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ABSTRACT
Two kinds of polyurethane elastomers were synthesized. One containing acylhydrazone bonds was named TPIA. The other containing both acylhydrazone and disulfide bonds was named TPID. Self-repairable ability and reprocessability of these two elastomers were studied. The results show that: The polyurethane elastomer TPIA can automatically repair damage to it under acidic conditions. After self-healing for 24 h, the strength and the elongation value at break recovered to 32% and 55% of the originality, respectively. The polyurethane elastomer TPID can automatically repair damage to it under visible light at room temperature. After 24 h of self-healing time, 75% of the original strength and 100% of the original elongation values at break were obtained. These two polyurethane elastomers can be reprocessed in their cured state by just applying temperature and pressure.

1. Introduction
Polyurethanes are widely used in foams, adhesives and other fields for their excellent properties. However, like other polymer materials, micro-cracking will inevitably produce within matrix during the production and application of polyurethane materials. Micro-cracks will develop into cracks and eventually lead to the destruction of polymeric materials. Besides, Micro-cracking is also the direct cause of material property deterioration continuously. This is a very valuable method for polymeric structural materials to incorporate the self-healing property into polymeric materials since it effectively expands the lifetime use of the product and has desirable economic and human safety attributes. Self-healing polymeric materials are currently the subject of active research. A particularly useful approach to generate self-healable polymers has been the introduction of dynamic covalent bonds such as Diels–Alder reaction, acylhydrazone bonds, imine, disulfide bonds, reversible C–ON bonds, trithioesters, diarylbenzofuranone, phenylboronic acid ester bonds into the polymeric materials. In addition to normal properties of conventional polymers such as strength and stability, these dynamic covalent polymers have shown the ability to exchange components between different polymer chains by the exchange reaction of the dynamic covalent bonds. In the majority of cases, an appropriate external stimulus such as pH, light, temperature and catalysts is required, in order to promote the exchange reaction of the dynamic covalent bonds. This feature enables these dynamic covalent polymers to repair their damage.

Acylhydrazone bonds were firstly used by Lehn and co-workers to prepare dynamic covalent polymers, which showed better thermal stability and solvent stability due to the stronger bond energy. Also, Deng and his coworkers synthesized dynamic polymer gels based on acylhydrazone bonds. The dynamic polymer gels possess self-healing properties by the exchange reaction of acylhydrazone bonds. The self-healing properties already occurred after simply putting the cracked gels together and keeping contact without any outside stimulus at room temperature. The heated gel was strong enough to sustain severe deformation. And the dynamic polymer gels also displayed reversible sol-gel phase transitions by adjusting the acidity of the system. Alaitz Rekondo and his coworkers synthesized a poly (urea-urethane) elastomeric material based on aromatic disulfides, which is able to self-mend by simple contact at room-temperature. Also, the poly (urea-urethane) elastomeric material could be reprocessed by applying temperature and pressure. Besides, the combination of disulfide and acylhydrazones reported by Zhang et al was also a breakthrough for the application of self-healing materials. The synthesized materials above based on acylhydrazones only or both disulfide and acylhydrazones were weak in mechanical strength, which restrict their applications.

However, the room-temperature self-healing and reprocessability of polyurethane elastomers own better mechanical strength based on acylhydrazone bonds has, to the best of our knowledge, not been reported so far. For this purpose, two kinds of polyurethane elastomers were synthesized. One containing acylhydrazone bonds is named TPIA. The other containing both acylhydrazone and disulfide bonds in order to improve the self-repairable ability of TPIA is named TPID. Self-repairable ability and the reprocessability of these two elastomers were studied.
2. Experimental

2.1. Materials

Dimethyl 3,3'-dithiobispropionate (purity = 96%) was purchased from Shanghai Aladdin Biochemical Technologies Co., Ltd. Adipic dihydrazide (98%) was purchased from Shanghai Macklin Biochemical Technologies Co., Ltd. TEP-240 (Mn = 7300; Polyether triol) was purchased from Tianjin Third Petrochemical Co., Ltd. Isophorone diisocyanate (IPDI; >99.5%) was purchased from Bayer, Germany. Polypropylene glycol 2000 (PPG2000; >99.9%) was purchased from Jiangsu Haian Petrochemical Co., Ltd. Methanol, Hydrazine hydrate 80%, p-Hydroxybenzaldehyde, Isopropanol, Ethanol, Glacial acetic acid, Dimethyl sulfoxide (DMSO), Dibutyl tin dilaurate (DBTDL) were of analytical grade and used as received.

