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Super-Tough, Self-Healing Polyurethane Based on Diels-Alder Bonds and Dynamic Zinc–Ligand Interactions

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Self-healing polymer materials have attracted extensive attention and have been explored due to their ability of crack repairing in materials. This paper aims to develop a novel polyurethane-based material with high self-healing efficiency and excellent mechanical properties under 80 °C on the basis of reversible Diels–Alder bonds as well as zinc–ligand structure (DA-ZN-PU). By integrating DA bonds and zinc–ligand structure, as-prepared DA-ZN-PU samples reach the maximum tensile strength as much as 28.45 MPa. After self-healing, the tensile strength is 25.85 MPa, leading to the high self-healing efficiency of 90.8%. In addition, by introducing carbonyl iron powder (CIP), a new polyurethane containing carbonyl iron powder (DA-ZN-CIP-PU) can be achieved, exhibiting microwave-assisted self-healing property. And the self-healing efficiency can be reached to 92.6% in 3 min. Due to high self-healing efficiency and excellent mechanical properties of the prepared novel polyurethane, it has application attributes in crack repair of functional composite materials.

1. Research Purposes and Methods

Self-healing is a beneficial feature of biological tissues, enabling them to effectively repair themselves after mechanical damage.[1] Inspired by nature, there is a growing interest in the design of self-healing materials, which can extend the life of polymer materials and reduce maintenance. Self-healing polymer is an intelligent material that can automatically recover some or all functions after suffering from external mechanical damage or harsh conditions (such as high temperature or radiation).[2] By introducing self-healing property into synthetic materials, the life span and stability of materials can be greatly improved, leading to cost reduction as well as new applications. So far, various materials with self-healing property have been successfully applied in field effect transistors,[3] solar cells,[4] electronic skin,[5] electrochemical sensor,[6] supercapacitors,[7] coatings etc.[8]

At present, materials can achieve the ability of self-healing in two ways: external and internal self-healing. The first and most studied method for preparing exogenous self-healing polymer materials is microencapsulation, in which reactive consolidants are first embedded in microcapsules and then added to the polymer matrix.[9] Fractures can be healed by the polymerization of healing agents released during the process of fracture formation and vessel rupture. The disadvantages of this external self-healing approach are nonrepeatable healing and the obvious complexity of the operation. Meanwhile, another approach is to construct a network of microvessels to the polymer.[10] Despite exhibiting recyclable self-healing capabilities, microvascular self-healing materials typically have impaired initial properties, limited by embedding techniques. In addition, different chemical and physical properties between the polymer matrix and the healing zone may lead to poor compatibility and compromise healing properties. In contrast, the inherent self-healing system based on reversible interactions can achieve repetitive self-healing performance, extending the service life of the material.

Supramolecular chemistry and dynamic covalent chemistry are two main strategies for manufacturing self-healing materials.[11] Separately, for supramolecular systems, noncovalent interactions, including hydrogen bonds,[12] host–guest interactions,[13] π–π stacking, and metal ion binding interactions,[14,15] have been used to synthesize self-healing body materials.[16] In addition, a variety of self-healing polymers have been developed based on reversible dynamic covalent bonds, including imine bonds,[17] disulfide bonds,[18] Diels–Alder reactions,[19] and reversible free radical reactions.[20] In contrast, covalent self-healing materials have attracted more and more attention due to their excellent functional properties. In general, the healing process

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of covalent self-healing materials can be accomplished through reversible fracture and recombination of covalent bonds, most of which require external conditions to initiate, such as pH,[21] heating,[22] ultrasonic,[23] light, and magnetic field.[24,25]

In general, the self-healing ability and mechanical properties of materials are mutually exclusive in nature, in other words, achieving high mechanical strength and the healing efficiency remain a formidable challenge, especially under environmental conditions, as their requirements for molecular structure are often contradictory. Nevertheless, due to the poor mechanical properties, engineering applications of self-healing polymers are extremely narrow. Therefore, self-healing polymers with high efficiency of healing and high mechanical properties must be developed for certain fields such as military and construction industries.[26]

Polyurethane holds great promise to extend its application fields, such as building insulation, traffic vehicles, medical materials, repairable super capacitors, due to its excellent acid resistance, low temperature resistance, and interesting mechanical properties. Polyurethane materials will endure for a long time in the chemical, external force in the use process, such as thermal effect inevitably damage, which leading to fracture, the production of micro cracks. As a consequence, the cracks not only decreased the basic performance of material, but also provided a channel to accelerate the chemical corrosion, which had a serious influence the service life of the material. To solve this problem, making polyurethane materials have self-healing ability is one of the most effective methods. Yubin synthesized a new polyurethane by cross-linking Diels–Alder reaction with bismaleimide from isocyanate-terminated prepolymer and furamide.[27] The initial tensile strength of self-healing was 13.5 MPa and the tensile strength of healing was 12.2 MPa under heating at about 125 °C. Luzhi developed a new type of copper(ii)-dimethylglyoxime-polyurethane composite polyurethane elastomer with synergistic triple dynamic bond.[28,29] The maximum initial tensile strength of the self-healing elastomer at room temperature was 14.8 MPa and the healing tensile strength was 13.8 MPa.

