Self-Healing Mechanism of Microcracks on Waterborne Polyurethane with Tunable Disulfide Bond Contents

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ABSTRACT: Self-healing mechanism of microcracks on waterborne polyurethane (WPU) with varied disulfide bond contents was investigated thoroughly in this paper. The self-healing process could be observed by an optical microscope, which was divided into two steps. The first step was the cohesive healing movement, closely related with microphase separations and further characterized by the Fourier transform infrared peak fitting, differential scanning calorimetry, and dynamic mechanical thermal analysis. The second step of the exchange reactions of disulfide bonds could be confirmed by in situ Raman and tensile mechanics. In addition, the cohesive healing behavior was quantitatively described by the kinetic method, and the exchange reaction active energies of disulfide bonds were also calculated to be 20.42 kJ/mol by gel permeation chromatography tests. The best self-healing performance of SHWPUs was WPU-8, and it could be healed at 75 °C in 15 min with 100% self-healing efficiency. Combining the self-healing process observation with the kinetic analysis can provide deep insights into the self-healing mechanism of microcracks.

INTRODUCTION

When structural materials are exposed to harsh environments or suffer external stimuli, microcracks will form, which will threaten the integrity of the material matrix and even lead to mechanical failure.1−5 These microcracks are difficult to detect, thereby troubling engineers. Many advanced detection technologies have been developed to solve the problem of microcracks.6,5 To a large extent, the implementations of these technologies should recourse to manual interventions. The newly emerging concepts of self-healing provide an elegant route for self-healing of microcracks.6 Recently, considerable progress for self-healing materials has been obtained,6−25 which shows great advantages in prolonging the service life and lessening maintenance costs.

Waterborne polyurethane (WPU), a kind of engineering material, also suffers from microcrack problems. Combining the self-healing function and WPU is greatly advantageous for the recovery of mechanical integrity. Given that the molecular structure of WPU is versatile and tunable, the most direct method is to introduce self-healing functional groups to the main chains. In general, these self-healing functional groups are attributed to the field of reversible chemistry. If they are distributed around the microcracks, they will bind the crack faces through reversible reactions under suitable conditions. On the basis of these premises, some self-healing waterborne polyurethanes (SHWPUs) have been successfully prepared.26−31 Moreover, high-quality SHWPUs can be synthesized by importing the disulfide bonds to the structures,27,28 which exhibited excellent self-healing performance.

In recent years, disulfide chemistry has been applied in the field of polymer materials.32 Given that the exchange reactions of disulfide bonds are easy to carry out, many self-healing materials based on disulfide bonds have been prepared. Canadell et al.16 synthesized a kind of coating with commercial epoxy resins containing disulfide bonds. By changing the ratios of disulfide with other components, different self-healing degrees can be acquired, among which the highest disulfide concentration demonstrated the optimum self-healing efficiency. Regardless of disulfide content, the mobility of the molecular chains also showed great effects. Generally, rigid matrix can inhibit the movements of disulfide bonds, as well as weaken the cohesion and adhesion abilities. Lafont et al.33 explored the influence of different extenders to the self-healing performance of material matrix, demonstrating that the introduction of more cross-linking points to the system would promote the self-healing of disulfide bonds. In addition, the self-healing process depends on the state of microcracks. Garcia et al.34 proved the self-healing property of vulcanized natural rubber by tuning the disulfide/polyisulfide ratio and found that the self-healing efficiency was related with the postcuring storage time, time between damage creation and re-establishment of mechanical contact, and actual healing time. Given that self-healing is a complex topic, exploring the self-healing chemical functional groups, matrix structures, and...
The earliest research on the disulfide exchange reactions were confirmed by chemorheology. The earliest research on the disulfide exchange reactions were confirmed by chemorheology. To date, chemorheology remains a classical method to demonstrate the existence of the exchange reactions of dynamic reversible chemical bonds, such as disulfides. With the development of disulfide chemistry in the field of materials, more and more technologies are being used to explain the nature of this self-healing principle. Odriozola et al. synthesized a kind of self-healing polyurethane by incorporating aromatic disulfide compounds, which can be healed at room temperature without manual interventions. As the synergism of exchange reactions of disulfides with the aid of quadrupole hydrogen bonds formed, the self-healing activation energy was found to be 55 kJ/mol by the stress relaxation method, demonstrating the possibilities of self-healing at room temperature. By combining rheology and mechanical concepts, Garcia found that hydrogen-bonding self-healing efficiency was separated from the aromatic disulfide exchange reactions, which can be both described quantitatively. Given that the occurrences of exchange reactions can change the molecular features such as molecular weight, Zhang et al. utilized this property to characterize the dynamic nature of polymers containing disulfide bonds. In addition, dynamic mechanical thermal analysis (DMTA) can also disclose the existence of exchange reactions for disulfide bonds. Although all the above-mentioned methods can characterize the self-healing phenomenon, self-healing process analysis of microcracks was still lacking. Hence, a kinetic approach to observe microcracks was established, and the self-healing mechanism for SHWPUs was also improved, which could be an effective way to gain further comprehension of the self-healing mechanism.