2.2. Methods

2.2.1. Synthesis of dihydric alcohol PA containing acylhydrazone bonds

p-Hydroxybenzaldehyde (24.4 g, 0.2 mol-CHO) was dissolved in isopropanol (48.8 g), Adipic dihydrazide (17.4 g, 0.2 mol-CONHNH2) was dissolved in glacial acetic acid (87.0 g). Afterwards, the two solutions were mixed and refluxed for 1 h at 70°C under stirring. The resulting mixture was filtered under reduced pressure. The resulting product was washed three times with 50 g of ethanol and 200 g of deionized water at 70°C, respectively. Afterwards, the resulting product was dried under vacuum to a constant weight. The product was obtained in the form of a yellowish solid powder, which is named PA. Yield: 96%. PA was synthesized as shown in Scheme 1a.

2.2.2. Synthesis of 3,3'-dithiobis (propionohydrazide)

To a solution of dimethyl 3,3'-dithiobispropionate (14.95 g, 0.06 mol) in methanol (30 g, 0.48 mol), hydrazine hydrate 80% (30 g, 0.24 mol) was added. The mixture reacted for 1 h at room-temperature. The resulting mixture was filtered under reduced pressure. The resulting product was washed with 50 g of methanol, 50 g of deionized water and 50 g of methanol respectively. Afterwards, the resulting product was dried under vacuum to a constant weight. The resulting product was obtained in the form of a white solid powder. Yield: 86%. 3,3'-dithiobis (propionohydrazide) was synthesized as shown in Scheme 1b.

2.2.3. Synthesis of dihydric alcohol PD containing acylhydrazone and disulfide bonds

p-Hydroxybenzaldehyde (24.4 g, 0.2 mol-CHO) was dissolved in isopropanol (48.8 g), 3,3'-dithiobis (propionohydrazide) (23.8 g, 0.2 mol-CONHNH2) was dissolved in glacial acetic acid (120.0 g). Afterwards, the two solutions were mixed and refluxed for 2 h at 70°C under stirring. The resulting mixture was filtered under reduced pressure. The resulting product was washed three times with 50 g of ethanol and 200 g of deionized water at 70°C, respectively. Afterwards, the resulting product was dried under vacuum to a constant weight. The product was obtained in the form of a yellowish solid powder, which is named PD. Yield: 65%. PD was synthesized as shown in Scheme 1b.

Scheme 1. (a) Synthesis of PA. (b) Synthesis of 3,3'-dithiobis (propionohydrazide) and PD. (c) Synthetic procedure of TPIA and TPID.
2.2.4. Synthesis of tris-isocyanate-terminated prepolymer TEP-IPDI

TEP-240 (100 g), IPDI (9.14 g) and DBTDL (0.55 g) were added in a 250 ml three-necked flask. The mixture was stirred under vacuum at 70°C for 2 h. The product was obtained in the form of a colourless liquid (Theoretical content of -NCO: 1.58%). TEP-IPDI was synthesized as shown in Scheme 1c.

2.2.5. Synthesis of bis-isocyanate-terminated prepolymer PPG-IPDI

PPG2000 (100 g), IPDI (22.23 g) and DBTDL (0.61 g) were added in a 250 ml three-necked flask. The mixture was stirred under vacuum at 70°C for 2 h. The product was obtained in the form of a milky liquid (Theoretical content of -NCO: 3.44%). PPG-IPDI was synthesized as shown in Scheme 1c.

2.2.6. Synthesis of polyurethane elastomer TPIA

To a solution of PA (3.82 g) in DMSO (7.64 g), TEP-IPDI (27.49 g) and PPG-IPDI (11.78 g) were added. The mixture was mixed well and then degassed under vacuum for 30 minutes. Afterwards, the mixture was placed into an open glass mold. The curing was allowed to proceed for 6 h at 70°C. Polyurethane elastomer TPIA was obtained in the form of a milky elastomeric material. (Theoretical content of DMSO: w_DMSO = 15.06%). TPIA was synthesized as shown in Scheme 1c.