Here, we presented a super-tough polyurethane with self-healing behavior, which is on the basis of Diels–Alder bonds and dynamic zinc–ligand interactions. Specifically, 4,4-diphenyl methane diisocyanate (MDI), polytetrahydrofuran (PTFEG), and 2,2-dimethylolpropionic acid (DMPA) were mingled under the chain extender, and subsequently reacted with furanmethanol and isophorone diisocyanate (IPDI) by Diels–Alder reaction. PTFEG was used to be the soft segment to magnify the flexibility of the chain segment, which can increase the chain mobility for better self-healing. MDI was used to be the hard segment, and IPDI was used to decrease the crystallization performance of the entire system relied on its bulky structure. The polyurethane had a good performance about intensity for the addition of IPDI, MDI, and' the anhydride ring. DA bond reversible reaction and zinc–ligand interaction were used to form a crosslinking structure, and healing materials were prepared with excellent mechanical properties.

As shown in **Figure 1**, the hybrid dynamic network that constituted by DA bonds, hydrogen bonds and zinc–ligand makes the polyurethane become a self-healing material. The key is *N*-2,3-dihydroxypropyl maleimide in the design of DA-ZN-PU, which acts as the chain extender to introduce reversible DA bonds. Its bulky structure restrains the crystallization of the hard segment and accelerates the chain motion. Besides, The dissociation of the weaker hydrogen bonds introduced by the DA reaction can absorb energy immensely during mechanical deformation result in high toughness, which plays the same function of zinc–ligand interactions in the system. Moreover, those weaker bonds promote the reconfiguration of DA bonds to facilitate the self-healing process. At the beginning of the fracture, the DA bond on the chain segment was decomposed into maleimide and furan groups through rDA reaction. Furthermore, the DA reaction occurred again between maleimide on the one chain segment and furan group on the other chain segment with the attraction of zinc–ligand and hydrogen bond, which will form a stable DA bond, make the material healing at the macro level. The composite effect of hybrid dynamic network ensures our materials possess both good mechanical properties and self-healing properties.

2. Results and Discussions

2.1. Preparation of FA-ID and DA-ZN-PU

The reaction formula for the preparation of DA-ZN-PU is shown in Figure S1 in the Supporting Information. Whether the product is the expected product has been verified by comparing the peaks of various groups in ^{1}H NMR spectrum. The result shows we get the expected product, *N*-dihydroxypropyl maleimide (Figure S2, Supporting Information).

Additionally, the formation of zinc–ligand structure is verified by observing the absorption peaks of C—N—C and C═O in the Fourier transform infrared spectroscopy, which means the DA-ZN-PU was synthesized successfully (Figure S3, Supporting Information).

As shown in Figure S4 (Supporting Information), the introduction of zinc ions not only plays a role of dynamic crosslinking, but also leads to a better degree of microphase separation between the hard segment and the soft segment of polyurethane by comparing the AFM picture of DA-ZN-PU and DA-PU, thus leading to a better tensile strength.

2.2. Thermal Reversibility of Polyurethane

In order to study the potential reversibility and self-healing ability of synthetic polymers, Differential scanning calorimetry (DSC) has been used for measurement. As shown in **Figure 2b**, the second heating cycle curve of DA-ZN-PU, DA-PU, and ZN-PU in the DSC test of 40180 °C. The glass transition temperature was observed at about 72 °C from the DSC curve of the DA-ZN-PU (Figure S5a, Supporting Information). Compared with Li's work,[27] the glass transition temperature of our polyurethane was about 95 °C and that of DA-ZN-PU was 72 °C, which should be caused by the joint action of the added FA-ID prepolymer and zinc ion bond (the process of analysis was shown in Figure S5 in the Supporting Information). The heating–cooling cycle curve in DSC clearly shows that the DA-ZN-PU polymer is thermally reversible, enabling self-healing behavior.