In this study, a series of SHWPUs with varied contents of disulfide bonds was synthesized using prepolymer mixing. The SHWPU is a kind of thermoplastic elastomer that has inherent self-healing ability with intense molecular diffusion ability. The exchange reactions of disulfide bonds in the structure of Table 1. Formulas of Samples Used in This Study (Mol)

| sample | PPG | IPDI | DMPA | BDO | HEDS | TEA | EDA |
|--------|-----|------|------|-----|------|-----|-----|
| WPU-5  | 0.300 | 0.900 | 0.224 | 0.100 | 0.100 | 0.224 | 0.166 |
| WPU-6  | 0.300 | 0.900 | 0.224 | 0.080 | 0.120 | 0.224 | 0.166 |
| WPU-7  | 0.300 | 0.900 | 0.224 | 0.060 | 0.140 | 0.224 | 0.166 |
| WPU-8  | 0.300 | 0.900 | 0.224 | 0.040 | 0.160 | 0.224 | 0.166 |
| WPU-9  | 0.300 | 0.900 | 0.224 | 0.020 | 0.180 | 0.224 | 0.166 |
| WPU-10 | 0.300 | 0.900 | 0.224 | 0.000 | 0.200 | 0.224 | 0.166 |
| WPU-L  | 0.600 | 0.900 | 0.224 | 0.000 | 0.200 | 0.224 | 0.166 |
| WPU-C  | 0.300 | 0.900 | 0.224 | 0.200 | 0.000 | 0.224 | 0.166 |

Table 1. Formulas of Samples Used in This Study (Mol)

Molecular weight of PPG used for WPU-L was 2000. WPU-C did not contain the self-healing component HEDS, which was used as a control sample.

Scheme 1. Synthesis of Self-Healing Waterborne Polyurethane with HEDS

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SHWPU can promote the self-healing performance. Therefore, a dual functional self-healing material can be obtained. Except for the basic physical property characterizations, the self-healing mechanism and their self-healing kinetics were mainly analyzed by optical microscopy and gel permeation chromatography (GPC). The optimum formulation and conditions were also obtained through mechanical tests. The relationships between structures and performance were explored, providing theoretical guidance for forming highly effective self-healing materials.

**EXPERIMENTAL METHODS**

**Materials.** Poly(propylene glycol) (PPG, $M_n = 1000$, industrial grade, Tianjin Petrochemical Co., Ltd, China) was dehydrated at 120 °C for 6 h before use. Isophorone diisocyanate (IPDI, industrial grade, Bayer AG, Germany) and 2-hydroxyethyl disulfide (HEDS, industrial grade, Aldrich) were used as received. 2-Bis(hydroxyethyl)propionic acid (DMPA, industrial grade, Beijing Linshi Fine Chemical & New Material Co., Ltd, China) was dried at 100 °C for 12 h. Butanone (MEK, analytical grade, Beijing Chemical Works, China), triethylamine (TEA, analytical grade, Tianjin Fuchen Co., China), ethylenediamine (EDA, analytical grade, Tianjin Fuchen Co., China), and 1,4-butylen glycol (BDO, analytical grade, Tianjin Fuchen Co., China) were also used as received.

**Experiments.** SHWPUs with different amounts of HEDS in the main chains were synthesized by the prepolymer mixing process. First, PPG, DMPA, and IPDI were sequentially added in a 250 mL three-necked flask connected with a mechanical stirrer, a nitrogen inlet, and a condenser. The mixture was heated to 85 °C and reacted for 3 h. Then, the temperature was lowered to 60 °C, and different mole ratios of BDO and HEDS (5:5, 4:6, 3:7, 2:8, 1:9, and 0:10) were added in the above reaction system. The mixture was heated for another 6 h to obtain the prepolymer. Then, 20 g MEK should be added into the mixtures if the viscosity was high. TEA was next added to the prepolymer to neutralize the carboxylic acids for 30 min and form ionic groups below 40 °C. The prepolymer was subsequently emulsified by deionized (DI) water with EDA at 2000 rpm for 30 min. The prepolymer was then added into the emulsions to obtain the prepolymer. The emulsions were tested using the Labram HR Evolution spectrometer, and the synthesis diagram is shown in Scheme 1.

**Preparation of Films.** Emulsions of SHWPUs (20 g) were poured into Teflon molds to dry at room temperature for 7 days. After the evaporation of water, dried films were obtained with thickness of 0.5–1 mm. These films were placed in a vacuum oven for further maturation. The temperature was set at approximately 45 °C, and the maturation time was 12 h.

**Characterization.** $^1$H NMR and $^{13}$C NMR. Both $^1$H NMR and $^{13}$C NMR spectra of the WPU-10 and WPU-C were measured by an Avance III HD 400 MHz Instrument (Bruker Co., Germany) with deuterated dimethyl sulfoxide (DMSO-$d_6$) as the solvent.

**Fourier Transform Infrared (FTIR).** The SHWPUs films were tested using Fourier infrared transform spectroscopy of Nicolet 8700 FTIR (Thermo Nicolet Corporation). The scan range was from 4000 to 650 cm$^{-1}$ with a resolution ratio of 4 cm$^{-1}$ for a total of 48 times.

