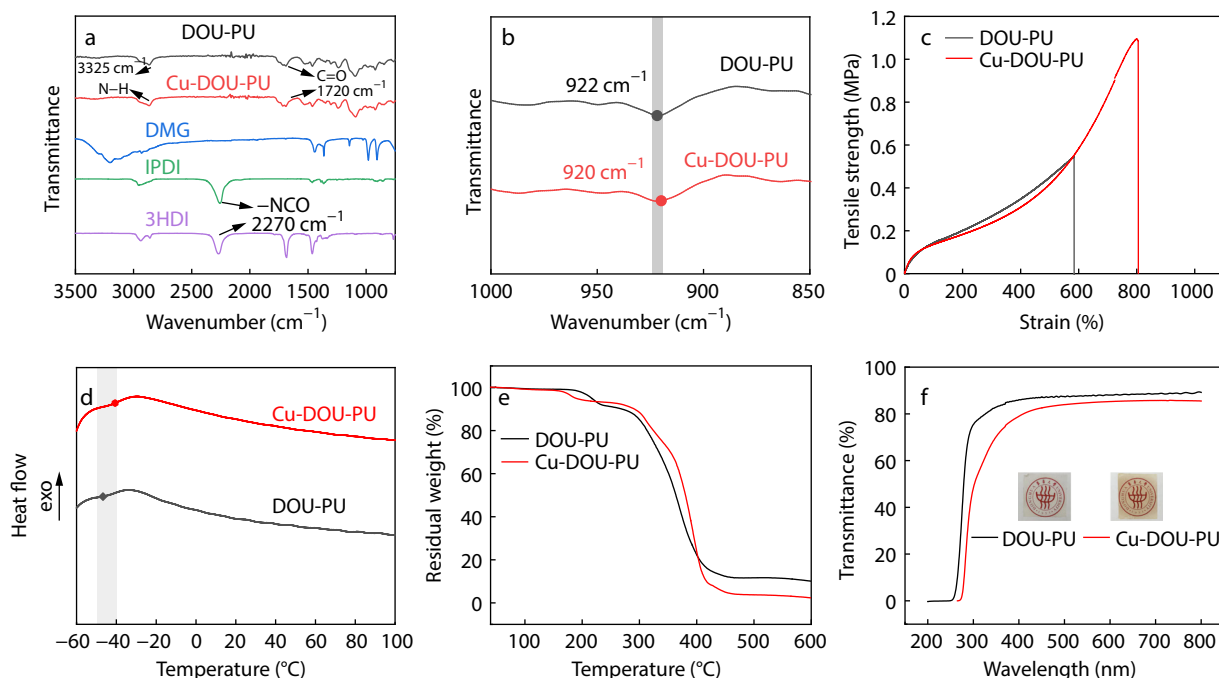


Fig. 2 Structural characterization and comparison of material properties of DOU-PU and Cu-DOU-PU. (a) FTIR spectra of DOU-PU, Cu-DOU-PU, DMG, IPDI and 3HDI at room temperature; (b) FTIR spectra of DOU-PU and Cu-DOU-PU at room temperature; (c) Tensile stress-strain curves of DOU-PU and Cu-DOU-PU; (d) DSC curves of DOU-PU and Cu-DOU-PU; (e) TGA curves of DOU-PU and Cu-DOU-PU; (f) Transmittance spectra of DOU-PU and Cu-DOU-PU with a thickness of 200 μm .