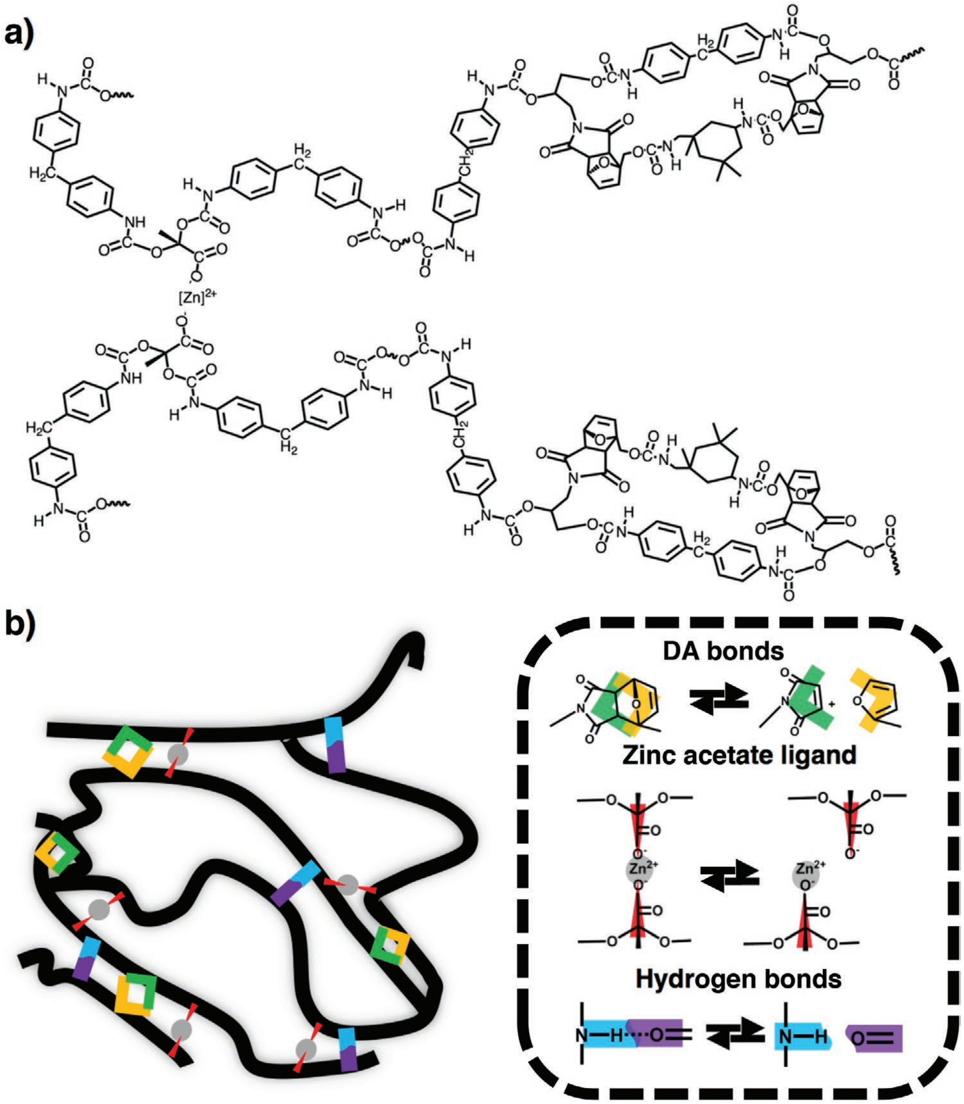

Figure 1. a) Chemical structure of the novel polyurethane. b) The hybrid dynamic network contains of triple dynamic bonds, including reversible covalent bonds, zinc–ligand and hydrogen bonds.

The TG and DTG curves of DA-ZN-PU, DA-PU, and ZN-PU from 25 to 600 °C was shown in Figure 2c,d, which exhibited that the polymer had three thermal decomposition stages. The first decomposition stage at about 200 °C, which has shown lower thermal stability, likely due to the presence of ligand structure formed by zinc acetate. In the second stage, the increase of decomposition rate was observed from 300 to 350 °C. At temperatures above 400 °C, the third stage of decomposition is based on the breaking of the chain which was formed in above stages of decomposition, as well as secondary reactions in the dehydrogenation and gasification processes. The complete decomposition of ZN-PU polymer was observed at 588 °C. The temperatures of DA-ZN-PU, DA-PU, and ZN-PU polymers were respectively 220, 249, and 197 °C when they lost 10% mass, indicated the addition of furan ring improved the thermal stability of polyurethane. The mass fractions of the remaining samples in the crucible were 9.35%, 6.27%, and 0.10% after DA-ZN-PU, DA-PU, and ZN-PU samples were heated to 600 °C. The synthesized polyurethane had better thermal stability based on the large number of furan-benzene ring structures produced by the DA reaction, which made the DA-ZN-PU and DA-PU samples significantly less decomposed than the ZN-PU samples after the final heated to 600 °C. In addition, the cross-linked network system constructed by various active functional groups DA-ZN-PU samples enhanced the thermal stability of the samples to some extent.