2.2.7. Synthesis of polyurethane elastomer TPID

To a solution of PD (4.46 g) in DMSO (2.23 g), TEP-IPDI (27.49 g) and PPG-IPDI (11.78 g) were added. The mixture was mixed well and then degassed under vacuum for 30 minutes. Afterwards, the mixture was placed into an open glass mold. The curing was allowed to proceed for 12 h at 70°C. Polyurethane elastomer TPID was obtained in the form of a milky elastomeric material. (Theoretical content of DMSO: w_DMSO = 4.85%). TPID was synthesized as shown in Scheme 1c.

3. Characterization

3.1. Analysis of FTIR spectra

p-hydroxybenzaldehyde, adipic dihydrazide, PA, 3, 3'-dithiobis (propionohydrazide) and PD were measured using a KBr tablet method at room-temperature. The FTIR spectra of TPIA and TPID were measured using a total reflection method at room-temperature. Dimethyl 3, 3'-dithiobispipronate, IPDI, PPG2000, TEP-240, TEP-IPDI and PPG-IPDI were coated on a KBr wafer in order to test their FTIR spectra. All the samples were measured by a same Fourier transform infrared spectrometer (Bruker, Germany).

3.2. Analysis of 1H NMR spectra

The 1H NMR spectra of PA and PD were measured using a AC500 (500 MHz) nuclear magnetic resonance instrument (Bruker, Germany). The solvent used in NMR experiments are DMSO-d6.

3.3. Tensile tests

Tensile tests were performed on dumbbell-shaped specimens according to ISO527-2 and using a Zwick/Roell/005 universal tester (Zwick/Roell, Germany) at a speed of 500 mm/min.

3.4. Swelling ratio tests

Polyurethane elastomer TPID (2.47 g) was immersed into DMSO (125 g) at 25°C. The swollen TPID was weighed at a regular interval with a microbalance quickly after the excess of DMSO on the surfaces was absorbed with filter paper until equilibrium of swelling had been reached. The swelling ratio (SR) was calculated using the following equation:

$$SR = \frac{(w-w_0)}{w_0} \times 100\%,$$

where, w and w_0 are the weights of the polyurethane elastomer TPID at equilibrium swelling state and original state, respectively.

Polyurethane elastomer TPIA (0.62 g) was immersed into DMSO (30 g) at 25°C. The swelling ratio of TPIA was calculated by the same method as we have described above.

3.5. Gel content tests

The polyurethane elastomer TPID/TPIA reached a state of equilibrium swelling was immersed into 50 times the mass of deionized water at 80°C for 2 h in order to displace the DMSO. This step needs to be repeated twice. Afterwards, these elastomers were dried under vacuum to a constant weight at 110°C. The gel content was calculated using the following equation:

$$\text{Gel content} = \frac{w_0 \times (1 - w_{\text{DMSO}}) - w'}{w_0 \times (1 - w_{\text{DMSO}})} \times 100\%,$$

here, w_0 and w' are the weights of the polyurethane elastomer TPID/TPIA at original state and dry state.

3.6. Dynamic rheological measurements

All dynamic rheological measurements were carried out with an Advance Rheological Expansion System (ARES) (TA Instruments, America) equipped with a parallel plate fixture of a diameter of 8 mm at 140°C. And the polyurethane samples used were film samples matched the thickness of the instrument. Prior to the frequency sweep experiments, strain sweep experiments were performed at fixed frequency of 1 rad/s to determine the linear viscoelastic region and then the frequency sweep experiments from 0.01 to 100 rad/s at strain of 0.05% were conducted at 140°C.

4. Results and discussion

4.1. Analysis of the structure of PA

4.1.1. FTIR spectra of PA

The peaks at 1668 cm⁻¹ on curve c are derived from the carbonyl stretching vibrations of p-hydroxybenzaldehyde. The peak at 1632 cm⁻¹ on curve b is derived from carbonyl stretching vibrations of adipic dihydrazide. The peaks at 3291 cm⁻¹ and 3316 cm⁻¹ are derived from the N-H symmetric and asymmetric stretching vibrations of -NH₂ in adipic dihydrazide, respectively.
The FTIR spectra of p-hydroxybenzaldehyde, adipic dihydrazide and PA proved the occurrence of condensation reaction between acylhydrazine and aldehyde groups in PA. The absorption from aldehyde groups of p-hydroxybenzaldehyde on curve c at 1668 cm\(^{-1}\) became invisible on the curve a of PA, indicating the formation of the acylhydrazone bonds. The broad peak at around 1624–1562 cm\(^{-1}\) was formed due to the stacking of C\(_N\) and C\(_O\) stretching vibrations in PA.