largely unchanged after the introduction of copper ions. Additionally, the band in Fig. 2(b), which corresponds to the stretching vibration of N—O bonds in DMG, shifts from 922 cm^{-1} in DOU-PU to 920 cm^{-1} in Cu-DOU-PU due to the coordination of copper ions with DMG. These results indicated the successful formation of carbamate groups and the successful introduction of dynamic oxime carbamate linkages into polyurethanes. DMG was the key to the design of POUs. L-DOU-PU with lower DMG content had less content of dynamic covalent bonds, so its self-healing efficiency and recycling efficiency were lower than those of DOU-PU and H-DOU-PU (Tables S1 and S2, in the electronic supplementary information, ESI). By increasing the DMG content, the mechanical properties can be adjusted, and the self-healing and recycling ability of POUs can be improved. According to the design, the coordination of copper ions and DMG will enhance the mechanical properties of polyurethane by increasing the dynamic crosslinking points.^[31] The tensile strength and elongation at break of Cu-DOU-PU ($1.03\pm0.03\text{ MPa}$ and $829.6\%\pm80.7\%$) are found to be approximately twice that of DOU-PU ($0.54\pm0.07\text{ MPa}$ and $527.0\%\pm48.9\%$) (Fig. 2c and Fig. S1 in ESI). Moreover, the coordination of copper ions did not change the Young's modulus, and the Young's moduli of DOU-PU and Cu-DOU-PU are 236.7 ± 19.2 and $238.6\pm18.6\text{ kPa}$, respectively. In addition, the incorporation of PEG endowed DOU-PU and Cu-DOU-PU good hydrophilicity with water absorption rates of $111.6\%\pm0.6\%$ and $107.9\%\pm1.7\%$, respectively.

In order to investigate the impact of copper ions on the thermal and optical properties of Cu-DOU-PU, we conducted a series of tests including DSC, TGA, DMA, oscillatory rheological analysis and ultraviolet spectrophotometry. The results show that both DOU-PU and Cu-DOU-PU have low glass transition temperatures (DOU-PU: $T_g=-47.1\text{ }^\circ\text{C}$, Cu-DOU-PU: $T_g=-40.6\text{ }^\circ\text{C}$) without crystallization or melting peaks between -60 and $100\text{ }^\circ\text{C}$ (Fig. 2d). The coordination of copper ions elevated the glass transition temperature (T_g) as indicated by DSC, which has the same conclusion in the DMA test (Fig. S2 in ESI). The results show that the dynamic cross-linking introduced by the Cu^{2+} coordination bonds restrict the movement of polymer chain segments. The TGA results show that the thermal decomposition temperature (T_d) of Cu-DOU-PU is $28\text{ }^\circ\text{C}$ lower than that of DOU-PU (DOU-PU: $T_d=216\text{ }^\circ\text{C}$, Cu-DOU-PU: $T_d=188\text{ }^\circ\text{C}$), which can be attributed to the enhanced dynamic dissociation of the reversible DOU bonds facilitated by the coordination of copper ions (Fig. 2e). The oscillatory rheology curve shows that both the storage modulus (G') of DOU-PU and Cu-DOU-PU drop sharply at $125\text{ }^\circ\text{C}$ (Fig. S3 in ESI). However, in the test range from $40\text{ }^\circ\text{C}$ to $160\text{ }^\circ\text{C}$, G' of the two polyurethanes remained higher than G'' (loss modulus), which indicated that both POUs remained solid at elevated temperatures and had high thermal stability. Additionally, both DOU-PU and Cu-DOU-PU exhibit high transparency in the visible region of the ultraviolet spectrophotometer, with a transmittance rate exceeding 80%, and the addition of copper ions does not significantly affect the material's transparency (Fig. 2f).

As shown in Figs. 3(a) and 3(b), both types of POUs were able to self-heal after being cut, with the mechanical proper-

ties almost completely restored upon reconnection. In the scratch self-healing test conducted at $80\text{ }^\circ\text{C}$ (Fig. S4a in ESI), the scratches were able to fully heal within 120 min. To assess the impact of copper ions on the dynamic properties of Cu-DOU-PU, the self-healing capabilities of both Cu-DOU-PU and DOU-PU were thoroughly evaluated. During the uniaxial tensile test of self-healing samples, after 2 h of healing at $80\text{ }^\circ\text{C}$, the tensile strength and breaking strain of DOU-PU were able to recover to 85.5% and 81.5% of their initial values (Fig. 3c). Cu-DOU-PU demonstrated even better self-healing performance, reaching 91.8% and 92.4%. The results demonstrate that Cu-DOU-PU has better dynamic properties than DOU-PU. In addition, given that the DOU bonds and metal coordination bonds can dynamically exchange even at room temperature, Cu-DOU-PU has the ability to self-heal at room temperature. As shown in Fig. S4(b) (in ESI), the material self-heals over time at $25\text{ }^\circ\text{C}$ and the tensile strength and breaking strain are able to recover to 94.4% and 95.5% of their original values after 120 h.

