express polymer letters

Research article

Wide-temperature-range and anti-aging self-healing polyurethane enabled by dual cooperative cross-linking strategy

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Received 1 July 2022; accepted in revised form 26 September 2022

Abstract. The development of skin-compatible polyurethane materials with excellent wide-temperature range and anti-aging self-healing properties is considered crucial for modern applications. However, few polyurethane materials can achieve these characteristics simultaneously because of the chemical bond activity. Here, we report a wide-temperature range and anti-aging self-healing polyurethane material with superior mechanical features. At $-40 \,^{\circ}$ C, the polyurethane exhibits a self-healing efficiency of 72.6%, with a tensile strength of ~7.4 MPa and elongation at break of ~1424.5%. At 60 $^{\circ}$ C, its self-healing efficiency reached 93.6%, with an elongation at break of 1922.2% without significant reduction of the tensile strength. Notably, its low-temperature self-healing efficiency was 79.3 and 72.6%, respectively, at –20 and–40 $^{\circ}$ C, and the samples showed some degree of self-healing, even at –60 and –80 $^{\circ}$ C. Meanwhile, the polyurethane showed excellent anti-aging performance, and its self-healing properties were sufficiently high after aging at 60 $^{\circ}$ C for 7 days. The designed polyurethane is expected to offer a promising platform for fabricating materials for electronic skin applications, wearable electronic devices, flexible displays, and soft robotics.

Keywords: polyurethane, self-healing, mechanical properties, wide temperature range, anti-aging

1. Introduction

Electronic skin (e-skin), a novel technology that can monitor many kinds of signals and exhibits high sensitivity and wide detection range [1-4], has significant potential in wearable electronic devices, flexible displays, and soft robotics [5-13]. Elastic polyurethane substrates are often used to endow e-skins with excellent mechanical elasticity; however, during the application, polyurethane is inevitably subjected to accidental damage, such as scratches and penetrations, and therefore highly susceptible to tearing [14, 15]. Inspired by the rapid and efficient self-healing ability of human skin after injury, researchers have attempted to incorporate self-healing functionality into e-skin [7, 16].

In recent decades, significant progress has been achieved in the field of self-healing materials, and two types of such materials have been developed

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based on extrinsic or intrinsic healing mechanisms [17, 18]. Extrinsic self-healing materials generally rely on a healing agent in implanted microcapsules [19–21]. As the amount of the implanted healing agent is fixed, it can only provide limited repairs, and the preparation process is relatively complicated [22]. In contrast, intrinsic self-healing materials are realized by the reversible exchange reaction of dynamic bonds, such as metal coordination bonds [23-27], hydrogen bonds [28–30], disulfide bonds [31– 35], D-A reactions [36, 37], imine bonds [38], and boron-ester bonds [39, 40]. Theoretically, intrinsic self-healing materials can be repaired countless times and have more stable self-healing properties than extrinsic self-healing materials; therefore, intrinsic self-healing has received more attention. Through the introduction of self-healing technology, some self-healing polyurethanes with excellent mechanical properties have been successfully synthesized [41–45]. Wu et al. [43] successfully prepared an elastomer with excellent tensile strength, high toughness, high self-healing efficiency, and good puncture resistance by introducing an asymmetric alicyclic structure adjacent to an aromatic disulfide into polyurethane. The tensile strength and toughness of this elastomer were as high as 46.4 MPa and 109.1 MJ/m³, respectively, and it also had a selfhealing efficiency of 90.3%. Liu et al. [44] developed a nanofiber-reinforced self-healing polymer matrix that mainly mimics the structure and function of human skin. Significantly, its tensile strength and toughness were improved by 836 and 1000%, respectively, compared with those of the pure matrix, while its healing efficiency was largely preserved. Wei et al. [45] successfully developed a novel selfhealing elastomer enhanced by dynamic supramolecular nanosheets with switchable interfacial interactions. The elastomer has a high self-healing efficiency (91.2%). In addition, supramolecular nanosheets, as layered nanofillers, possess strong interfacial interactions and endow elastomers with outstanding mechanical properties, water insensitivity, and gas barrier properties.

However, these polyurethane materials can only accomplish self-healing at room temperature or high temperatures. At low temperatures, where the molecular chain movement is significantly hindered, the self-healing efficiency of polyurethane decreases abruptly [46]. At present, despite the constantly

increasing number of studies on low-temperature self-healing materials, the contradiction between the strength of the material and its low-temperature selfhealing performance persists. Most materials with excellent low-temperature self-healing properties are extremely soft hydrogels, which have extremely low tensile strength, despite their excellent molecular chain mobility. In contrast, high-strength polymer materials have poor low-temperature self-healing properties owing to their high cross-linking density. Li *et al.* [47] synthesized a polydimethylsiloxane polymer chain network cross-linked by coordination compounds, which showed an elongation at break of ~1825% and tensile strength of ~0.23 MPa at 25 °C. However, owing to its high cross-link density and strong Fe-pyridine coordination bonds, its repair efficiency reached only ~68% after self-healing at -20 °C for 72 h. Wang et al. [48] prepared a multifunctional ionic hydrogel with a repair efficiency of up to 68.6% at -80 °C with a repair time of only 30 min and an ultra-long elongation at break of >7000%. These features were attributed to the extremely soft hydrogel structure that facilitated the exchange reactions of dynamic bonds (e.g., ionic bonds); however, the material strength was extremely low (~ 0.02 MPa). Therefore, the design of polyurethane with excellent self-healing and mechanical properties over a wide temperature range is paramount. However, another aspect of the durability of polyurethane, the anti-aging performance, has seldom been studied. In fact, anti-aging is as important as other durability factors because the polyurethane matrix may need to resist ultraviolet rays, humidity, and other environmental factors during its lifecycle. In this study, dual-dynamic-bond cross-linking and copolymerization strategies were synergistically introduced into a polyurethane polymer to prepare an anti-aging material with superior self-healing and mechanical performance over a wide temperature range. The method included the copolymerization of hydroxyl-terminated polyethylene glycol-tetrahydrofuran co-polyether (HTPE) with hydroxyl-terminated polybutadiene (HTPB), followed by the addition of aliphatic disulfides (HEDS) to form ligands; finally, zinc chloride (ZnCl₂) was added to cross-link with the ligands and form polyurethane. The mechanical, self-healing, and anti-aging properties of the synthesized polyurethane were analyzed considering various aspects.