**In Situ Raman Spectroscopy.** The Raman spectroscopies were tested using the Labram HR Evolution spectrometer, and the wavelength of the laser was 536 nm. The special wave position was approximately 510 cm$^{-1}$, which is the signal of disulfide bonds.

**Particle Size and Zeta-ζ.** Particle size and Zeta-ζ were characterized using a laser particle size instrument (Malvern Zetasizer Nano ZS90). The SHWPUs emulsions were diluted to 1 wt % using DI water. The equilibrium time was set for 120 s, and the emulsions were tested three times for sequential analysis.

**Viscosity.** Viscosity was measured using the Brookfield Programmable DV-II+Pro Viscometer. The rotor is zero size at 150 s$^{-1}$. The temperature was 25 °C, and the data of the last 100 points were averaged.

**Centrifugal Stability.** Equal amounts of emulsions were placed in two centrifuge tubes that were positioned symmetrically in the high-speed centrifuge (ZONKIA, HC-3018). The speed was set to 3000 rpm, and the centrifugal force was 1.5 kg. After centrifuging for 5 min, no precipitations were observed, indicating that the emulsions were stable.

**Differential Scanning Calorimetry (DSC).** The thermal properties were tested by DSC (Mettler Toledo). A total of 10 mg of sample was placed in an alumina crucible with the temperature increasing from −80 to 150 °C. The heating rate was 10 °C/min, and the nitrogen purging rate was 30 mL/min. The temperature range was from −80 to 80 °C under nitrogen atmosphere with a heating rate of 5 °C/min. The dimensions of the test specimens were square samples with the length 4 mm and thickness 0.4 mm.

**GPC.** The molecular weight was obtained using GPC (LC-20A, Shimadzu) at 35 °C with tetrahydrofuran as the mobile phase and flow rate of 1 mL/min. The raw data were calibrated using a universal calibration with polystyrene standards.

**Optical Microscopy.** The self-healing processes of the microcracks on samples were observed using the Leica optical microscope DM 2500P, and the samples were heated with a Linkam hot stage. To observe the self-healing process, the temperatures were set at 70, 75, and 80 °C with heating rate of 10 °C/min.

**Mechanical Property.** Dumbbell-shaped samples were divided into two groups. The first group was composed of samples scratched with 300 μm-deep cracks using a micro-meter scratch instrument. The samples in the second group were used as the control. They were both placed in an oven at different temperatures (70, 75, and 80 °C) for 20 min. Then, the tensile strength ($\sigma_m$) and elongation at break ($\varepsilon_m$) of the specimens were measured using a universal testing machine (Instron-6022, Shimadzu Co., Ltd.) with a tensile rate of 100 mm/min. The final results were expressed as the average of three samples.

**RESULTS AND DISCUSSION**

**Analysis of Emulsion Properties.** The fundamental properties of SHWPU emulsions are summarized in Table 2. With the growth of disulfide bond contents from WPU-5 to WPU-10, the mean particle size showed an increase and then decreased trend, of which the maximum value is 73.33 nm for WPU-8. Many factors influence the particle sizes, such as ionic amount, molecular flexibility, solid content, etc. So in the formula design, the contents of PPG, IPDI, DMPA, TEA, EDA, and solid content were all set at the same levels. Through
changing the amounts of BDO and HEDS, a series of SHWPUs were made at $R = 1.243$. Working as extenders, BDO and HEDS could increase the rigidity and toughness of the molecules. So incorporations of BDO and HEDS will change the flexibility of the molecules. In general, the more flexible the molecules are, the smaller are the particle sizes. When the content of HEDS introduced was little, the molecules were still keeping their stiffness, which made the particle size increase. However, when the content of HEDS was more, the flexibility of the molecules increased, which could not be ignored by the disulfide bond in HEDS with better flexibility than BDO. Therefore, the synergistic effects of BDO and HEDS made the particle size increase first and then decrease. As can be seen in Figure 1, particle size distributions are unimodal and narrow as well as the polydispersity index $D$ is relatively small, indicating that the emulsion particle sizes are homogenous. Zeta-$\zeta$ is a critical parameter that can reflect the stability of SHWPU emulsions, the absolute values of which were all larger than 30 mV, demonstrating that the emulsions were in stable states. In general, the small particles had thick hydrated electric double layers, which exhibited stronger interactions with water molecules, increasing the viscosity of emulsions. In addition, no precipitants were found at the bottom of the centrifugal tubes, indicating that the emulsions reached the stable standards.