To demonstrate the improved dynamic properties of Cu-DOU-PU, we conducted temperature-variable Fourier transform infrared (FTIR) spectroscopy, and oscillatory rheological analysis. The results of the temperature-variable FTIR show that at high temperatures, a small amount of free isocyanate (2270 cm^{-1}) can dissociate from the DOU bonds (Figs. 3d and 3e). The initial dissociation temperature of DOU-PU is high, exceeding $100\text{ }^\circ\text{C}$. However, the catalysis of copper ions on the DOU bonds lowers the initial dissociation temperature for Cu-DOU-PU, with a characteristic band of dissociated isocyanate already evident at $80\text{ }^\circ\text{C}$. Above $120\text{ }^\circ\text{C}$, the DOU bonds in both DOU-PU and Cu-DOU-PU have obvious dissociation, which makes the complex viscosity of the material decrease rapidly when the temperature rises (Fig. 3f). This demonstrates that copper ions catalyze the dissociation of DOU bonds, thus enhancing the dynamic properties of Cu-DOU-PU.

The dynamic property is closely related to the activation energy of dynamic covalent network dissociation.^[32,33] For further research, stress-relaxation tests were performed on DOU-PU and Cu-DOU-PU at different temperatures (Figs. 3g and 3h). The results show that at a test temperature of $100\text{ }^\circ\text{C}$, Cu-DOU-PU is able to relax stress almost completely within 2500 s, while DOU-PU fails to exhibit complete stress relaxation under the same conditions, suggesting that Cu-DOU-PU has better dynamic properties. As the stress relaxation is determined by dynamic bond exchange, the relaxation time-temperature relationship displays an Arrhenius-like dependence.^[34] Based on the Maxwell model for viscoelastic fluids, the characteristic relaxation time (τ^*) can be extracted as the time when the normalized residual stress (G/G_0) is $1/e$.^[28,35] The activation energy (E_a) was then calculated using the Arrhenius equation and found to be significantly lower in Cu-DOU-PU than that of DOU-PU (DOU-PU: $E_a=119.6\text{ kJ}\cdot\text{mol}^{-1}$, Cu-DOU-PU: $E_a=95.4\text{ kJ}\cdot\text{mol}^{-1}$) (Fig. 3i), which further confirms the catalytic effect of copper ions on the dissociation of DOU bonds.

To confirm its crosslinked structure, we conducted swelling experiments on DOU-PU and Cu-DOU-PU. The swelling ratios of DOU-PU and Cu-DOU-PU are $475.5\%\pm36.1\%$ and