2. Materials and methods

2.1. Materials

HTPB (hydroxyl value = $0.75 \text{ mmol} \cdot \text{g}^{-1}$, functionality (f) = 2,99% purity), 1,4-butanediol (BDO, 99%) purity), ZnCl₂, and N,N-dimethylformamide (DMF, ≥99.8% purity) were purchased from Jining Huakai Resin Co., Ltd. (Jining, China). HTPE (hydroxyl value = 0.68 mmol \cdot g⁻¹, f = 2, 99.5% purity) was purchased from Luoyang Liming Chemical Research and Design Institute Co., Ltd. (Luoyang, China), whose relative molecular weights ($M_{\rm w} = 3217 \, {\rm g} \cdot {\rm mol}^{-1}$, $M_{\rm n} = 2925 \text{ g} \cdot \text{mol}^{-1}, D = 1.10$) were determined by gel permeation chromatography (GPC, PL-GPC50) (Yuzhong Industrial Co., Ltd., Shanghai, China) (Figure 1). Dibutyl phthalate (DBP, 99.5% purity) was provided by the Tianjin Damao Chemical Reagent Factory (Tianjin, China). Triphenylbismuth (TPB), HEDS (90% purity), isophorone diisocyanate (IPDI, 99% purity), and tetrahydrofuran (THF) were obtained from Shanghai McLean Biochemical Technology Co., Ltd. (Shanghai, China).

2.2. Synthesis of HEPU-Zn polyurethane

First, 2.4 g of HTPB was added to a 100 ml threenecked flask and dried overnight at 60 °C in a vacuum environment. Then, 1.8 mg of TPB (catalyst), 0.39 g of DBP (plasticizer), and 0.49 g of IPDI (curing agent) were thoroughly mixed, added to the flask, and stirred at 60 °C under nitrogen protection for 2 h. Thereafter, 0.6 g of HTPE was mixed well with 1 ml of DMF, and the mixture was added to the flask to conduct the copolymerization reaction for 1 h. Next, 0.27 g of HEDS (chain extender) was gradually added to the mixture, followed by stirring for 2 h to obtain the ligand. Finally, 58.6 mg of ZnCl₂ was fully dissolved in 2 ml of THF and added to the mixture, reacted at 25 °C for 12 h, poured into a polytetrafluoroethylene mold, and dried in a vacuum



Figure 1. GPC chromatogram of HTPE.

Table 1. Formula and name of samples (mass ratio).

Sample	HTPB	HTPE	IPDI	HEDS	BDO	ZnCl ₂
PU	3.0	0.0	0.50	0.00	0.101	0.0000
EPU	2.4	0.6	0.49	0.00	0.099	0.0000
HEPU	2.4	0.6	0.49	0.17	0.000	0.0000
HEPU-Zn	2.4	0.6	0.49	0.17	0.000	0.0586

oven at 60 °C for 24 h to evaporate the solvent and obtain the sample (labeled as HEPU-Zn). In addition, three control groups were fabricated, namely, the PU (only HTPB was cross-linked with IPDI, and BDO was used instead of HEDS as the chain extender), the EPU (without HEDS and ZnCl₂, and BDO was used instead of HEDS as the chain extender) and the HEPU (without ZnCl₂) groups. In our experiments, the R-value (ratio of the isocyanate group to hydroxyl group) of each group was 1. The mass ratios of the formulations for all samples were shown in Table 1.

2.3. Characterization

The structure of the coordination bonds was characterized using a Horiba Labram Raman spectrometer (Horiba Company, Paris, France) equipped with an Ar laser source (excitation wavelength = 633 nm, scanning range = $200-800 \text{ cm}^{-1}$). The absorption spectra in the wavelength range of 400–4000 cm⁻¹ were analyzed via Fourier transform infrared spectroscopy (FTIR) using an infrared spectrometer (NICOLET iS10) (Bruker Corporation, Germany) with a resolution of 4 cm⁻¹. The proton nuclear magnetic resonance (¹H NMR) spectrum was collected using a BRUKER AVANCE 400 instrument (NMR), with a supply of DMSO- d_6 as the solvent. Dynamic characteristic analysis was conducted on a dynamic mechanical analyzer (DMA, Q800) (TA Instruments Corporation, USA). Frequency scanning tests were performed on both the original and repaired samples, while temperature scanning and stress-relaxation experiments were performed on the original samples. For the frequency scanning tests, the frequency sweep range was 0.1–100 Hz, and the temperature was set to 60, 25, -20, or -40 °C. For the temperature scanning tests, the temperature sweep range was -90-60 C; the heating rate was $3 \degree C \cdot min^{-1}$, and the test frequency was 1 Hz. In the stress-relaxation experiments, the temperature was set to 60, 25, -20, -40,-60, or -80 °C, and the strain was set to 50%. The relaxation time (τ) of the polyurethane network was defined as the time required for the stress-relaxation



Figure 2. Synthesis of HEPU-Zn polyurethane.

modulus to reach 37% of its original value and was plotted on the curve. In accordance with the GB/ T528-92 standard, the tensile tests at -40, -20, 25, and $60 \,^{\circ}\text{C}$ were performed at a speed of $100 \, \text{mm} \cdot \text{min}^{-1}$ on an Instron 5982 material testing machine (Instron Corporation, USA), and the results were averaged with at least three measured data. Optical microscope images of the healing process of the samples were obtained using an AOSVI polarizing microscope (CM2000-3M100) (AOSVI Optical Instrument Co., Ltd., Shenzhen, China). For the self-healing experiments, the samples were cut into two pieces, contacted without an external force at each set temperature (60, 25, -20, or -40 °C), and left to repair at this temperature for 12 h. Subsequently, they were tested on an Instron 5982 material testing machine. The tensile experiments were performed at each temperature at a speed of 100 mm \cdot min⁻¹, and the tensile strength (σ_b) and elongation at break (ε_b) values were recorded.