### 4.1.2. 1H NMR spectra of PA

The peaks at \(\delta = 11.15\) ppm and 11.02 ppm are derived from the absorption of H in -CONH-. The peaks at \(\delta = 8.03\) ppm and 7.86 ppm are derived from the absorption of H in -CH\(_N\)-. The H in these two groups have two chemical shifts are due to the fact that the acylhydrazone bond has cis and trans isomers and \(\delta_{\text{cis}} > \delta_{\text{trans}}\). The presence of these absorption peaks indicates the formation of an acylhydrazone bond, thus indicating that the compound containing acylhydrazone bonds have been synthesized. Besides, the peak at \(\delta = 9.87\) ppm is derived from the absorption of H in -OH; The peaks at \(\delta = 7.47\) ppm and 6.79 ppm are derived from the absorption of H in benzene ring; The peaks at \(\delta = 2.62\) ppm, 2.20 ppm and 1.61 ppm are derived from the absorption of H in DMSO. The peaks at \(\delta = 3.36\) ppm is derived from the absorption of H in water.

### 4.2. Analysis of the structure of 3, 3'-dithiobis(propionohydrazide)

#### 4.2.1. FTIR spectra of 3, 3'-dithiobis(propionohydrazide)

The peak at 1735 cm\(^{-1}\) on curve a is derived from carbonyl stretching vibrations of dimethyl 3, 3'-dithiobis-propionate. The peak at around 1243-1142 cm\(^{-1}\) is derived from asymmetric stretching vibrations of C-O-C in ester groups. The peak at 2953 cm\(^{-1}\) is derived from C-H stretching vibrations of methyl groups. The peaks at 1437 cm\(^{-1}\) and 1357 cm\(^{-1}\) are derived from asymmetric and symmetric bending vibrations of C-H in methyl groups, respectively.

The peak at around 1665–1630 cm\(^{-1}\) on curve b is derived from carbonyl stretching vibrations of 3, 3'-dithiobis(propionohydrazide). The peak at 3178 cm\(^{-1}\) is derived from the N-H stretching vibrations of -NH- in 3, 3'-dithiobis (propionohydrazide). The peaks at 3291 cm\(^{-1}\) and 3323 cm\(^{-1}\) are derived from the N-H symmetric and asymmetric stretching vibrations of -NH\(_2\) in 3, 3'-dithiobis (propionohydrazide), respectively.

The absorption from methyl and ester groups on curve a became invisible on the curve b of 3, 3'-dithiobis (propionohydrazide), which was used as criteria to prove the generation of 3, 3'-dithiobis(propionohydrazide).
4.2.2. $^1$H NMR spectra of 3, 3'-dithiobis (propionohydrazide)
The peaks at $\delta = 2.55$ ppm and 2.87 ppm are derived from the absorption of H at the $\alpha$ and $\beta$ positions of the hydrazide groups, respectively. The reason why the absorption peaks of hydrogen in the hydrazide groups are not shown in this figure is that the solvent used is heavy water. The peaks at $\delta = 4.68$ is derived from the absorption of H in water.

4.3. Analysis of the structure of PD

4.3.1. FTIR spectra of PD

The FTIR spectra of p-hydroxybenzaldehyde, 3, 3'-dithiobis (propionohydrazide) and PD proved the occurrence of condensation reaction between acylhydrazine and aldehyde groups in PD. The absorption from aldehyde groups of p-hydroxybenzaldehyde on curve $a$ at 1668 cm$^{-1}$ became invisible on the curve $c$ of PD, while a new peak appeared around 1651 cm$^{-1}$ on the curve $c$ of PD. Besides, the absorption from the N-H symmetric and asymmetric stretching vibrations of $-\text{NH}_2$ in 3, 3'-dithiobis (propionohydrazide) became invisible on the curve $a$ of PD. These indicated the formation of the acylhydrazone bonds. The peak at 3182 cm$^{-1}$ on curve $c$ is derived from O-H stretching vibrations of PD.