**Structure Characterization.** The chemical structures of SHWPU films characterized by FTIR and Raman spectroscopy are shown in Figure 2. Compared with conventional WPUs, some common FTIR peaks can be found in Figure 2a, involving peaks at 3330, 2920, and 1104 cm$^{-1}$, which are attributed to the stretching vibrations of the $-\text{NH}_2$, $-\text{CH}_2-\text{CH}_3$, and $-\text{C}==\text{O}$ groups, respectively. For the unique structural features of the $-\text{C}==\text{O}$ groups in urethane and urea, the stretching vibration peaks at 1707 and 1650 cm$^{-1}$ were also detected. The peaks at 1560 cm$^{-1}$ were assigned to the bending vibrations of $-\text{NH}_2$. In addition, the complete disappearance of vibrations at 2270 cm$^{-1}$ related to the $-\text{NCO}$ groups demonstrated that SHWPU films were cured completely. In addition, no peaks of $-\text{OH}$ groups were observed, confirming that all the diols participated in the reactions, especially for the self-healing component of HEDS. The intensity of the disulfide bonds of HEDS is weak and cannot be detected in the FTIR spectra. To determine whether the disulfide bonds are accurately inserted into the main chains of WPUs, Raman spectra were used to detect the existence of disulfide bonds. In Figure 2b, the obvious stretching vibration peaks at 510 cm$^{-1}$ for disulfide bonds can be observed. As the content of disulfide bonds increased, the intensities of these peaks were also enhanced, further showing that SHWPUs were successfully synthesized.

**$^1$H NMR and $^{13}$C NMR.** The structures of WPU-10 and WPU-C confirmed by $^1$H NMR and $^{13}$C NMR spectra are shown in Figures 3 and 4, respectively. In the $^1$H NMR spectra, the signal of methylene closest to the disulfide bond was at 2.6–3.0 ppm, exhibiting multipeak distributions. However, the signal of the second nearest methylene shifted to high frequency with the distance of 1.0 ppm, which was also due to the influences of disulfide bonds. As can be seen in Figure 4, $^{13}$C NMR spectra of WPU-10 had some differences about the methylenes near disulfide bonds compared with WPU-C. There are two peaks at 41.57 and 59.88 ppm, which did not exist in WPU-C. These two peaks were, respectively, attributed to the second and first nearest methylenes to the disulfide

![Figure 1. Particle size distributions of SHWPUs.](image1)

![Figure 2. Structure characterization of SHWPUs: (a) FTIR and (b) Raman spectra.](image2)
bonds, demonstrating that the HEDS were successfully introduced into the macromolecules of WPU.

**Degree of Hydrogen Bonding.** The degree of hydrogen bonding was characterized by infrared peak fitting and was used to obtain the relationship between the microphase separation and varied disulfide contents further. In general, hydrogen bonds can be formed between the hydrogen of the \(-\text{NH}^-\) groups and oxygen from the urethane or urea of hard segments (HS) and ether of soft segments (SS). The higher the degree of hydrogen bonding in hard segments is, the higher the degree of microphase separation. Meanwhile, the hydrogen bonds formed between the soft segments and hard segments will cause the phase mixing. The wavenumbers at 1600–1800 cm\(^{-1}\) are typically assigned to the stretching vibrations of \(-\text{C}==\text{O}\), whereas the wavenumbers at 3100–3600 cm\(^{-1}\) are for \(-\text{NH}^-\). Then, these peaks were deconvoluted with a number of iterations to obtain the best fit for Gaussian peaks, the area percentages and positions of which are also listed in Tables 3 and 4. As shown in Table 3, the degree of hydrogen bonding in hard segments could be described by parameters of \(X_H\) and Harvey–Bradshaw index (HBI) reaching the minimum values as 44.27% and 0.8 for WPU-8 indicates that the degree of
microphase separation of WPU-8 is the smallest and the hydrogen-bonding interactions are relatively weak. In Table 4, the hydrogen bonds of hard segments (HS) for SHWPUs occupy a large proportion, and the trend is in accordance with the HBI indexes. The indexes of SS/HS for —NH— groups show an opposite trend, suggesting that the phase mixing of WPU-8 is large. The aggregations of hydrogen bonds result in the hydrogen bonds did not play major roles in this self-healing system. Hence, the self-healing degree is dominated by microphase separation, that is, molecular diffusion mobility.

Glass-Transition Temperatures for SHWPUs. Figure 5a shows the DSC test results for SHWPUs. Obviously, there are two $T_g$’s for every SHWPU sample exhibited in this figure. One was $T_g^1$ of soft segments at low temperature, which were in the range of $-33$ to $-37$ °C. The other was $T_g^2$ of hard segments at high temperature in the range of 84–99 °C. $T_g^1$ increased to the maximum value of $-33.0$ °C for WPU-8 and then decreased, whereas $T_g^2$ exhibited the opposite trend. As $\Delta T_g = T_g^2 - T_g^1$ can be used to measure the degree of microphase separation, the smallest $\Delta T_g$ of WPU-8 indicates that it possesses a weak degree of microphase separation, further indicating strong molecular diffusion mobility. Generally, self-healing happens above the temperature of $T_g^1$. High self-healing temperature is favorable to promote cohesive recovery.33 If the temperature is higher than $T_g^1$, the material matrix starts becoming soft, which is not suitable for use. Some studies had detected that the beginning of self-healing temperature was at 65 °C. So the appropriate self-healing