The self-healing efficiency based on either the strength or elongation at break (η_{σ} and η_{ϵ} , respectively) was defined according to Equations (1) and (2), respectively. The accelerated aging experiments were performed in a constant-temperature blast box, which simulated the daily sun and wind through heating and airflow. During the anti-aging experiments, the mechanical and self-healing properties of the samples were evaluated. Two sets of samples were placed in a constant-temperature blast box (60 °C) and aged for 7 d. After the aging treatment was completed, the samples were cooled to 25 °C, and then one group of samples was subjected to tensile testing using an Instron 5982 material testing machine, while the other group of samples was first cut in half and then repaired at 25 °C for 12 h after contact. Finally, the self-healing performance after aging was evaluated according to Equations (1) and (2):

Healing efficiency,
$$\eta_{\epsilon} [\%] = \frac{\varepsilon_{b} \text{ of healing sample}}{\varepsilon_{b} \text{ of original sample}} \cdot 100\%$$
 (1)

Healing efficiency,
$$\eta_{\sigma} [\%] = \frac{\sigma_{b} \text{ of healing sample}}{\sigma_{b} \text{ of original sample}} \cdot 100\%$$
 (2)

3. Results and discussion

3.1. Material design and structural characterization

The main purpose of this study was to develop a wide-temperature range and anti-aging self-healing polyurethane material with superior mechanical performance. To achieve this objective, dynamic bond cross-linking and copolymerization strategies were simultaneously applied to the polyurethane network (Figure 2). Initially, HTPB and IPDI were used as raw materials to synthesize long chains terminated with isocyanate groups. After the chains were copolymerized with HTPE, HEDS was added to form HEPU ligands. Finally, HEPU ligands were cross-linked with Zn^{2+} to obtain polyurethane (HEPU-Zn). The introduction of HTPE into HTPB effectively reduced the cross-linking density, which benefited the molecular chain mobility of polyurethane [49]. In addition, HEDS provided disulfide bonds and introduced self-healing properties to polyurethane. Concurrently, the dynamic disulfide bonds effectively eliminated free radicals, endowing polyurethane with antiaging capabilities [50-54]. Moreover, the ZnCl₂ formed Zn-coordination bonds with the ligands, where the zinc ions have an alternating configuration, where transformation between the tetrahedral and octahedral structure is possible. This endowed the zinc coordination bonds with high dynamic exchange characteristics and provided excellent selfrepairing properties for polyurethane, especially at low temperatures [55].

Figure 3a shows the Raman spectra of HEPU-Zn, where the characteristic peaks at 245 and 319 cm^{-1} correspond to the stretching vibrations of Zn-N and Zn–O coordination bonds, respectively, indicating the presence of Zn-ligand bonds. The characteristic peak at $\sim 626 \text{ cm}^{-1}$ is due to the tensile vibration of the S-S covalent bond [56, 57], suggesting the successful introduction of disulfide bonds into HEPU-Zn. Figure 3b shows the FTIR spectra of EPU, HEPU, and HEPU-Zn. Compared with the HEPU spectrum, new absorption peaks at 1526 and 520 cm⁻¹ were observed for HEPU-Zn, which are attributed to the stretching vibrations of Zn-N and Zn-O, respectively [55]; this further indicates the existence of Zn-ligand bonds. In addition, the spectrum of EPU had a prominent absorption peak at 2257 cm⁻¹, which was due to the excess of -NCO groups. However, HEPU and HEPU-Zn showed no characteristic -NCO peak, which indicates that -NCO was completely

consumed, and the disulfide bonds were successfully introduced. From the above characterization results, it is concluded that the HEPU-Zn polyurethane samples containing Zn-coordination bonds and disulfide bonds were successfully synthesized.

As shown in Figure 3c, the chemical structures of HEDS, HTPE and HEPU were characterized by proton nuclear magnetic resonance. HEDS: δ 2.19 (s, 1H), 3.92 (s, 2H) and 2.91 (s, 3H) ppm; HTPE: δ 1.62 (s, 1H), 3.41 (s, 2H) and 3.64 (s, 3H) ppm. The chemical shift at 7.28 ppm for three samples was due to the deuterated solvent CDCl₃. HEPU contains the unique chemical shifts of HEDS and HTPE, and it does not show the chemical shift of protons in the hydroxyl groups belonging to HEDS at 2.19 ppm. These indicate that HEDS and HTPE have been successfully introduced into HEPU, which provides a necessary condition for the next preparation of HEPU-Zn.

3.2. Dynamic characteristic analysis

The superior self-repairing properties of the prepared HEPU-Zn polyurethane suggested that it might also have good dynamic properties. To verify this, rigorous temperature and frequency scanning tests were comparatively conducted between HEPU-Zn and the control group (PU) (Figures 4–6). In the temperature scanning curves (Figure 4), negligible differences were observed in the glass transition temperatures (T_g) of PU and HEPU-Zn (approximately -64 to -82 °C for HEPU-Zn and -66 to -83 °C for PU). However, the loss factor $(\tan \delta = G''/G')$ of HEPU-Zn showed a gradual increase when the temperature rose above -40 °C, indicating the better molecular chain fluidity of HEPU-Zn than that of PU. Figure 5 shows the frequency scanning curves of PU and HEPU-Zn. Generally, higher G''/G' ratios indicate better flexibility of the molecular chain of polyurethane [58]. From Figures 5, and 6, the G''/G'ratio in both HEPU-Zn and PU decreased with decreasing temperature in general trend, implying that the fluidity of the polyurethane molecular chain was impaired at lower temperatures. In addition, the G''/G' ratio of HEPU-Zn was higher than that of PU in general trend at -40, -20, 25, and 60 °C, thereby indicating the overall higher molecular chain mobility of HEPU-Zn, which was consistent with our previous conclusion. This behavior was theoretically attributed to the simultaneous introduction of the HTPE long chains and dual dynamic bonds in the



Figure 3. a) Raman spectra of HEPU and HEPU-Zn. b) FTIR spectra of EPU, HEPU, and HEPU-Zn. c) ¹H NMR spectra of HEDS, HTPE, and HEPU.

HEPU-Zn structure. On the one hand, the copolymerization with HTPE increases the length of the molecular chain and reduces its cross-linking density; on the other hand, the dynamic exchange reactions between dual dynamic bonds enhance energy dissipation and promote the flow of the molecular chain.

3.3. Mechanical performances

Table 2 shows the tensile mechanical properties of the HEPU-Zn, HEPU, and PU samples at -40, -20, 25, and 60 °C. PU exhibited the highest tensile strength and lowest elongation at break, which can be attributed to its poor molecular chain mobility and irreversible cross-linked network. At all tested



Figure 4. Temperature scanning curves of a) HEPU-Zn and b) PU from -90 to 60 °C.