2.3. Mechanical Properties of Polyurethane

As different amounts of DA-rDA units can have great influence in mechanical properties of DA-ZN-PU polymers. The mechanical properties of DA-ZN-PU samples with different FA-ID addition amounts were prepared by changing FA-ID

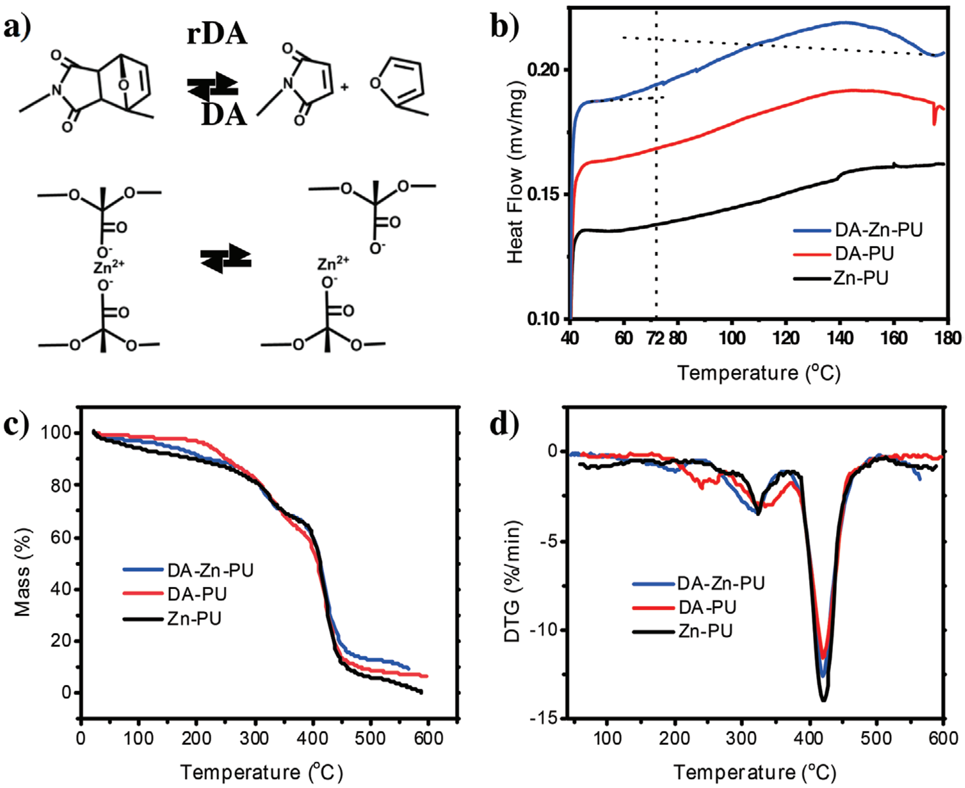

Figure 2. a) Proposed mechanism of bonds break and formation during thermal treatment, b) DSC, c) TG, and d) DTG Characterization of DA-ZN-PU, DA-PU, and ZN-PU.

content of furan methanol and IPDI products (Table S1, Supporting Information). As shown in **Figure 3**, the hardness of DA-ZN-PU samples decreased first and then increased within the increasing of FA-ID content. While the tensile strength, elongation at break as well as toughness went the opposite trend. Initially, a large number of DA bonds generated based on the DA reaction increased with the content of FA-ID, which makes a significant increase in the cross-linking degree of the polymer, resulting in an increase in the toughness of the polymer. With the further increase of FA-ID content, the excessive amount of FA-ID could not fully react with polyurethane, which formed a similar island structure in the system as an impurity in the system reduced the toughness of polyurethane. At the same time, the contrary trend of polyurethane hardness test also proves the above conjecture. As samples with 7% FA-ID have best tensile strength of 28.45 MPa, proper toughness of 106.42 MPa $m^{1/2}$ and hardness of 16 SH, they were chosen for the following tests.

2.4. Self-Healing Behavior of Polyurethane

Due to the DA bond from the DA reaction, the cross-linking degree of polyurethane was increased after the addition of FA-ID. Some FA-ID in the polyurethane system could not participate in the DA reaction, may disperse in the polyurethane system as the island structure to enhance and toughened with the increasing amount of FA-ID. And then those FA-ID participated in the DA reaction faster in the self-healing process, which improved the self-healing efficiency of polyurethane. The self-healing efficiency was characterized by measuring the recovery rate of tensile strength as well as fracture elongation. As shown in **Figure 4b**, the self-healing efficiency of the DA-ZN-PU samples decreased at first and then remained basically unchanged with the increase of FA-ID. One possible reason is that polyurethane system became a continuous phase and turned into the main structure gradually with the increasing of FA-ID.