| Table 3. Statistical Results for Peak Fitting of —C=O Group |
|--------------------------------------------------------------|
| Sample | $v$ (cm$^{-1}$) | Area (%) | $v$ (cm$^{-1}$) | Area (%) | $X_H$ (%) | HBI$^b$ (%) |
|--------|----------------|----------|----------------|----------|-----------|-------------|
| WPU-5  | 1723.97        | 20.11    | 1703.09        | 54.07    |            |             |
| WPU-6  | 1722.13        | 27.89    | 1700.31        | 48.48    |            |             |
| WPU-7  | 1722.11        | 28.46    | 1700.49        | 48.22    | 1662.39   | 17.80       |
| WPU-8  | 1722.90        | 36.10    | 1699.11        | 39.17    | 1665.83   | 19.52       |
| WPU-9  | 1722.62        | 25.56    | 1701.05        | 39.17    | 1667.92   | 17.65       |
| WPU-10 | 1722.87        | 25.38    | 1701.03        | 51.36    | 1668.88   | 17.80       |

“$X_H$ is the percent ratio between bonded and total areas for —C=O. $^b$HBI is the ratio between the total bonded and total free —C=O.”

| Table 4. Statistical Results for Peak Fitting of the —NH— Group |
|---------------------------------------------------------------|
| Sample            | $v$ (cm$^{-1}$) | Bonded with SS$^a$ | $v$ (cm$^{-1}$) | Bonded with HS$^b$ | Overtone$^c$ |
|-------------------|----------------|-------------------|----------------|-------------------|-------------|
|                   | $v$ (cm$^{-1}$) | Bonded with SS$^a$ | $v$ (cm$^{-1}$) | Bonded with HS$^b$ | Bonded with HS$^b$ |
| WPU-5             | 3525.72        | 6.03              | 3453.96        | 3.02              | 3329.06     | 86.06       |
| WPU-6             | 3550.05        | 1.51              | 3482.62        | 5.68              | 3300.79     | 89.50       |
| WPU-7             | 3514.89        | 1.95              | 3437.39        | 7.12              | 3336.00     | 72.43       |
| WPU-8             | 3534.23        | 0.54              | 3459.56        | 8.93              | 3332.07     | 83.78       |
| WPU-9             | 3500.71        | 4.48              | 3444.34        | 7.03              | 3330.92     | 82.18       |
| WPU-10            | 3552.12        | 0.63              | 3472.95        | 8.02              | 3330.54     | 86.11       |

“$SS$ is the soft segment of WPU. $^b$HS is the hard segment of WPU. $^c$SS/HS is the ratio of —NH— bonded in soft and hard segments.”

Figure 5. (a) $T_g$ of SHWPUs by DSC measurements; (b) self-healing time with various $T - \Delta T_g$ values.
temperature should be chosen between 65 and 80 °C. In addition, the effect of self-healing time is plotted in Figure 5b as a function of $T - \Delta T_g$. With the increment of disulfide bond contents, the value of $T - \Delta T_g$ shifts from high temperature to low temperature, then shifts to high temperature again. This was due to the influences of material structure like microphase separations. Meanwhile, the self-healing time decreased with increasing $T - \Delta T_g$ for the same sample, confirming that high temperature is beneficial to the cohesive self-healing. Besides this, higher value of $T - \Delta T_g$ indicates that the molecular diffusions occur easily. Hence, $T_g$ also influences the self-healing performance in a potential way.

**Dynamic Mechanical Thermal Analysis (DMTA).** Figure 6 shows the results of DMTA tests about the storage modulus $E'$ and loss factor $\tan \delta$ for SHWPUs. From Figure 6a, $E'$ of SHWPUs exhibited a decreasing and then increasing trend with the varied contents of HEDS. The $E'$ of WPU-8 was the lowest, indicating that the nature of material itself was soft and difficult to resist to deformations compared with other samples. However, in Figure 6b, the values of $\tan \delta$ for SHWPUs were increasing as the temperature increased, along which there were two peaks attributed to the $T_g$ of soft segments and hard segments. The details about the $T_g$ are listed in Table 5. In this study, the DMA curves were measured on the square samples using a micrometer scratch instrument. These samples were placed in the hot stage to observe the microcrack changes at constant temperatures, 70, 75, and 80 °C. Finally, the varied microcracks were photographed using a Leica camera every 30 s. As shown in Figure 7, the self-healing processes of WPU-8 and WPU-C at 75 °C are listed in Figure 7. As shown in Figure 7a, the two faces of the microcrack approached slowly before 6 min; then, it was narrowed and became shallower after 6 min. This was because molecular chain movements were activated gradually by the stimuli of temperature. Especially in the later stage, the movements of molecular chains were more intense, which accelerated the velocity of self-healing. At 15 min, the traces of the microcrack were almost invisible, indicating that this film had the self-healing ability. Compared with the self-healing process of WPU-8, the light traces of the microcrack on the control sample of WPU-C in Figure 7b still existed after heating for 15 min. Given that these environmental conditions were all set at the same levels (including the samples’ shape, method of heating, operation process), the sole different element between the structures of WPU-8 and WPU-C was only the presence of disulfide bonds. Hence, the disulfide bonds were concluded to play important roles in the self-healing process.