Figure 5. Frequency scanning curves of PU and HEPU-Zn at a) -40 °C, b) -20 °C, c) 25 °C, and d) 60 °C.

temperatures, the HEPU samples showed an evidently improved ε_b compared with that of PU, but its σ_b was significantly impaired. This was theoretically attributed to the significantly improved molecular chain fluidity that provided by both the copolymerization with HTPE and the dynamic exchange reactions of disulfide bonds. In parallel, owing to the decrease in the cross-linking density, the σ_b of HEPU decreased. However, compared with those of HEPU, the ε_b and σ_b of HEPU-Zn were significantly higher, and the σ_b was even close to that of PU. This was attributed to the fact that the Zn-coordination bonds formed by Zn²⁺ and the ligands increased the crosslinking density of the polyurethane network, thereby increasing its strength. Furthermore, the alternating configuration of zinc ions that can change from tetrahedral to octahedral endowed the zinc coordination bonds with high dynamic exchange characteristics, thereby further increasing the molecular chain fluidity of polyurethane. Specifically, the ε_b of HEPU-Zn



Figure 6. The curve of G''/G' ratio of a) HEPU-Zn and b) PU samples at different temperatures.

Table 2. Elongation at break [%] and tensile strength [MPa] of polyurethane samples at -40, -20, 25, and 60 °C.

Sample	-40 °C		−20 °C		25°C		60 °C	
	ε _b [%]	σ _b [MPa]						
PU	302.9	9.37	466.7	6.29	656.2	0.50	324.6	0.23
HEPU	622.0	5.13	883.4	3.30	1401.2	0.27	1053.8	0.17
HEPU-Zn	1424.5	7.40	1618.9	4.40	2723.6	0.40	19222	0.19

at -40, -20, 25, and $60 \,^{\circ}$ C was ~ 1424.5 , 1618.9, 2723.6, and 1922.2%, respectively (all values >1400%), while its σ_b was 7.4, 4.4, 0.4, and 0.19 MPa, respectively. Therefore, it was inferred that the combined introduction of copolymerization and dual-dynamic bond cross-linking strategies into polyure-thane effectively enhanced its mechanical properties over a wide temperature range.

3.4. Wide-temperature-range self-healing performance

Figure 7a shows the self-healing properties of HEPU-Zn, HEPU, and PU at 60 °C. The self-healing efficiency of PU was extremely low, even at 60 °C, primarily attributed to its irreversible cross-linked network. Although its healing performance was improved after copolymerization and the introduction of disulfide bonds, the healing efficiency was only ~65%. When Zn^{2+} species were further introduced, its self-healing efficiency was significantly increased, with η_{ϵ} and η_{σ} reaching 93.6 and 89.5%, respectively. This was attributed to the synergistic effect of the disulfide and Zn-coordination bonds that both enhanced the self-healing ability of polyurethane. According to the images demonstrating the self-healing performance (Figure 7b-7d), the selfhealing efficiency of HEPU-Zn at all four temperatures remained considerably high; particularly, its η_{σ}

and η_{ϵ} values at -40 °C were ~87.8 and ~72.6%, respectively. These results suggest its excellent selfhealing efficiency over a wide temperature range that could be attributed to the following factors: first, the low cross-linking density and segmentation effect of the disulfide bonds endowed polyurethane with high molecular chain mobility; second, the cross-linked network formed by the disulfide and Zn-ligand bonds provides good dynamic mechanical properties, enhancing the self-healing ability of polyurethane over a wide temperature range. Finally, the dynamic exchange reactions of the Zn-ligand bonds facilitate the reduction of the energy barrier of the polymer chain slip, thereby endowing the polyurethane network with good self-healing properties, even at low temperatures.

Figure 8 shows the frequency scanning curves of the original and healed HEPU-Zn polyurethanes. The self-healing performance of polyurethane can be further characterized by comparing the frequency scanning curves before and after repair [59, 60]. According to Figure 8, the G' and G'' of the repaired HEPU-Zn samples were lower than those of the original samples, which is theoretically ascribed to the incomplete healing of the crack. In addition, as the healing degree of the crack increased with increasing temperature, the gap between the G' and G'' values of the healed and original specimens gradually



Figure 7. a) Self-healing performance of PU, HEPU, and HEPU-Zn at 60 °C. b, c) Self-healing performances of HEPU-Zn at -40, -20, 25, and 60 °C. d) Self-healing efficiency (η) of HEPU-Zn at different temperatures.

decreased as the temperature increased. Notably, the frequency scanning curves of the original and healed samples were very similar at 60 °C, indicating that the healing efficiency was close to 100%. This is because HEPU-Zn has excellent molecular chain mobility at 60 °C, and the dynamic reversibility of disulfide bonds and Zn-urethane coordination bonds are also extremely high currently, which greatly promotes HEPU-Zn self-healing process. This is consistent with the results in Figure 6, further validating the excellent self-healing properties conferred by the dual cooperative cross-linking strategy. Figure 9a illustrates the healing mechanism of the HEPU-Zn polyurethane. When the HEPU-Zn polyurethane is damaged, there will be many reversible active groups on the fractured surface, which is the key to realize self-healing. When the fracture surfaces contact each other, with the help of the rapid migration of molecular chains, the active groups contact each other to form new coordination bonds and disulfide bonds and finally realize self-healing. The corresponding microscopy images (Figure 9b) verify that the healed cracks at 60 and 25 °C were almost indistinguishable, and the healing degree decreased with decreasing temperature. The polyurethane evidently achieved a relatively high degree of healing above -40°C, which proves our previous conclusions. Significantly, the polyurethane showed partial healing capabilities, even at ultra-low temperatures (-60 and -80 °C). To visualize the self-healing ability at -60and -80 °C, manual tensile experiments of HEPU-Zn polyurethane were carried out, and the results are shown in Figure 9c. After healing at -60 and -80 °C, the polyurethane was relatively intact, highlighting its excellent molecular chain fluidity and self-repairing ability at low temperatures, which is of great application value.

Subsequently, stress-relaxation experiments were carried out at a constant temperature and deformation rate, and the recombination ability of the polyure-thane network was evaluated to reflect its healing ability. A shorter τ value implies a higher reorganization



Figure 8. DMA frequency sweep curves of the original and repaired HEPU-Zn polyurethanes at a) -40 °C, b) -20 °C, c) 25 °C, and d) 60 °C.