4.3.2. $^1$H NMR spectra of PD

The peaks at $\delta = 11.28$ ppm and 11.21 ppm are derived from the absorption of H in $-\text{CONH}-$. The peaks at $\delta = 8.04$ ppm and 7.88 ppm are derived from the absorption of H in $-\text{CH} = \text{N}-$. The H in these two groups have two chemical shifts are due to the fact that the acylhydrazone bond has cis and trans isomers and $\delta_{\text{cis}} > \delta_{\text{trans}}$. The presence of these absorption peaks indicates the formation of an acylhydrazone bond, thus indicating that the compound containing acylhydrazone bonds have been synthesized. Besides, the peak at $\delta = 9.89$ ppm is derived from the absorption of H in $-\text{OH}$; The peaks at $\delta = 7.49$ ppm and 6.81 ppm are derived from the absorption of H in benzene ring; The peaks at $\delta = 3.01$ ppm, 2.60 ppm and 2.54 ppm are derived from the absorption of H in -CH$_2$-; The peaks at $\delta = 3.50$ ppm is derived from the absorption of H in DMSO. The peaks at $\delta = 3.39$ ppm is derived from the absorption of H in water.

4.4. Analysis of the structure of TEP-IPDI

The peak at 3492 cm$^{-1}$ on curve $c$ is derived from O-H stretching vibrations of TEP-240. The peak at 2258 cm$^{-1}$ on curve $b$ is derived from the characteristic absorption of $-\text{NCO}$ in IPDI. The peaks at 1720 cm$^{-1}$ and 3332 cm$^{-1}$ on curve $a$ are derived from carbonyl and N-H stretching vibrations of TEP-IPDI, respectively. Besides, the peak at 2266 cm$^{-1}$ on curve $a$ is derived from the characteristic absorption of $-\text{NCO}$ in TEP-IPDI.

The absorption derived from O-H groups on curve $c$ became invisible on the curve $a$ of TEP-IPDI, while a new absorption derived from N-H groups appeared on the curve $a$ of TEP-IPDI. Moreover, a displacement of the $-\text{NCO}$ stretching band from 2258 cm$^{-1}$ to 2266 cm$^{-1}$ can be observed, which was used as criteria to establish that the reaction was finished.

4.5. Analysis of the structure of PPG-IPDI

The peak at 3480 cm$^{-1}$ on curve $c$ is derived from O-H stretching vibrations of PPG2000. The peak at 2258 cm$^{-1}$ on curve $b$ is derived from the characteristic absorption of $-\text{NCO}$ in IPDI. The peaks at 1719 cm$^{-1}$ and 3335 cm$^{-1}$ on curve $a$ are derived from carbonyl and N-H stretching vibrations of PPG-IPDI, respectively. Besides, the peak at 2263 cm$^{-1}$ on curve $a$ is derived from the characteristic absorption of $-\text{NCO}$ in PPG-IPDI.

The absorption from O-H groups on curve $c$ became invisible on the curve $a$ of PPG-IPDI, while a new absorption derived from N-H groups appeared on the curve $a$ of PPG-IPDI. Moreover, a displacement of the $-\text{NCO}$ stretching band from...
Figure 6. $^1$H NMR spectra of PD.

Figure 7. FTIR spectra of TEP-IPDI (curve a), IPDI (curve b) and TEP-240 (curve c).

Figure 8. FTIR spectra of PPG-IPDI (curve a), IPDI (curve b) and PPG 2000 (curve c).

Figure 9. FTIR spectra of TPID.

Figure 10. FTIR spectra of TPIA.

Figure 11. The relation curve of TPID (curve a) and TPIA (curve b) swelling ratio and swelling time in DMSO.
4.7. Analysis of the structure of polyurethane elastomer TPID

The disappearance of the characteristic absorption of -NCO in TPID was used as criteria to establish that the reaction among TEP-IPDI, PPG-IPDI and PD was finished.

4.8. Analysis of the cross-linked structure of polyurethane elastomer TPID and TPIA

The relation curve of TPID (curve a) and TPIA (curve b) swelling ratio and swelling time in DMSO at 25°C is shown in Figure 10.

As shown in Figure 11a, the swelling ratio of TPID in DMSO increased to the peak value 129% within 24 h and kept a plateau with further increasing time. The volume of TPID expanded but kepted structure integrity, which was used as criteria to prove the cross-linked structure of TPID.