The self-healing behavior of polyurethane samples was firstly analyzed by hot-table microscope by taking self-healing test for 40 min at 80 °C, and the optical microscope images was shown in Figure 4c, during which the sample was intentionally damaged by the blade. The result indicates that this furan-maleimide polymer requires critical heat (80 °C) to carry out self-healing ability. As shown in Figure 4d, the tensile strength of the pristine polyurethane sample was 28.45 MPa, the elongation at break was 640 °C, and the fracture toughness obtained by integral was 106.70 MPa $m^{1/2}$. After heating at 80 °C for 40 min, the tensile strength of DA-ZN-PU was about 25.85 MPa, elongation at break was 509% and the fracture toughness was 78.64 MPa $m^{1/2}$. The tensile strength was 90.86% of the pristine polyurethane sample, the elongation at break was 79.53% of the pristine polyurethane sample, and the fracture toughness was 73.70% of the pristine polyurethane sample. It should be pointed out that the tensile strength does not reach 100% healing efficiency due to the lack of force to

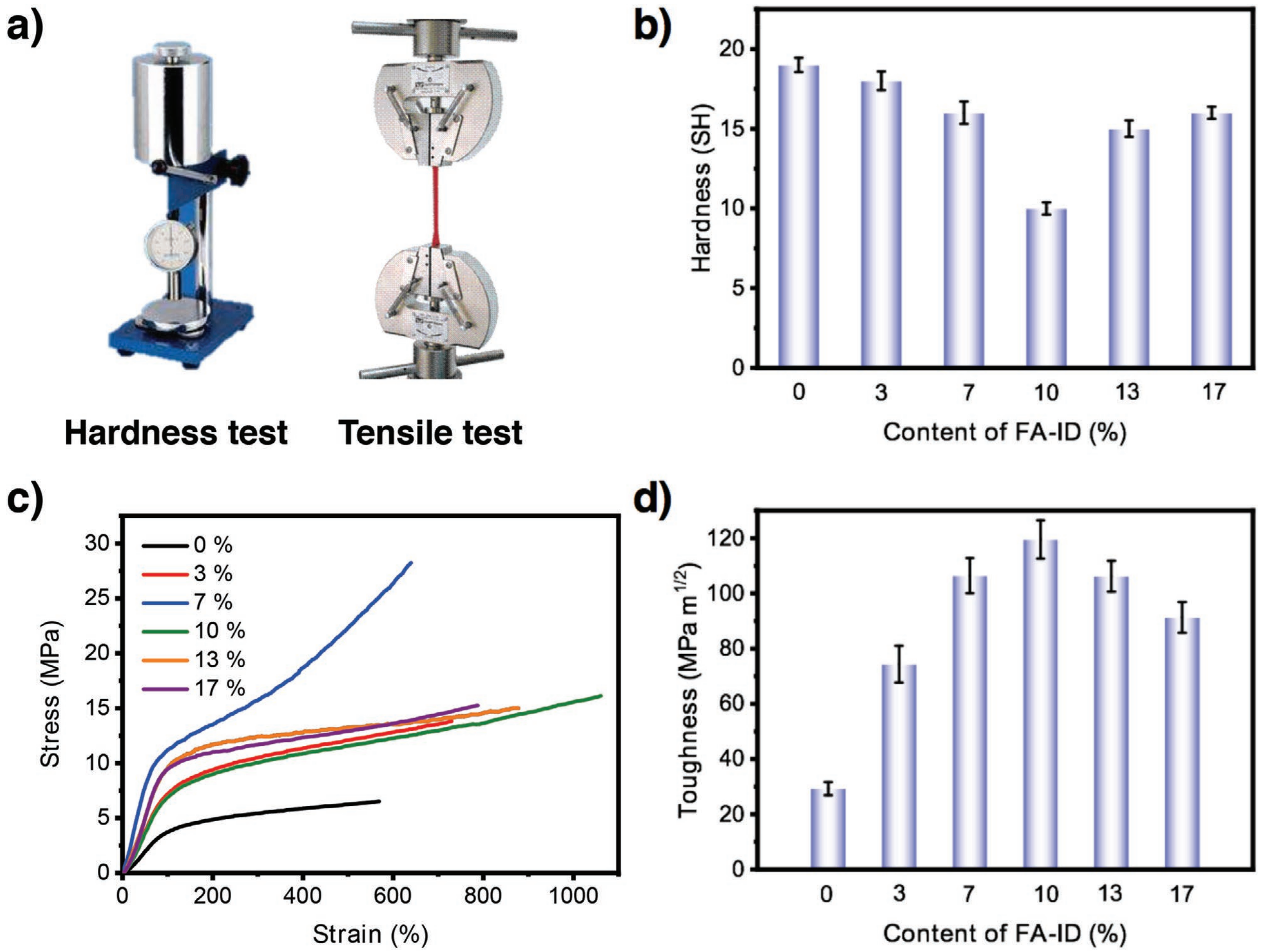

Figure 3. a) Images of hardness test and tensile test, b) hardness, c) stress–strain curves, and d) toughness of DA-ZN-PU polymers with different content of FA-ID.