**Table 5. Two $T_g$ of Soft Segments and Hard Segments for SHWPUs (°C)**

|          | WPU-5 | WPU-6 | WPU-7 | WPU-8 | WPU-9 | WPU-10 |
|----------|-------|-------|-------|-------|-------|--------|
| $T_g$    | −20.90| −20.87| −18.77| −18.18| −22.02| −22.14 |
| $\Delta T_g$ | 78.99 | 77.31 | 73.75 | 71.95 | 75.48 | 81.47  |

The $T_g$ decreased and then increased in the temperature range of −18 to −23 °C, whereas the trend of $T_g$ was opposite in the temperature range of 53–60 °C. If the values of $T_g$ were still smaller, it indicated that the degree of microphase separation was smaller. The values of $T_g$ are also listed in Table 5, among which $T_g$ of WPU-8 was the smallest, showing that WPU-8 had the smallest degree of microphase separation. This further indicated that the molecular chains of WPU-8 moved more easily, which was more helpful to achieve the cohesive behaviors. When the temperature was higher than the $T_g$, the materials were found to be in the viscous flow state, especially WPU-8 should have a higher $\tan \delta$ value. In fact, the $\tan \delta$ values of WPU-8 to WPU-10 were relatively lower than the other samples due to the exchange reactions of disulfide bonds, which limited the movements of molecular chains and signaled the occurrence of this reaction.

**Optical Microscope Analysis.** The self-healing process was monitored using an optical microscope equipped with a Linkam hot stage. First, the films of SHWPUs were cut into 4 mm × 4 mm squares. Then, 300 μm-deep microcracks were made on the square samples using a micrometer scratch instrument. These samples were placed in the hot stage to observe the microcrack changes at constant temperatures, 70, 75, and 80 °C. Finally, the varied microcracks were photographed using a Leica camera every 30 s. Here, the self-healing processes of WPU-8 and WPU-C at 75 °C are listed in Figure 7. As shown in Figure 7a, the two faces of the microcrack approached slowly before 6 min; then, it was narrowed and became shallower after 6 min. This was because molecular chain movements were activated gradually by the stimuli of temperature. Especially in the later stage, the movements of molecular chains were more intense, which accelerated the velocity of self-healing. At 15 min, the traces of the microcrack were almost invisible, indicating that this film had the self-healing ability. Compared with the self-healing process of WPU-8, the light traces of the microcrack on the control sample of WPU-C in Figure 7b still existed after heating for 15 min. Given that these environmental conditions were all set at the same levels (including the samples’ shape, method of heating, operation process), the sole different element between the structures of WPU-8 and WPU-C was only the presence of disulfide bonds. Hence, the disulfide bonds were concluded to play important roles in the self-healing process.

The disulfide content will increase with the self-healing process of the microcrack. To detect the traces of disulfide bonds, in situ Raman was used to monitor this change in sample WPU-8, as shown in Figure 8. As can be seen from
Self-Healing Mechanical Property. Tensile test is a common method used to quantify the self-healing efficiencies. The dumbbell-shaped samples were divided into two groups. The sample in the first group was scratched with a microcrack as shown in Figure 9a–d using a micrometer scratch instrument. Then, it was placed in the oven with the control sample and heated to the target temperature. After 20 min, the samples were taken out to rest at room temperature. Tensile tests were carried out after 24 h using the machine shown in Figure 9e. Given that the sample with the microcrack can heal to some degree, the self-healing efficiency can be calculated using eq 1.

\[
\text{SH} \% = \frac{\sigma_{\text{self-healing}}}{\sigma_{\text{original}}} \times 100\%
\]  

(1)

Self-healing experiments for WPU-5–WPU-10 at different temperatures, 70, 75, and 80 °C, were conducted. The tensile curves are shown in Figure 10, and the calculated self-healing efficiencies are listed in Table 6. The self-healing efficiencies demonstrated the same trend with the microphase separations at the same temperature because the self-healing process was greatly affected by the molecular chain diffusion movements, which are limited by microphase separations. Thus, molecular chain diffusions played significant roles in the self-healing process. Moreover, disulfide bonds also had important effects. When the contents of the disulfide bonds were minimal, such as that of WPU-5, the disulfide bonds could not take exchange reactions effectively, leading to weak break points, which decreased the tensile strength. Compared with the mechanical property of WPU-C, the self-healing efficiencies were higher for WPU-7–WPU-10, indicating that the self-healing efficiencies can be improved by disulfide bonds.

Furthermore, the self-healing efficiencies were improved by the disulfide bonds, which can be found in WPU-8 and WPU-9. Generally, the self-healing efficiencies of the same sample for gradually increasing temperatures showed a decreasing trend. For WPU-8 and WPU-9, the tensile strengths were increased to the maximum value at 75 °C, which was obviously different from other samples. This finding was because the tensile strength of self-healing samples was related not only to the strength of the matrix itself but also to the self-healing reactions of disulfide bonds. The material matrix provided the major strength of the tensile stress. When the temperature increased closely to \( T_g \), the material matrix was soft. Hence, the tensile stress decreased such as that of WPU-C. The self-healing efficiencies of WPU-8 and WPU-9 further increased, especially at 75 °C, which was abnormal. Given that the influence of the self-healing degree by the exchange reactions of disulfide bonds was higher than the softening degree, the self-healing efficiencies increased. Overall, the synergies in strength of matrix and self-healing degrees through disulfide bonds determined the final performance. Similarly, the elongation at break also displayed the same trend due to the same reasons.