ability of the polyurethane network, which is conducive to self-healing [55, 61]. Figure 10a shows the stress-relaxation curves of HEPU-Zn polyurethane at 60, 25, -20, -40, -60, and -80 °C, and the stress relaxation experimental results of PU at 60, 25, and -20 °C are shown in Figure 10b. The τ value of HEPU-Zn is named τ_1 and that of PU is τ_2 . The τ_2 values of PU at 60 and 25 °C are 15.89 and 44.32 min, respectively, while the internal stress at -20 °C can only decrease to ~63% of its initial value. Note that τ_1 was extremely small, with values of only 0.89 and 1.79 min at 60 and 25 °C, respectively, which indicates that HEPU-Zn has excellent dynamic properties at 60 and 25 °C. When the temperature decreased to -20 and -40 °C, τ_1 increased to 7.02 and 22.46 min, respectively. This is because the molecular chain movement is hindered at low temperatures, the recombination ability of the polyurethane network is weakened, thus τ value increased as the temperature decreased. While compared with PU, HEPU-Zn still had strong molecular chain fluidity at

this time. When the temperature decreased from -40 to $-60 \,^{\circ}\text{C}$, τ_1 increased from 22.46 to 45.65 min, and the corresponding self-healing ability decreased significantly, but it was still close to the molecular chain mobility of PU at 25 °C. When the temperature decreased to -80 °C, although the internal stress of the polyurethane could not even reach up to 37% of the original stress, it could decrease to ~62% within 60 min. This demonstrated that at -80 °C, the polyurethane still had a certain healing ability, which was consistent with the results obtained from optical microscopy. These results further illustrated that the synergistic cross-linking strategy of copolymerization and dual dynamic bonds endowed polyurethane with excellent wide-temperature-range self-healing performance.

3.5. Anti-aging properties

In addition to the self-healing ability, an excellent anti-aging performance is paramount for the longterm use of polyurethane. Figure 11a depicts the



Figure 9. a) Self-healing mechanism of HEPU-Zn. b) Repair of HEPU-Zn occurring under optical microscopy observation. c) Photographs of manual tensile testing of HEPU-Zn samples repaired at -60 and -80 °C.



Figure 10. Stress-relaxation curves of a) HEPU-Zn and b) PU at different temperatures.

stress-strain curves of PU aged for 7 d at 60 °C under airflow. Both the tensile strength and elongation at break of the aged PU decreased significantly. This is because of the degrading influence of external factors such as heat and oxygen; the groups containing active hydrogen in polyurethane molecules are easily attacked by oxidizing components to form macromolecular free radicals, resulting in a series of freeradical chain reactions that promote aging. In contrast, no significant degradation of the tensile strength and elongation at break of the aged HEPU-Zn polyurethane samples was observed (Figure 11b); the



Figure 11. Stress-strain curves of a) PU and b) HEPU-Zn aged for 7 d under air flow at 60 °C. c) Stress-strain curves of HEPU-Zn samples aged at 60 °C for 7 d, cut in half, and healed at 25 °C for 12 h after contact.

tensile strength was ~0.37 MPa, which was 92.5% of the original value, while the elongation at break was $\sim 2437.2\%$, which was 89.4% of the original value. This superior anti-aging performance is attributed to the anti-aging property of disulfide bonds, which effectively prevented free-radical generation in the polyurethane network [54, 62–64]. These results show that HEPU-Zn polyurethane has relatively stable mechanical properties. To further study the stability of the self-healing properties of HEPU-Zn, after accelerated aging for 7 d, HEPU-Zn samples were cooled to 25 °C, cut in half and contacted, and then healed at 25 °C for 12 h. Their tensile mechanical properties were then measured, as shown in Figure 11c. The η_{ϵ} and η_{σ} of the aged HEPU-Zn samples reached 79.9 and 77.5%, respectively. Compared with the original sample (87.9%/85.0%), the healing ability decreased to some extent, but remained at a high level, which further proves the excellent anti-aging characteristics of disulfide bonds. As for the slight decrease in self-healing efficiency, this may be due to the molecular chain fluidity. The active groups on the fracture surface directly form new bonds with the adjacent groups, thus reducing the number of new bonds that can be formed between the two fracture surfaces, which shows the decline of tensile strength, elongation, and self-repairing efficiency in a macroscopic view. The above results show that HEPU-Zn polyurethane can maintain relatively high mechanical and self-healing performance, even after accelerated aging for 7 d. This will enable this material to be used in practical operating environments for a sufficiently long time.

4. Conclusions

In this study, dual-dynamic-bond cross-linking and copolymerization strategies were synergistically applied to polyurethane materials to provide wide-temperature-range and anti-aging self-healing performance. The final obtained polyurethane had a self-healing efficiency of ~93.6% and an elongation at break of ~1922% at 60 °C, and its tensile strength

was like that of the PU control group. At -40 °C, it had a tensile strength of ~7.4 MPa and an elongation at break of ~1425%, along with a high self-healing efficiency. Significantly, the low-temperature selfhealing efficiencies of the polyurethane were 79.3 and 72.6% at -20 and -40 °C, respectively, and intact samples were achieved after healing, even at -60 and -80 °C. Furthermore, when the polyurethane was aged at 60 °C for 7 d, its mechanical and self-healing properties were still relatively high. The findings presented here highlight the feasibility of polyurethane as a potential material for applications in wearable electronics, flexible displays, and soft robotics.

Acknowledgements

This work was supported by the National Defense Pre-Research Projects (Grant No. LJ20212A031130), NSFC (Grant No. 11732012), and NSSFC (Grant No.2020SKJJC108).

References

- [1] Jin M. L., Park S., Lee Y., Lee J. H., Chung J., Kim J. S., Kim J-S., Kim S. Y., Jee E., Kim D. W., Chung J. W., Lee S. G., Choi D., Jung H. T., Kim D. H.: An ultrasensitive, visco-poroelastic artificial mechanotransducer skin inspired by Piezo2 protein in mammalian merkel cells. Advanced Materials, **29**, 1605973 (2017). <u>https://doi.org/10.1002/adma.201605973</u>
- [2] Liu R., Lai Y., Li S., Wu F., Shao J., Liu D., Dong X., Wang J., Wang Z. L.: Ultrathin, transparent, and robust self-healing electronic skins for tactile and non-contact sensing. Nano Energy, 95, 107056 (2022). https://doi.org/10.1016/j.nanoen.2022.107056
- [3] Han T-Y., Lin C-H., Lin Y-S., Yeh C-M., Chen Y-A., Li H-Y., Xiao Y-T., Chang J-W., Su A-C., Jeng U-S., Chou H-H.: Autonomously self-healing and ultrafast highlystretching recoverable polymer through trans-octahedral metal-ligand coordination for skin-inspired tactile sensing. Chemical Engineering Journal, 438, 135592 (2022).

https://doi.org/10.1016/j.cej.2022.135592

[4] Amoli V., Kim J. S., Kim S. Y., Koo J., Chung Y. S., Choi H., Kim D. H.: Ionic tactile sensors for emerging human-interactive technologies: A review of recent progress. Advanced Functional Materials, 30, 1904532 (2019).