promote fracture surface to contact closely during the repair process. Therefore, the degree of DA reversible reaction and the dissociation of zinc ions at the interface were insufficient. The better recovery of elongation at break may be caused by the entanglement between the DA-ZN-PU chain and zinc–ligand at 80 °C.

Additionally, we introduced CIP into DA-ZN-PU that contains 7% FA-ID to form a novel polyurethane material (DA-ZN-CIP-PU), which could be healed more effective under microwave. The DA-ZN-CIP-PU sample scratched for 0.25 mm in deeps was shown in Figure 4e, which was bended into 30° after being heated in microwave with 600 W for 3 min, showing that the crack has been basically healed. As shown in Figure 4f, DA-ZN-CIP-PU made up of 2% CIP exhibited pristine (15.98 MPa) and healed (14.79 MPa) tensile strength, which means the recovery efficiency of tensile is 92.6%, both of which exceed other additive amounts of CIP. Similarly, it showed a pristine (82.17 MPa m$^{1/2}$) and healed (69.66 MPa m$^{1/2}$) toughness, indicated that DA-ZN-CIP-PU could be healed and restore physical properties basically after heating under microwave for 3 min.

2.5. Application of Polyurethane

As a preliminary demonstration, we used our novel polyurethane as a stretchable and self-healable substrate for constructing flexible electronics. As shown in **Figure 5**, the sample of DA-ZN-PU was symmetrically coated with Galinstan alloy on the surface and introduced into the circuit to verify whether the surface crack has healed completely or not. As shown in Figure 5b, the LED emitted light at first. The blade was used to cut a crack about 0.25 mm in the polyurethane, also cutting off the Galinstan alloy coating, leading the breakage of the circuit and the extinguishment of LED. The scratched sample was heated in an oven at 80 °C for 36 h. The DA-ZN-PU has healed, and the surface of DA-ZN-PU has reconnected to the circuit. Gleamy LED indicates that the healing in the surface of DA-ZN-PU promotes the motion of Galinstan alloy.

In a conductive circuit containing LED, a sample of DA-ZN-PU coated with Galinstan alloy on the surface was tensile tested, and the LED emitted light initially as shown in Figure S6a in the Support information. Later, the 2 cm area which had healed early in the sample was stretched unidirectional, and