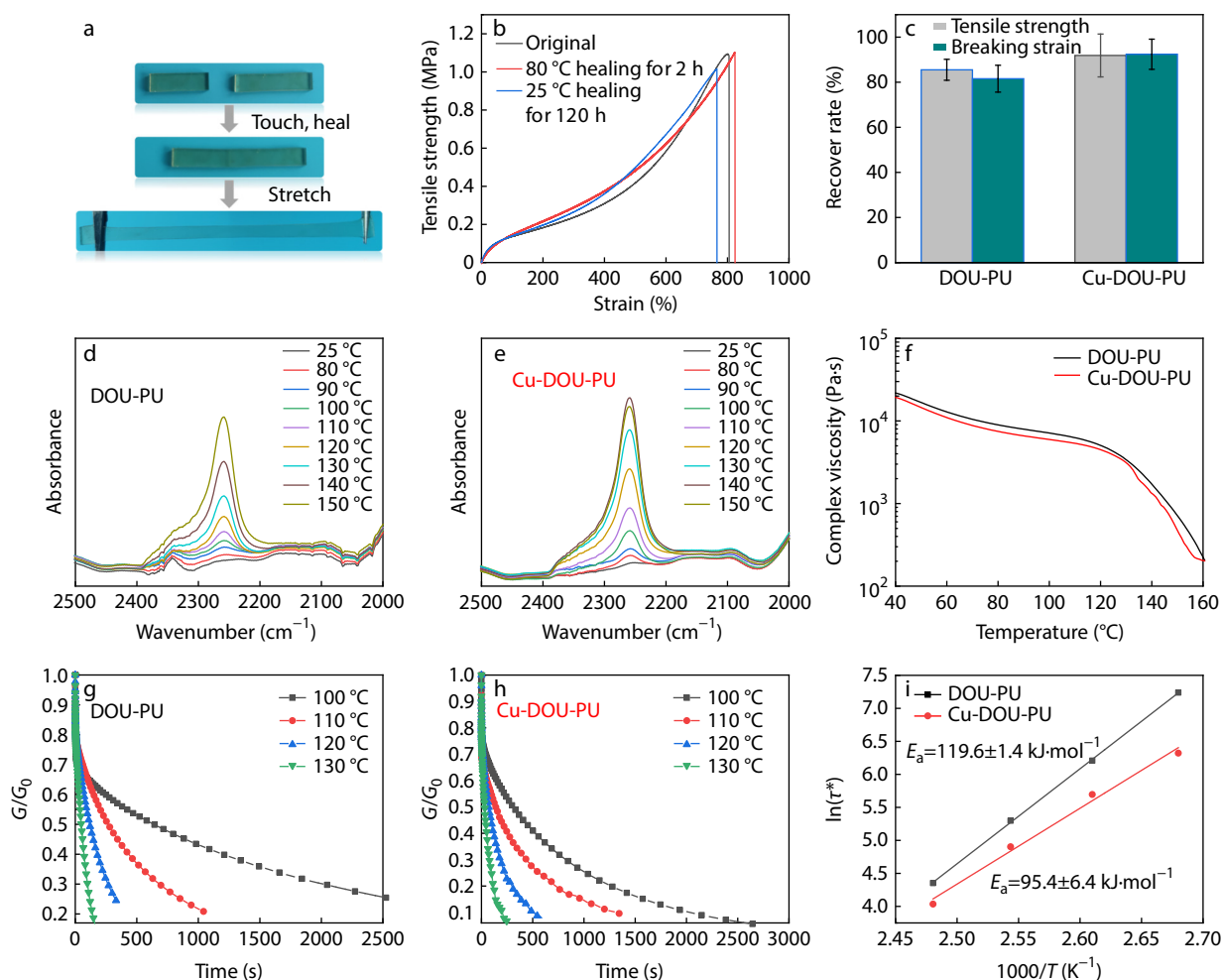


Fig. 3 Dynamic properties characteristics of DOU-PU and Cu-DOU-PU. (a) Optical pictures of Cu-DOU-PU cut in half, reattached, and healed at 80 °C for 2 h; (b) Stress-strain curves of self-healing of Cu-DOU-PU at 80 °C for 2 h and 25 °C for 120 h; (c) Comparison of recovery rates of Cu-DOU-PU and DOU-PU; Variable temperature FTIR spectra of (d) DOU-PU and (e) Cu-DOU-PU; (f) Complex viscosity of DOU-PU and Cu-DOU-PU by rheology test; Stress relaxation curves of (g) DOU-PU and (h) Cu-DOU-PU; (i) Arrhenius analysis of τ^* versus $1000/T$ of DOU-PU and Cu-DOU-PU.