Self-Healing Mechanism and Kinetic Analysis. SHWPUs synthesized here are thermoplastic materials, which have the self-healing ability inherently. Wool and O’Connor had discussed the self-healing mechanism of this kind material and proposed that the diffusion is the most important step to control the final self-healing performance. Combining the self-healing microscope observation and the theories proposed by previous research, the whole self-healing process is simplified and divided into three stages. The first stage is the cohesive movements of the two sides for microcracks. The second stage

Figure 8, the strength of peak \( \nu_{S-S} \) located at 510 cm\(^{-1}\) for disulfide bonds was enhanced on prolonging the time, indicating that disulfide bonds played important roles in binding the microcrack.

**Figure 8.** Raman spectra of microcrack on WPU-8 for self-healing at 80 °C.

**Figure 9.** (a) Dumbbell-shaped sample; (b) microcrack made using a micrometer scratch instrument; (c) and (d) samples with microcrack; and (e) tensile test.
is the diffusion of molecular chains cooperated with the exchange reactions of disulfide bonds. The third stage is the randomization of molecular chains. Details about the self-healing mechanism are shown in Figure 11. In this process, cohesive healing ability and the exchange reaction activation energy of disulfide bonds are two important parameters influencing the previous two self-healing stages. Cohesive healing ability, which defines the self-healing process of microcracks on the SHWPUs films monitored by the optical microscope, can be evaluated by the kinetic analysis method.

The data points of the self-healing cohesive recovery process are described by eq 2

\[ A = \frac{d_t}{d_0} \]  

where \( d_t \) is the width of the microcrack at time \( t \) and \( d_0 \) is the original width of the microcrack at initial time \( t_0 \). In general, polymers can transform from one kind of equilibrium state to another under the external influences of the environment. This

Table 6. Statistics for Self-Healing Efficiency at Different Temperatures

| Self-healing efficiency (%) | 70 °C tensile strength | 70 °C elongation at break | 75 °C tensile strength | 75 °C elongation at break | 80 °C tensile strength | 80 °C elongation at break |
|----------------------------|------------------------|--------------------------|-----------------------|--------------------------|-----------------------|--------------------------|
| WPU-5                     | 47.14                  | 42.30                    | 30.90                 | 11.96                    | 27.96                 | 7.69                     |
| WPU-6                     | 72.84                  | 74.61                    | 67.31                 | 71.18                    | 64.79                 | 71.21                    |
| WPU-7                     | 93.41                  | 90.60                    | 89.82                 | 82.25                    | 88.75                 | 83.32                    |
| WPU-8                     | 100.00                 | 100.00                   | 100.00                | 103.94                   | 94.56                 | 97.14                    |
| WPU-9                     | 89.61                  | 96.98                    | 97.92                 | 101.04                   | 57.61                 | 57.93                    |
| WPU-10                    | 98.95                  | 94.45                    | 91.76                 | 92.56                    | 88.27                 | 87.44                    |
| WPU-C                     | 84.36                  | 71.14                    | 66.65                 | 64.67                    | 69.90                 | 63.66                    |
transformation was time dependent, which can be described by the relation of deformations with relaxed time using eq 345
\[
d_d = d_0 e^{-\frac{t}{\tau}}
\] (3)

By fitting the self-healing data points, the fitting curves are shown in Figure 12, and the relaxed times \( \tau \) of WPU-5–WPU-10 for different temperatures are calculated and further listed in Table 7. Notably, the relaxed times were prolonged with decreasing temperature. However, at the same temperature, the relaxed times decreased and then increased, which was not only determined by the content of the disulfide bonds but also related to the molecular chain movements limited by microphase separations. When the microphase separation degree of WPU-8 was the smallest, the molecular chain movements were easier, which was in accordance with the trend of hydrogen bond analysis results. To calculate the cohesive healing activation energy, eq 4 of relaxation time \( \tau \) with these activation energies was also used
\[
\tau = \tau_0 e^{\frac{E_a}{R T}}
\] (4)

The parameter \( \tau_0 \) is a constant, whereas \( \tau \) is listed in Table 7. \( E_\text{a} \) is the cohesive healing activation energy, \( R \) is the gas constant, and \( T \) is the absolute temperature. Then, ln \( \tau \) at different temperatures is used to fit eq 4, and the final \( E_\text{a} \) values are also listed in Table 7. The smaller \( E_\text{a} \) value indicates high cohesive healing ability. The cohesive healing activation energy \( E_\text{a} \) decreased and then increased from WPU-5 to WPU-10 as the content of the disulfide bonds increased. WPU-8 showed the smallest \( E_\text{a} \) illustrating that WPU-8 more easily exhibited cohesive healing actions.