2.34 g of TPID at dry state was obtained when it was dried under vacuum to a constant weight at 110°C. Gel content $D_0$: $47 \%$; $D_2$: $47 \%$; $2$: $85 \%$; $D_3$: $43 \%$. This data proved the reaction among TEP-IPDI, PPG-IPDI and PD was very thorough.

From Figure 11b we can know that the swelling ratio of TPIA in DMSO increased to the peak value 42% within 24 h and kept a plateau with further increasing time. The volume of TPIA expanded but kept structure integrity, which was used as criteria to prove the cross-linked structure of TPIA. The gel content of TPIA was calculated by the same method as we have described above. The gel content of TPIA $= 3.77\%$, this data proved that the reaction among TEP-IPDI, PPG-IPDI and PA was very thorough.

The equilibrium swelling rate of TPID is two times higher than TPIA, just because the molecular structure of TPID contains disulfide bonds. This result may be due to the possibility that the disulfide bonds have a good compatibility with DMSO.

2258 cm$^{-1}$ to 2263 cm$^{-1}$ can be observed, which was used as criteria to establish that the reaction was finished.

4.6. Analysis of the structure of polyurethane elastomer TPID

The disappearance of the characteristic absorption of -NCO in TPID was used as criteria to establish that the reaction among TEP-IPDI, PPG-IPDI and PD was finished.

4.10. Self-healing property

4.10.1. Self-healing property of TPIA

As shown in Figure 12, in each self-healing experiment, a dumbbell-shaped specimen was first cut into two pieces with a razor blade. The two broken surfaces were then brought
together, subjected to a pressure of about 5 N on the top of them after 3 drops of glacial acetic acid were added to the incision, and stored horizontally at room temperature for 24 h.

Figure 13 shows stress-strain curves obtained for original samples, healed samples after 12 and 24 h of healing time under neutral conditions and the samples healed for 12 h and 24 h under acidic conditions.

The healed samples after 24 h of healing time under neutral conditions have a tensile strength of 0.29 MPa and an elongation at a breaking point of 187.70%, which are only 12.75% and 16.48% of the values of the original samples, respectively. However, the healed samples after 24 h of healing time under acidic conditions have a tensile strength of 0.74 MPa and an elongation at a breaking point of 626.75%, which are 32% and 55% of the values of the original samples, respectively.

Self-healing efficiency was calculated using the following equation:

$$ R(\sigma) = \frac{\sigma_{\text{healed}}}{\sigma_{\text{initial}}} \quad \text{and} \quad R(\varepsilon) = \frac{\varepsilon_{\text{healed}}}{\varepsilon_{\text{initial}}} $$

here, $\sigma_{\text{healed}}$ and $\sigma_{\text{initial}}$ are the tensile strength of the healed and original samples, respectively; $\varepsilon_{\text{healed}}$ and $\varepsilon_{\text{initial}}$ are the failure strain of the healed and original samples, respectively.

The self-healing efficiency of the healed samples after 24 h of healing time under acidic conditions is $R(\sigma) = 32\%$, $R(\varepsilon) = 55\%$.

The self-healing efficiency of TPIA could be attributed to two aspects: (1) the cleavage and the exchange reaction of the acylhydrazone bonds at room-temperature and (2) the H-bonds in TPIA. As shown in Figure 13, the self-healing efficiency of the healed samples under acidic conditions is much larger than the self-healing efficiency under neutral conditions. This result could be explained by the reason that the cleavage and exchange reaction of the acylhydrazone bonds was promoted under acidic conditions. The sources of self-healing efficiency in the self-healing process of TPIA are shown in Figure 14.

4.10.2. Self-healing property of TPID

As shown in Figure 15, in each self-healing experiment, a dumbbell-shaped specimen was first cut into two pieces with a razor blade. The two broken surfaces were then brought together, irradiated by visible light at room temperature for 24 h. The light source was a commercial tabletop lamp.

Figure 16 shows stress-strain curves obtained for original and self-healed samples at different healing times.

The relationship between the self-healing efficiency and healing time is shown in Table 1.

As shown in Table 1, the healing efficiency increases with increasing time. After self-healing for 24 h, 75% of the original strength and 100% of the elongation values at break are obtained.