434.9%±28.2%, respectively. The gel fractions of DOU-PU and Cu-DOU-PU are 73.3%±2.7% and 75.1%±3.2%, respectively. In addition, the crosslinking density of DOU-PU and Cu-DOU-PU are 32.77 and 34.05 mol·m⁻³, respectively (Table S3 in ESI). The data show that the degree of crosslinking of DOU-PU and Cu-DOU-PU was basically equal. The stable structure endows it with excellent solvent resistance and elasticity, which is demonstrated by taking Cu-DOU-PU as an example. After being soaked in acetone, tetrahydrofuran, and *N,N*-dimethylformamide for three days, we observed that Cu-DOU-PU remained intact, suggesting that it has a stable crosslinked structure (Fig. S5 in ESI). This stable structure gives Cu-DOU-PU excellent elasticity. As demonstrated in Fig. S6 (in ESI), we stretched samples using a universal testing machine until fracture, and the results indicated that the length of Cu-DOU-PU remained unchanged before and after stretching, demonstrating its impressive deformation recovery ability. Furthermore, the continuous cycle incremental stretching experiment of Cu-DOU-PU revealed a residual strain of less than 35% even after being stretched up to 400%, which confirms its remarkable resilience (Fig. S7 in ESI).

The rheological tests reveal that despite its stable cross-linked structure, Cu-DOU-PU possesses excellent dynamic properties and has the potential for recycling. To demonstrate this, we conducted a recycling test by cutting the sample into smaller pieces and then remolding them at 120 °C under a pressure of 5 MPa for 10 min. At this temperature, as shown in Fig. 4(a), the chopped samples were rapidly hot-pressed into intact and defect-free materials, a feat that cannot be achieved with conventional cross-linked polyurethanes. We repeated the molding process three times under the same conditions and conducted FTIR spectra tests and tensile tests. The results showed that the FTIR spectra and stress-strain curves of the recycled Cu-DOU-PU were virtually identical to those of the initial curves, indicating that the material retained its original chemical structure and mechanical properties (Figs. 4b and 4c).

The results show that the introduction of copper ions endowed Cu-DOU-PU higher tensile strength and dynamic properties at the same time. Furthermore, we varied the concentration of CuCl₂ to investigate its effect on the materials properties (Tables S1 and S2 in ESI). We prepared H-Cu-DOU-