Once the two sides of the microcrack are close enough with the favorable temperature conditions, the exchange reactions of disulfide bonds would take place, which is a critical factor in the self-healing process. Otsuka et al.46 explored this exchange reaction using photoirradiation and found that the molecular weight tended to be at the middle of the two different molecules as time passed. Similarly, in this study, experiments designed by testing the molecular weight can be used to characterize the exchange reactions of disulfide bonds under the influence of temperature. The high and low molecular weights of SHWPUs were mixed, and the chains were altered at the suitable temperatures in a long period to ensure that the exchange reactions of disulfide bonds could reach the new equilibrium. On the basis of this premise, equal amounts of WPU-L (\( M_n = 31\,372 \text{ g/mol} \)) and WPU-10 (\( M_n = 18\,113 \text{ g/mol} \)) emulsions were mixed. The samples were placed in the oven at different temperatures, 65, 70, 75, and 80 °C. With the time interval of 12 h,47 the molecular weights of these samples were tested by GPC. Each sample was tested five times with a total time of 60 h, and the results are listed in Table 8. In fact, the molecular weights were all changed with the varied temperatures and times, indicating that the exchange reactions of disulfide bonds occurred.

### Table 7. Relaxed Time \( \tau \) and Cohesive Healing \( E_\text{a} \) Obtained by Fitting Equations 3 and 4

| time (min) | WPU-5 | WPU-6 | WPU-7 | WPU-8 | WPU-9 | WPU-10 |
|-----------|-------|-------|-------|-------|-------|--------|
| 343 K     | 41.63 | 24.17 | 16.05 | 11.22 | 16.17 | 20.94  |
| 348 K     | 16.80 | 12.99 | 9.76  | 5.55  | 7.22  | 13.58  |
| 353 K     | 6.07  | 5.29  | 4.20  | 3.32  | 3.85  | 4.41   |
| \( E_\text{a} \) (kJ/mol) | 193.80 | 152.80 | 134.78 | 122.67 | 144.54 | 156.47 |

![Figure 12. Self-healing data points of A and self-healing fitting curves.](image-url)
To calculate the active energy of the disulfide bonds in SHWPUs, the molecular weight should be converted to mole values using eq 5

\[ c = n/t \times \frac{1}{M_n}/t \]  

(5)

where \( n \) stands for moles, \( t \) is time, and \( M_n \) is the molecular weight. Meanwhile, the reactant concentration \( c \) is proportional to \( 1/M_n \). The reactant concentration \( c \) is related with the reactive velocity constant \( k \) by the reaction order relationship as follows

\[ \frac{dc}{dt} = kc^n \]  

(6)

where \( k \) is the reactive velocity constant and \( n \) represents the reactive orders. As \( n \) could take 0, 1, 2, and so on, the integration formulas are listed in Table 9. On the basis of these relationships, the reactive velocity constant \( k \) could be obtained by fitting the integration relationships. Then, the reactive activation energies \( E_a \) of different orders could be obtained based on the Arrhenius eq 7 and 8, which are also listed in Table 9. The best fitting result was 20.42 kJ/mol with \( n = 0 \).

\[ k = A \exp \left( -\frac{E_a}{RT} \right) \]  

(7)

\[ \ln k = \ln A - \frac{E_a}{RT} \]  

(8)

On the basis of the results in Table 9, the best fitting reactive activation energy was 20.42 kJ/mol with the highest R-square of 0.9953, indicating that exchange reaction of disulfide bonds in this system was zero order. The ref 48 reported that the self-healing disulfide bond was about 23.1 kJ/mol for first-order kinetics, which was higher than the reactive activation energy of this system. It may be that the molecular movements were activated by temperature, which made the molecular chains more flexible and mobile,49,50 further aiding the exchange reaction of disulfide bonds, so the \( E_a \) was relatively lower. To achieve the self-healing goals for the samples, some heat should be conveyed to facilitate the cohesive healing movements. Once the microcrack faces were close enough, the disulfide bonds could undergo exchange reactions with a small amount of heat. Hence, the self-healing process was dominated by the molecule chain movements and cooperated with the aid of disulfide bond exchange reactions.

## CONCLUSIONS

SHWPUs were successfully synthesized by importing disulfide bonds. The self-healing mechanism was affected by the amount of disulfide bonds, microstructure, and external factors such as temperature. By tuning the content of disulfide bonds in the WPUs and the temperature, the optimum self-healing conditions were obtained at 75 °C with WPU-8 for 15 min, and the self-healing efficiency was 100%. The self-healing kinetics demonstrated that the cohesive healing activation energy of WPU-8 was the smallest due to the faster molecular diffusion mobility. GPC can be used to calculate the reactive activation energy of disulfide bond exchange reactions, which was approximately 20.42 kJ/mol. So self-healing was closely related with the cohesive healing behavior of microcracks and exchange reactions of disulfide bonds. The analysis of mechanism and kinetics provided deep insights into the self-healing process, and the relations between structure and the properties of SHWPUs provide a reference for creating self-healing materials.

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The manuscript was written through contributions of all authors. All authors had given approval of the manuscript.

### Notes

The authors declare no competing financial interest.

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