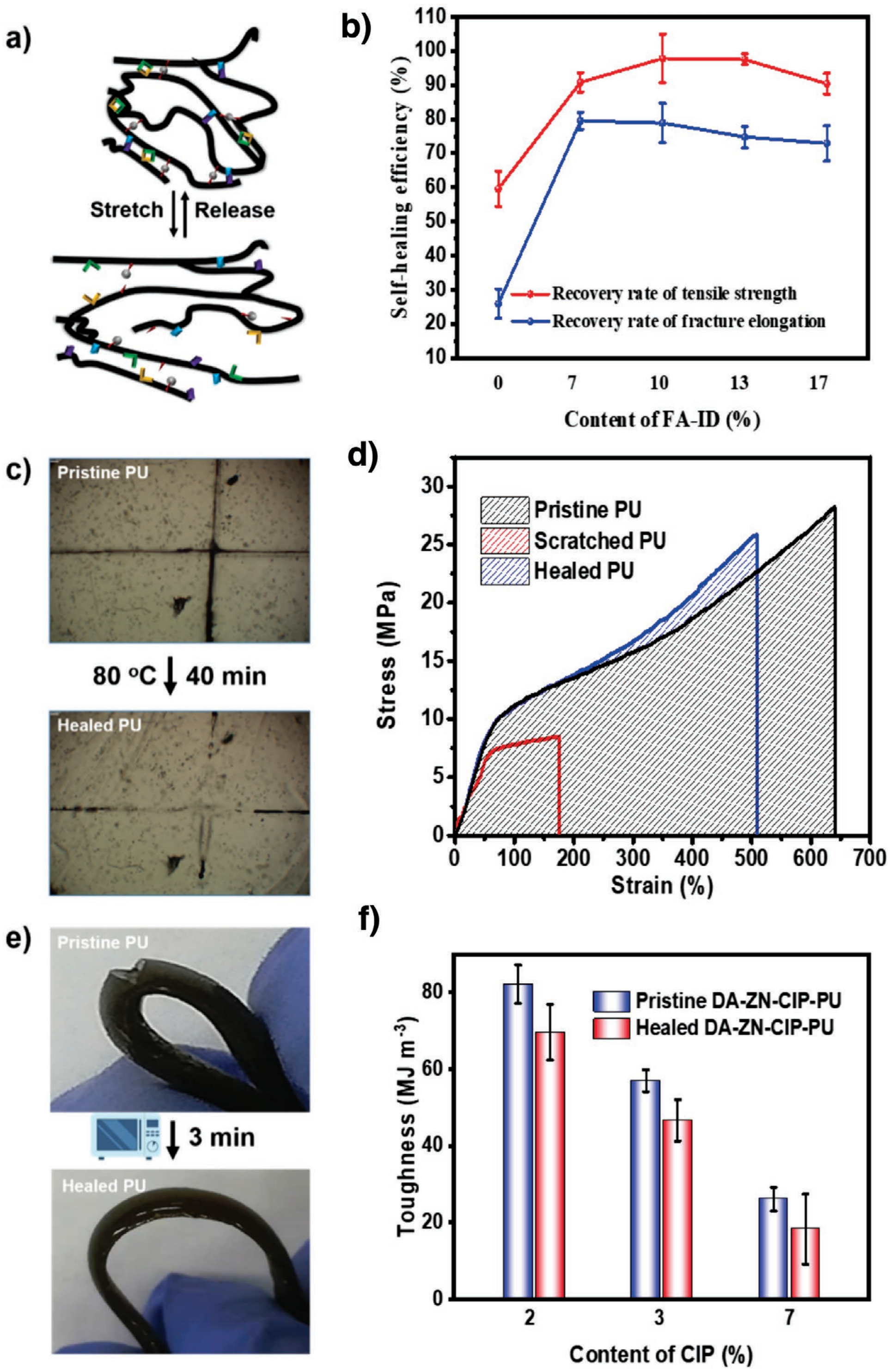

Figure 4. a) Schematic images of dynamic network during stretching and releasing, b) Self-efficiency of DA-ZN-PU with different content of FA-ID after annealing for 40 min at 80 °C, c) Microscope photos of films before and after annealing for 40 min at 80 °C, d) Tensile test of pristine, scratched, and healed DA-ZN-PU, e) photos of damaged DA-ZN-CIP-PU before and after microwave treating for 3 min, f) the toughness of pristine and healed DA-ZN-CIP-PU with different content of CIP.

when the stretch area was stretched to 8 cm (elongation reached 400%), the circuit was broken due to the absence of Galinstan alloy on the polyurethane surface, which making the LED not emit light, as shown in Figure S6b in the Support information. At that time, the polyurethane sample did not break and still had good ductility.

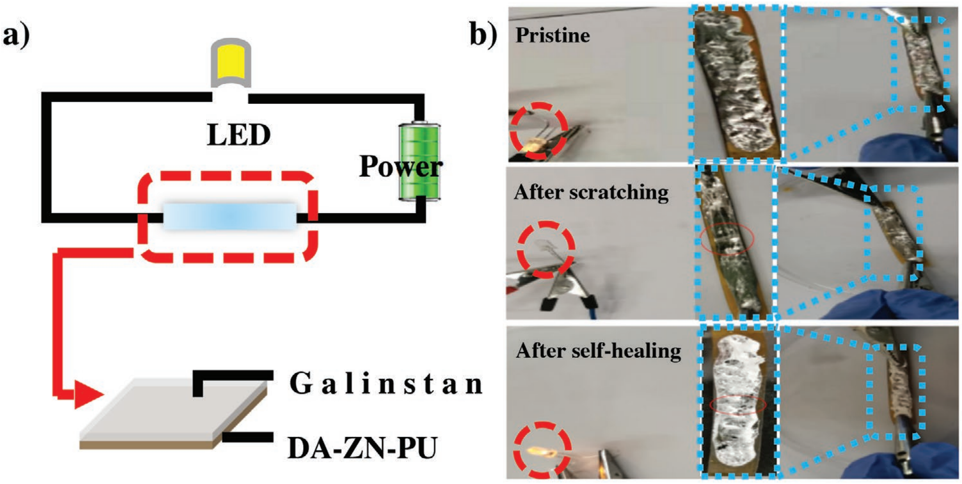

Figure 5. a) Schematic illustration of simple electronic circuit, b) the healing of Galinstan alloy loop was promoted by the self-healing of polyurethane.