### Table 1. The relationship between the self-healing efficiency and healing time.

<table>
<thead>
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<th>time/h</th>
<th>$R(\sigma)/%$</th>
<th>$R(\varepsilon)/%$</th>
</tr>
</thead>
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<tr>
<td>2</td>
<td>28</td>
<td>12</td>
</tr>
<tr>
<td>12</td>
<td>39</td>
<td>100</td>
</tr>
<tr>
<td>24</td>
<td>75</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 16. Stress-strain curves at different healing time obtained for self-healing elastomer TPID. Mending was performed by simple contact under visible light at room temperature.

Figure 17. Stress-strain curves of the elastomer TPID healed for 24 h in the absence of light.
The difference of self-healing properties between TPID and TPIA is hypothesized to be generated by the structural differences between TPID and TPIA, that is, the additional disulfide bonds in TPID. From 4.10.1, we can easily conclude that TPID could not repair itself through acylhydrazone bonds under neutral conditions. Therefore, the main source of self-healing efficiency in the self-healing process of TPID is derived from the disulfide bonds.

Figure 17 shows stress-strain curves of the elastomer TPID healed for 24 h in the absence of light at room temperature. As shown in Figure 17, the healed samples after healing for 24 h in the absence of light conditions have a tensile strength of 0.78 MPa and an elongation at a breaking point of 920.14%, which are much smaller than the healing efficiency under visible light. This result could be explained by the reason that the cleavage and exchange reaction of the disulfide bonds was promoted under visible light. Visible light can trigger hemolytic cleavage of the disulfide bond, the exchange reaction of the disulfide bonds in TPID is shown in Figure 18.

From this paper, we can easily know that the self-healing efficiency of TPIA is relatively low compared to TPID although the number of acylhydrazone bonds in TPIA is more than the number of disulfide bonds in TPID, which indicates that the cleavage and the exchange reaction of the disulfide bonds under visible light is faster than acylhydrazone bonds under acidic conditions.

4.4. Reprocessability

As we all know, conventional thermoset materials cannot be reprocessed in their cured state. However, some pioneering work has recently reported some reprocessable thermoset materials based on dynamic covalent bonds.[20,29] However, the
reprocessability of materials based on acylhydrazone bonds has, to the best of our knowledge, not been reported so far. In order to study the reprocessability of TPIA and TPID, these two kinds of cured materials were folded and then placed in a 2 mm thick mould and compressed in a hot press at 140°C and 5 MPa for 30 and 3 minutes respectively, resulting in two films (Figure 19). This result indicated that the acylhydrazone bonds were also sensitive to temperature.

4.5. Rheological characterization

The reprocessability of TPID and TPIA encouraged us to study the rheological properties of them. Figure 20 shows the relation curves of the storage modulus (G’) and loss modulus (G‘’), as a function of frequency. For these two samples, G’ exceeded G‘’ over the entire measured frequency, implying the existence of a chemically cross-linked network, which indicated that the reprocessability of TPID and TPIA was not from the melt flow at this temperature. Besides, G’ was dependent of oscillatory frequency to a certain degree, which should be attributed to the reversible properties of these two dynamic covalent bonds at this temperature. This result indicates that the self-healing property of TPID and TPIA at this temperature was primarily from the reversible properties of these two dynamic covalent bonds.

5. Conclusion

Compared with the two self-healing polyurethane elastomers synthesized in this paper, we can find TPID own higher self-healing efficiency (R(σ) = 75%, R(ε) = 100%) than TPIA (R(σ) = 32%, R(ε) = 55%), it can be benefitted by reversible reaction of disulfide bonds promoted by visible light. So we can determine essentially the efficiency of the disulfide bond was higher than that of the acylhydrazone bond due to that the cleavage and exchange reaction of the disulfide bonds under visible light is faster than the acylhydrazone bonds under acidic conditions. The self-healing processes of TPIA and TPID can be depicted by Figure 21. Besides, the polyurethane matrix synthesized by trifunctional polyether polyol (TEP-240) own better mechanical strength with tensile strength of 0.78 MPa and elongation at a breaking point of 920.14%, which can expand its application in load-bearing materials, especially mechanical materials. It was the purpose and significance to introduce self-healing ability to the polyurethane materials in our work.

Acknowledgments

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References

[34] Lei, Z.; Xiang, H.; Yuan, Y.; Rong, M.; Zhang, M. Chem. Mater. 2014, 26, 2038.
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