https://doi.org/10.1002/adfm.201904532

[5] Zhou K., Zhao Y., Sun X., Yuan Z., Zheng G., Dai K., Mi L., Pan C., Liu C., Shen C.: Ultra-stretchable triboelectric nanogenerator as high-sensitive and self-powered electronic skins for energy harvesting and tactile sensing. Nano Energy, **70**, 104546 (2020). https://doi.org/10.1016/j.nanoen.2020.104546

- [6] Rich S. I., Wood R. J., Majidi C.: Untethered soft robotics. Nature Electronics, 1, 102–112 (2018). https://doi.org/10.1038/s41928-018-0024-1
- [7] Kang J., Tok J. B-H., Bao Z.: Self-healing soft electronics. Nature Electronics, 2, 144–150 (2019). https://doi.org/10.1038/s41928-019-0235-0
- [8] Li G-Y., Li J., Li Z-J., Zhang Y-P., Zhang X., Wang Z-J., Han W-P., Sun B., Long Y-Z., Zhang H-D.: Hierarchical PVDF-HFP/ZnO composite nanofiber–based highly sensitive piezoelectric sensor for wireless workout monitoring. Advanced Composites and Hybrid Materials, 5, 766–775 (2021). https://doi.org/10.1007/s42114-021-00331-z
- [9] Huang X., Qin Q., Wang X., Xiang H., Zheng J., Lu Y., Lv C., Wu K., Yan L., Wang N., Xia C., Wang Z. L.: Piezoelectric nanogenerator for highly sensitive and synchronous multi-stimuli sensing. ACS Nano, 15, 19783– 19792 (2021).

https://doi.org/10.1021/acsnano.1c07236

- [10] Lu L., Jiang C., Hu G., Liu J., Yang B.: Flexible noncontact sensing for human-machine interaction. Advanced Materials, 33, 2100218 (2021). <u>https://doi.org/10.1002/adma.202100218</u>
- [11] Pu X., An S., Tang Q., Guo H., Hu C.: Wearable triboelectric sensors for biomedical monitoring and humanmachine interface. iScience, 24, 102027 (2021). <u>https://doi.org/10.1016/j.isci.2020.102027</u>
- [12] Chen J., Han K., Luo J., Xu L., Tang W., Wang Z. L.: Soft robots with self-powered configurational sensing. Nano Energy, 77, 105171 (2020). <u>https://doi.org/10.1016/j.nanoen.2020.105171</u>
- [13] Ounkaew A., Kasemsiri P., Srichiangsa N., Jetsrisuparb K., Knijnenburg J. T. N., Okhawilai M., Hiziroglu S., Theerakulpisut S.: Multifunctional gluten/guar gum copolymer with self-adhesion, self-healing, and remolding properties as smart strain sensor and self-powered device. Express Polymer Letters, 16, 607–623 (2022). https://doi.org/10.3144/expresspolymlett.2022.45
- [14] Du R., Xu Z., Zhu C., Jiang Y., Yan H., Wu H-C., Vardoulis O., Cai Y., Zhu X., Bao Z., Zhang Q., Jia X.: A highly stretchable and self-healing supramolecular elastomer based on sliding crosslinks and hydrogen bonds. Advanced Functional Materials, **30**, 1907139 (2019).

https://doi.org/10.1002/adfm.201907139

[15] Zhang Y., Zheng J., Zhang X., Du Y., Li K., Liu Y., Yu G., Jia Y., Song S.: Dual dynamic bonds self-healing polyurethane with superior mechanical properties over a wide temperature range. European Polymer Journal, 163, 110934 (2022).

https://doi.org/10.1016/j.eurpolymj.2021.110934

[16] Huynh T-P., Sonar P., Haick H.: Advanced materials for use in soft self-healing devices. Advanced Materials, 29, 1604973 (2017). https://doi.org/10.1002/adma.201604973

- [17] Cao J., Lu C., Zhuang J., Liu M., Zhang X., Yu Y., Tao Q.: Multiple hydrogen bonding enables the self-healing of sensors for human-machine interactions. Angewandte Chemie-International Edition, 56, 8795–8800 (2017). https://doi.org/10.1002/anie.201704217
- [18] Ying W. B., Liu H., Gao P., Kong Z., Hu H., Wang K., Shen A., Jin Z., Zheng L., Guo H., Zhang R., Zhu J.: An anti-stress relaxation, anti-fatigue, mildew proof and self-healing poly(thiourethane-urethane) for durably stretchable electronics. Chemical Engineering Journal, 420, 127691 (2021). https://doi.org/10.1016/j.cej.2020.127691
- [19] Romero-Sabat G., Gago-Benedí E., Rovira J. J. R., González-Gálvez D., Mateo A., Medel S., Chivite A. T.: Development of a highly efficient extrinsic and autonomous self-healing polymeric system at low and ultra-low temperatures for high-performance applications. Composites Part A: Applied Science and Manufacturing, 145, 106335 (2021). https://doi.org/10.1016/j.compositesa.2021.106335
- [20] Liu Y., Zheng J., Zhang X., Du Y., Li K., Yu G., Jia Y., Zhang Y.: Mussel-inspired and aromatic disulfide-mediated polyurea-urethane with rapid self-healing performance and water-resistance. Journal of Colloid and Interface Science, 593, 105–115 (2021). https://doi.org/10.1016/j.jcis.2021.03.003
- [21] Zhang M. Q.: Polymer self-heals in seconds. Express Polymer Letters, 9, 84 (2015). https://doi.org/10.3144/expresspolymlett.2015.9
- [22] Ambekar R. S., Kandasubramanian B.: Advancements in nanofibers for wound dressing: A review. European Polymer Journal, **117**, 304–336 (2019). https://doi.org/10.1016/j.eurpolymj.2019.05.020
- [23] Das M., Pal S., Naskar K.: Exploring various metal-ligand coordination bond formation in elastomers: Mechanical performance and self-healing behavior. Express Polymer Letters, 14, 860–880 (2020). https://doi.org/10.3144/expresspolymlett.2020.71
- [24] Lai J-C., Jia X-Y., Wang D-P., Deng Y-B., Zheng P., Li C-H., Zuo J-L., Bao Z.: Thermodynamically stable whilst kinetically labile coordination bonds lead to strong and tough self-healing polymers. Nature Communications, 10, 1164–1172 (2019).

https://doi.org/10.1038/s41467-019-09130-z

[25] Li C-H., Zuo J-L.: Self-healing polymers based on coordination bonds. Advanced Materials, **32**, 1903762 (2020).