3. Conclusion

In conclusion, a new self-healing polyurethane was prepared through the Diels–Alder reaction between FA-ID and dihydroxy propyl maleimide and the ligand interaction of zinc acetate. The self-healing property of polyurethane is proved by a series of tests. At the same time, the tensile test showed that DA-ZN-PU had excellent mechanical properties, the best tensile strength of the DA-ZN-PU sample was 28.45 MPa, the self-healing tensile strength was 25.85 MPa, and the self-healing efficiency of the tensile strength was 90.8%. The scratched DA-ZN-CIP-PU restores its mechanical properties more effective under microwave for 3 min. These new polyurethanes have high self-healing efficiency and remarkable mechanical properties, which have great potential as functional material for various military and civil applications.

4. Experimental Section

Materials: Polytetrahydrofuran (PTMEG), with a number-average molecular weight of 2000, (Jining baiyichemical limited-liability company) was vacuum dried at 110 °C for 3 h before using. DMPA, (Jining hongming chemical reagent) vacuum dried at 110 °C for 3 h before using; MDI, (Tokyo chemical industry co. LTD). *N*-methylpyrrolidone (NMP), (Shanghai Titan technology co. LTD) analytically pure; *N*-2,3-dihydroxypropyl maleimide, self-made; IPDI, Bayer, Germany; Furanmethanol, (Shanghai Titan technology co. LTD) analytically pure; zinc acetate dihydrate, (Shanghai Titan technology co. LTD) analytically pure; carbonyl iron powder (CIP), (Xinxiang sanyi metal material company).

Preparation of N-2,3-Dihydroxypropyl Maleimide: 60 mL ethanol was added to a 500 mL round bottom flask, followed by 45 g furan and 50 g maleic anhydride. After stirring at room temperature for 24 h, white crystals were obtained by vacuum filtration and transferred to the watch glass. After drying at room temperature for at least 24 h, 4,10-dioxytricyclic [5.2.1.02.6]-decy-8-ene-3,5-diketone (furan-A) was obtained. Then, furan-A 30 g was dissolved in 40 mL anhydrous ethanol and added into a 250 mL round bottom flask as a solution 1. 16.4 g 3-amino-1,2-propanediol, 10 mL anhydrous ethanol and 25 mL triethylamine were prepared as solution 2. The temperature was maintained at 0–2 °C in the ice bath, solution 2 was slowly dropped into solution 1, and the mixed solution was stirred for 2 h, then the solution was gradually heated up to 80–85 °C with nitrogen protection. After reacted for 3 h, the solution began to turn into white liquid and turned into yellow oily liquid as the reaction went on. The filtered solids were washed with a small amount of anhydrous ethanol and dried to obtain a white crystal of furan *N*-dihydroxypropyl maleimide. Finally, the new preparation of 5 g furan *N*-2 hydroxypropyl maleimide, 60 mL dry xylene, and trace antioxidant AO-80 to join with the agitator, the round bottom flask of spherical condenser pipe, reflux reaction 5 h under 125 °C, reaction in the process of continuously bubbled into nitrogen to prevent the oxidation reaction occur, at the same time take away the furan product. *N*-2,3-dihydroxypropyl maleimide was obtained by vacuum filtration.

Preparation of Furfuryl Alcohol and IPDI Reaction Product (FA-ID): 25 g furanmethanol and 100 mL dried dichloromethane were added into a four-mouth round-bottom flask with agitator and condensing tube, after which 1.2 g dibutyltin dilaurates as catalyst. Stirring the flask rapidly for 10 min under N_2, 28.3 g IPDI was added and reacted for another 2 h at room temperature, afterward reflux for 2 h at 40 °C to obtain the reaction product.

Preparation of DA-ZN-PU and DA-ZN-CIP-PU: PTMEG (20 g), DMPA (2.3 g), MDI (8.025 g), and NMP (50 mL) were added into 250 mL round bottom flask, and reacted for 1 h under 85 °C with N_2. *N*-2,3-dihydroxypropyl maleimide was added as chain extender under 60 °C for 1 h, PU solution was prepared by the introduction of FA-ID after reacted for 1 h. Zinc acetate dihydrate with equal molar ratio was added into PU solution, and the reaction was conducted at 100 °C for 0.5 h with a neutralization degree of 100%. The product was poured into polytetrafluoroethylene board and vacuum dried at 70 °C to obtain DA-ZN-PU. The different additive amounts of CIP with 2%, 3%, and 7% was added to the DA-ZN-PU solution which contain 7% FA-ID, and the reaction was conducted at 100 °C for another 0.5 h, vacuum dried at 70 °C to obtain DA-ZN-CIP-PU. All PU were prepared into 10 × 4 mm dumbbell tensile samples, and there have been at least five specimens for each sample. The maximum and minimum values in the data are discarded and then the average value of the remaining data is used in the paper.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Diels–Alder reactions, polyurethane, self-healing, zinc–ligand interactions

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