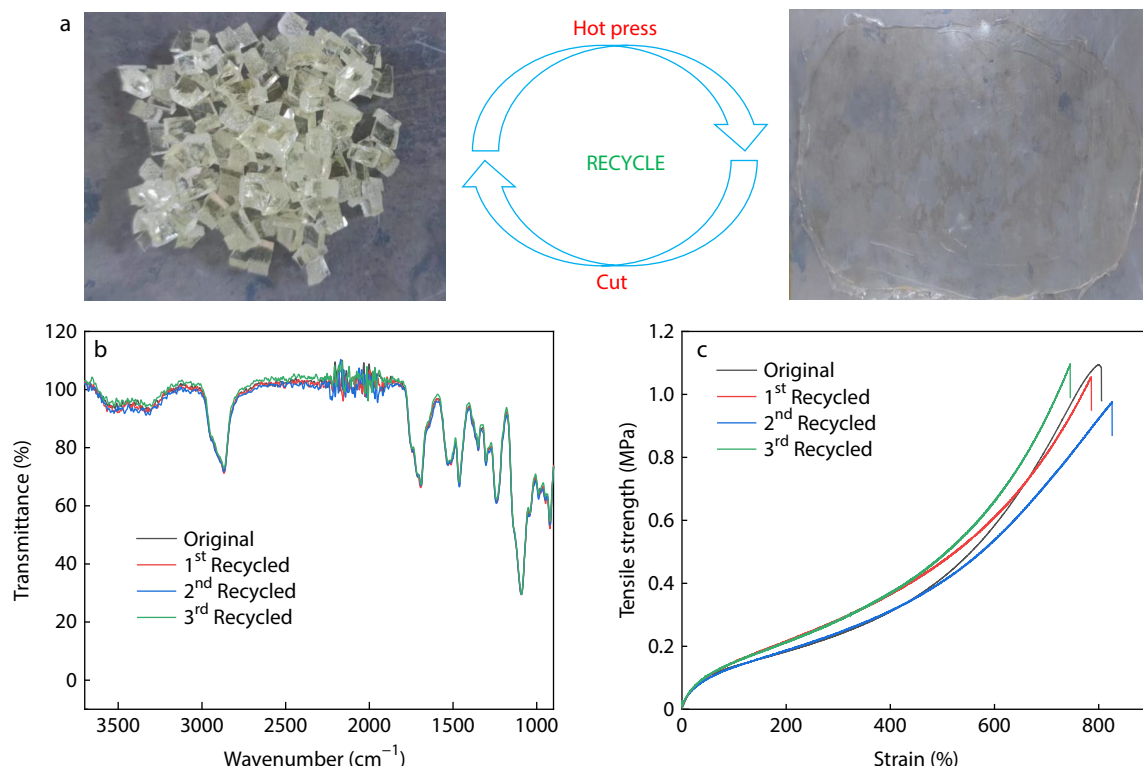


Fig. 4 The recycling of Cu-DOU-PU. (a) Photographs of Cu-DOU-PU pieces (left) and that after recycling (right); (b) FTIR spectra of the original and recycled Cu-DOU-PU; (c) Stress-strain curves of the original and recycled Cu-DOU-PU.

PU with higher CuCl_2 concentration and L-Cu-DOU-PU with lower concentration compared to aforementioned Cu-DOU-PU. The study found that the tensile strength and elongation at break of DOU-PU coordinated CuCl_2 at three concentrations were higher than those of DOU-PU, indicating that metal coordination could significantly improve the mechanical properties. Moreover, compared with DOU-PU, the self-healing efficiency and recycling efficiency of the all Cu-DOU-PU were improved. The self-healing efficiency of POUs gradually increased with the increase of CuCl_2 concentration, indicating that metal coordination could improve the dynamic properties of the POUs.

As a preliminary demonstration, we demonstrate the potential of Cu-DOU-PU as a stretchable and self-healing conductor that can be easily repaired after damage. A schematic diagram of the electronic circuit and composite conductor is presented in Fig. 5(a). Initially, a 1 mm thick Cu-DOU-PU film with a length of 3 cm and a width of 1 cm was obtained by hot pressing. Subsequently, the self-healing property of the material was utilized to firmly join the two sides of the film, resulting in a hollow outer sheath with a diameter of approximately 0.3 cm. This outer sheath was then filled with gallium indium tin eutectic liquid metal to produce the composite conductor. The composite conductor was used to connect power and LED to form a functional circuit. When the composite conductor was cut, the LED turned off. However, after the composite conductor was self-healed at 80 °C for 2 h, the LED was able to light up again and maintain its function even when stretched (Fig. 5b). These results highlight the promising potential of Cu-DOU-PU for use in the field of stretch-

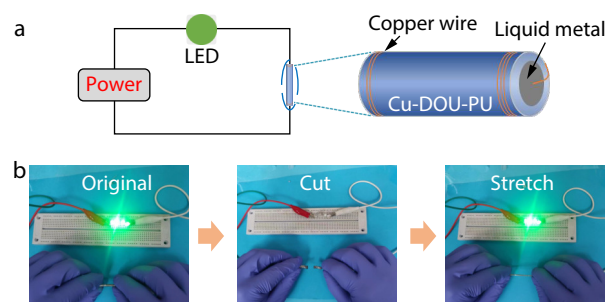


Fig. 5 Self-healing and stretchable composite conductor. (a) Schematic diagram of the electronic circuit and composite conductor; (b) Demonstration of the self-healing and stretchable properties for the composite conductor.

able and flexible electronics, making it a suitable choice for practical applications.

CONCLUSIONS

In summary, we have synthesized a recyclable and self-healing crosslinked polyurethane from industrial feedstocks without using solvents. By combining DOU bonds and metal coordination bonds in Cu-DOU-PU, we were able to achieve improved mechanical and dynamic properties of the polyurethane. The key to these improvements lies in the coordination and catalytic effects of copper ions, which increase the physical crosslinking points of the polyurethane for strengthened mechanical properties and catalyze the dissociation of DOU bonds for enhanced dynamic properties. In addition, the material's ability to self-heal at room temperature

was demonstrated, as well as its potential for rapid hot-press processing into defect-free materials during repeated processing. Overall, this work presents a promising approach to developing high-performance, environmentally friendly polyurethane materials for various applications.

Conflict of Interests

The authors declare no interest conflict.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-3009-0>.

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