https://doi.org/10.1002/adma.201903762

[26] Zhang L., Liu Z., Wu X., Guan Q., Chen S., Sun L., Guo Y., Wang S., Song J., Jeffries E. M., He C., Qing F-L., Bao X., You Z.: A highly efficient self-healing elastomer with unprecedented mechanical properties. Advanced Materials, **31**, 1901402 (2019). https://doi.org/10.1002/adma.201901402

- [27] Li M. X., Rong M. Z., Zhang M. Q.: Enhancement of mechanochemical self-blocking and self-healing of early minor damages in polymers through hyperbranched architecture. Express Polymer Letters, 15, 781–790 (2021). https://doi.org/10.3144/expresspolymlett.2021.62
- [28] Burattini S., Greenland B. W., Merino D. H., Weng W., Seppala J., Colquhoun H. M., Hayes W., Mackay M. E., Hamley I. W., Rowan S. J.: A Healable supramolecular polymer blend based on aromatic π–π stacking and hydrogen-bonding interactions. Journal of the American Chemical Society, **132**, 12051–12058 (2010). https://doi.org/10.1021/ja104446r
- [29] Wu X., Wang J., Huang J., Yang S.: Robust, stretchable, and self-healable supramolecular elastomers synergistically cross-linked by hydrogen bonds and coordination bonds. ACS Applied Materials & Interfaces, 11, 7387– 7396 (2019).

https://doi.org/10.1021/acsami.8b20303

[30] Yan X., Liu Z., Zhang Q., Lopez J., Wang H., Wu H-C., Niu S., Yan H., Wang S., Lei T., Li J., Qi D., Huang P., Huang J., Zhang Y., Wang Y., Li G., Tok J. B-H., Chen X., Bao Z.: Quadruple H-bonding cross-linked supramolecular polymeric materials as substrates for stretchable, antitearing, and self-healable thin film electrodes. Journal of the American Chemical Society, 140, 5280– 5289 (2018).

https://doi.org/10.1021/jacs.8b01682

[31] Rekondo A., Martin R., de Luzuriaga A. L., Cabañero G., Grande H. J., Odriozola I.: Catalyst-free room-temperature self-healing elastomers based on aromatic disulfide metathesis. Materials Horizons, 1, 237–240 (2014).

https://doi.org/10.1039/C3MH00061C

[32] Yang Y., Lu X., Wang W.: A tough polyurethane elastomer with self-healing ability. Materials & Design, 127, 30–36 (2017).

https://doi.org/10.1016/j.matdes.2017.04.015

[33] Wan T., Chen D.: Synthesis and properties of self-healing waterborne polyurethanes containing disulfide bonds in the main chain. Journal of Materials Science, 52, 197–207 (2016).

https://doi.org/10.1007/s10853-016-0321-x

[34] Liu M., Zhong J., Li Z., Rong J., Yang K., Zhou J., Shen L., Gao F., Huang X., He H.: A high stiffness and selfhealable polyurethane based on disulfide bonds and hydrogen bonding. European Polymer Journal, 124, 109475 (2020).

https://doi.org/10.1016/j.eurpolymj.2020.109475

[35] Aguirresarobe R. H., Martin L., Fernandez-Berridi M. J., Irusta L.: Autonomic healable waterborne organicinorganic polyurethane hybrids based on aromatic disulfide moieties. Express Polymer Letters, 11, 266–277 (2017).

https://doi.org/10.3144/expresspolymlett.2017.27

[36] Lin C., Sheng D., Liu X., Xu S., Ji F., Dong L., Zhou Y., Yang Y.: Effect of different sizes of graphene on Diels-Alder self-healing polyurethane. Polymer, 182, 121822 (2019).

https://doi.org/10.1016/j.polymer.2019.121822

- [37] Yang S., Du X., Deng S., Qiu J., Du Z., Cheng X., Wang H.: Recyclable and self-healing polyurethane composites based on Diels-Alder reaction for efficient solar-to-thermal energy storage. Chemical Engineering Journal, **398**, 125654 (2020). https://doi.org/10.1016/j.cej.2020.125654
- [38] Yang Z., Li H., Zhang L., Lai X., Zeng X.: Highly stretchable, transparent and room-temperature selfhealable polydimethylsiloxane elastomer for bending sensor. Journal of Colloid and Interface Science, 570, 1–10 (2020).

https://doi.org/10.1016/j.jcis.2020.02.107

[39] Chen Y., Tang Z., Zhang X., Liu Y., Wu S., Guo B.: Covalently cross-linked elastomers with self-healing and malleable abilities enabled by boronic ester bonds. ACS Applied Materials & Interfaces, 10, 24224–24231 (2018).

https://doi.org/10.1021/acsami.8b09863

- [40] Cromwell O. R., Chung J., Guan Z.: Malleable and selfhealing covalent polymer networks through tunable dynamic boronic ester bonds. Journal of the American Chemical Society, 137, 6492–6495 (2015). https://doi.org/10.1021/jacs.5b03551
- [41] Hussain I., Ma X., Luo Y., Luo Z.: Fabrication and characterization of glycogen-based elastic, self-healable, and conductive hydrogels as a wearable strain-sensor for flexible e-skin. Polymer, 210, 122961 (2020). https://doi.org/10.1016/j.polymer.2020.122961
- [42] Wu H., Jin B., Wang H., Wu W., Cao Z., Wu J., Huang G.: A degradable and self-healable vitrimer based on non-isocyanate polyurethane. Frontiers in Chemistry, 8, 585569 (2020).

https://doi.org/10.3389/fchem.2020.585569

- [43] Wu H-T., Jin B-Q., Wang H., Wu W-Q., Cao Z-X., Yuan Z-Y., Huang Y., Li W-H., Huang G-S., Liao L-S., Wu J-R.: A robust self-healing polyurethane elastomer enabled by tuning the molecular mobility and phase morphology through disulfide bonds. Chinese Journal of Polymer Science, **39**, 1299–1309 (2021). https://doi.org/10.1007/s10118-021-2607-y
- [44] Liu J., Zhang L., Wang N., Zhao H., Li C.: Nanofiberreinforced transparent, tough, and self-healing substrate for an electronic skin with damage detection and program-controlled autonomic repair. Nano Energy, 96, 107108 (2022).

https://doi.org/10.1016/j.nanoen.2022.107108

[45] Wei H., Yang Y., Huang X., Zhu Y., Wang H., Huang G., Wu J.: Transparent, robust, water-resistant and highbarrier self-healing elastomers reinforced with dynamic supramolecular nanosheets with switchable interfacial connections. Journal of Materials Chemistry A, 8, 9013– 9020 (2020).

https://doi.org/10.1039/D0TA01352H

- [46] Sun F., Xu J., Liu T., Li F., Poo Y., Zhang Y., Xiong R., Huang C., Fu J.: An autonomously ultrafast self-healing, highly colourless, tear-resistant and compliant elastomer tailored for transparent electromagnetic interference shielding films integrated in flexible and optical electronics. Materials Horizons, 8, 3356–3367 (2021). https://doi.org/10.1039/D1MH01199E
- [47] Li C-H., Wang C., Keplinger C., Zuo J-L., Jin L., Sun Y., Zheng P., Cao Y., Lissel F., Linder C., You X-Z., Bao Z.: A highly stretchable autonomous self-healing elastomer. Nature Chemistry, 8, 618–624 (2016). https://doi.org/10.1038/nchem.2492
- [48] Wang C., Liu Y., Qu X., Shi B., Zheng Q., Lin X., Chao S., Wang C., Zhou J., Sun Y., Mao G., Li Z.: Ultrastretchable and fast self-healing ionic hydrogel in cryogenic environments for artificial nerve fiber. Advanced Materials, 34, 2105416 (2022). https://doi.org/10.1002/adma.202105416
- [49] Zhang Y., Zheng J., Zhang X., Du Y., Li K., Yu G., Jia Y., Liu Y.: Effect of chemical copolymerization and mixed chain extenders on mechanical properties of HTPB polyurethane. IOP Conference Series: Materials Science and Engineering, **1167**, 012012 (2021). https://doi.org/10.1088/1757-899X/1167/1/012012
- [50] Li T., Xie Z., Xu J., Weng Y., Guo B-H.: Design of a self-healing cross-linked polyurea with dynamic crosslinks based on disulfide bonds and hydrogen bonding. European Polymer Journal, **107**, 249–257 (2018). https://doi.org/10.1016/j.eurpolymj.2018.08.005
- [51] Grande A. M., Bijleveld J. C., Garcia S. J., Zwaag S.: A combined fracture mechanical – rheological study to separate the contributions of hydrogen bonds and disulphide linkages to the healing of poly(urea-urethane) networks. Polymer, 96, 26–34 (2016). https://doi.org/10.1016/j.polymer.2016.05.004
- [52] Xie H., Sheng D., Zhou Y., Xu S., Wu H., Tian X., Sun Y., Liu X., Yang Y.: Thermally healable polyurethane with tailored mechanical performance using dynamic crosslinking motifs. New Journal of Chemistry, 44, 13584–13590 (2020).

https://doi.org/10.1039/D0NJ02671A

- [53] Xiao L., Shi J., Wu K., Lu M.: Self-healing supramolecular waterborne polyurethane based on host-guest interactions and multiple hydrogen bonds. Reactive and Functional Polymers, 148, 104482 (2020). https://doi.org/10.1016/j.reactfunctpolym.2020.104482
- [54] Li F., Xu Z., Hu H., Kong Z., Chen C., Tian Y., Zhang W., Ying W. B., Zhang R., Zhu J.: A polyurethane integrating self-healing, anti-aging and controlled degradation for durable and eco-friendly E-skin. Chemical Engineering Journal, 410, 128363 (2021). https://doi.org/10.1016/j.cej.2020.128363
- [55] Wu X., Luo R., Li Z., Wang J., Yang S.: Readily selfhealing polymers at subzero temperature enabled by dual cooperative crosslink strategy for smart paint. Chemical Engineering Journal, **398**, 125593 (2020). <u>https://doi.org/10.1016/j.cej.2020.125593</u>

[56] Zhang W., Wang M., Zhou J., Sheng Y., Xu M., Jiang X., Ma Y., Lu X.: Preparation of room-temperature selfhealing elastomers with high strength based on multiple dynamic bonds. European Polymer Journal, **156**, 110614 (2021).

https://doi.org/10.1016/j.eurpolymj.2021.110614

[57] Xu J., Chen W., Wang C., Zheng M., Ding C., Jiang W., Tan L., Fu J.: Extremely stretchable, self-healable elastomers with tunable mechanical properties: Synthesis and applications. Chemistry of Materials, **30**, 6026– 6039 (2018).

https://doi.org/10.1021/acs.chemmater.8b02320

- [58] Matxain J. M., Asua J. M., Ruiperez F.: Design of new disulfide-based organic compounds for the improvement of self-healing materials. Physical Chemistry Chemical Physics, 18, 1758–1770 (2016). https://doi.org/10.1039/C5CP06660C
- [59] Cui Y., Song S., Tang Y., Chen Y., Yang H., Yang B., Huang J.: Decoupling the roles of the catechol content from those of glass transition temperature and dynamic mechanical modulus in determining self-healing and anti-corrosion of mussel-inspired polymers. Polymer, 185, 121928 (2019).

https://doi.org/10.1016/j.polymer.2019.121928

[60] Gupta A., Simmons W., Schueneman G. T., Hylton D., Mintz E. A.: Rheological and thermo-mechanical properties of poly(lactic acid)/lignin-coated cellulose nanocrystal composites. ACS Sustainable Chemistry & Engineering, 5, 1711–1720 (2017). https://doi.org/10.1021/acssuschemeng.6b02458 [61] Zhang Y., Chen J., Zhang G., Xv J., Xv J., Hu Y., Guo H., Guo F., Fu J., Jiang W.: Mechanically robust, highly adhesive and autonomously low-temperature self-healing elastomer fabricated based on dynamic metal – ligand interactions tailored for functional energetic composites. Chemical Engineering Journal, 425, 130665 (2021).

https://doi.org/10.1016/j.cej.2021.130665

- [62] Marykutty C. V., Mathew G., Mathew E. J., Thomas S.: Studies on novel binary accelerator system in sulfur vulcanization of natural rubber. Journal of Applied Polymer Science, 90, 3173–3182 (2003). https://doi.org/10.1002/app.13023
- [63] Alam M. N., Mandal S. K., Debnath S. C.: Bis(N-benzyl piperazino) thiuram disulfide and dibenzothiazyl disulfide as synergistic safe accelerators in the vulcanization of natural rubber. Journal of Applied Polymer Science, 126, 1830–1836 (2012). https://doi.org/10.1002/app.36874
- [64] Das A., Naskar N., Basu D. K.: Thiophosphoryl disulfides as crosslinking agents for chloroprene rubber. Journal of Applied Polymer Science, 91, 1913–1919 (2004).

https://doi.org/10.1002/app.13300