Hydroxyl-Terminated Polybutadiene-Based Polyurethane with Self-Healing and Reprocessing Capabilities

Jiawei Li, † Zhao Ning, † Weiming Yang, Bin Yang, and Yanning Zeng*

ABSTRACT: Hydroxyl-terminated polybutadiene (HTPB)-based polyurethane (PU) networks play indispensable roles in a variety of applications; however, they cannot be reprocessed, resulting in environmental problems and unsustainable industrial development. In this work, recyclable HTPB-based PU vitrimer (HTPB-PU_V) networks are fabricated by introduction of a cross-linker 2,2′-(1,4-phenylene)-bis[4-mercaptan-1,3,2-dioxaborolane] (BDB) with dynamic boronic ester bonds into the network. Meanwhile, the BDB can stabilize the HTPB unit in the network by elimination of double bonds. The novel HTPB-PU_V networks are constructed by a thiol-ene "click" reaction and an addition reaction between HTPB and cross-linker BDB and isocyanates (HDI). The dynamic HTPB-PU_V networks are characterized by dynamic mechanical analysis (DMA) and Fourier transform infrared (FTIR). The obtained dynamic HTPB-PU_V networks possess superior thermostability. Moreover, due to the presence of dynamic boronic ester bonds, the HTPB-PU_V network topologies can be altered, contributing to the reprocessing, self-healing, and welding abilities of the final polymer. Through a hot press, the pulverized sample can be reprocessed for several cycles, and mechanical properties of the reprocessed samples are similar to those of the pristine one, with the tensile strength being even higher. The self-healed sample exhibits almost complete recovery from scratch after the healing treatment at 130 °C for 3 h. Moreover, a welding efficiency of 120% was achieved.

1. INTRODUCTION

With the 2020 worldwide annual production estimated to be more than 29 billion kg, polyurethanes (PUs) are the most widely used versatile polymers. PU is applied in the fields of coatings, adhesives, and cross-linked thermosets because of its high reactivity and flexibility in formulation, application technologies, adhesion properties, superior viscoelasticity, tenacity, and abrasion. Polyurethane-based binder systems consist of alternating soft and hard segments. A very useful characteristic associated with urethane binder systems in PU is that the ultimate properties can be varied with good control by adjusting the formulations. PU binders can provide the unique possibility of tailored polymer topology by varying the composition and R-value (equivalents of NCO/OH groups). On the other hand, hydroxyl-terminated polybutadiene (HTPB) having a number average molecular weight (M_n) of 1500−10,000 g/mol is a low-viscosity colorless liquid. The HTPB with reactive functional groups can be applied to build ABA triblock copolymers, toughened resins, cross-linked elastomers, PB vitrimers, and supermolecular polymer gels. Especially, HTPB-based PUs have been extensively utilized as binders for solid propellants, explosives, adhesives, foams, coatings, sealants, elastomers, unsaturated polyesters, toughened polymers, and gas separation membrane applications. HTPB as a soft segment of PU can react with isocyanate instead of polyether or polyester, giving excellent properties, such as low surface energy, low-temperature flexibility, superior abrasion resistance, high electrical insulation properties, high viscoelasticity, tenacity, and hydrolytic stability. However, the presence of double bonds results in the poor stability of HTPB-based PUs in the air. Besides, as a widely utilized thermoset, HTPB-based PUs, which originate from petroleum resources, cannot be recycled, leading to environmental pollution and unsustainable industrial development.

The PU thermoset with the incorporated dynamic covalent bonds can rearrange its network chains under a proper stimulus, thus allowing for network reprocessing. In terms of mechanism, the dynamic chemistries involved in the dissociative reversible reaction include the Diels−Alder addition and the associative exchange reactions, including the disulfide exchange reaction, transamination reaction, C−C exchange reaction, and dioxaborolane metathesis.
Based on the associative exchange mechanism, the recyclable PU thermosets are called PU vitrimers because of their capability to flow like glass when heated; meanwhile, the network integrity of PU vitrimers is maintained even after reprocessing. Among the mentioned exchange reactions for PU, dioxaborolane metathesis, as a type of B–O bond exchange reaction, can be simply adjusted by temperature. Moreover, vitrimers based on the B–O bond exchange reaction can provide high mechanical performance to the obtained PU.\textsuperscript{24–27}

HTPB-based PU vitrimers with disulfide bonds\textsuperscript{28–30} are developed for their striking self-healing performances. Herein, novel HTPB-based PU networks with dynamic boronic ester bonds as linkages are prepared by a facile one-pot reaction approach to obtain the reprocessing ability. HTPB can react with the cross-linker 2,2′-(1,4-phenylene)-bis[4-mercaptop1,3,2-dioxaborolane] (BDB) and isocyanates (HDI) by the thiol-ene “click” reaction and the addition reaction, providing a formation of the networks. Double bonds in HTPB react with –SH groups in BDB, giving high stability networks. Meanwhile, the obtained HTPB-PUv displays plasticity, reprocessing, self-healing, and shape memory abilities since the dioxaborolane metathesis reaction permits the PU network topology rearrangement. The effect of the cross-linker BDB’s content on the properties of HTPB-based HTPB-PUv is also investigated.

2. EXPERIMENTAL SECTION

2.1. Materials. 1-Thioglycerol (99%), 1,4-phenylenediboronic acid (97%), DBTDL (95%), HDI, and 4-dimethylaminopyridine (99%) were purchased from Aladdin. HTPB (\(M_w = 3000\) g/mol) was purchased from Energy Chemical. Tetrahydrofuran (THF) toluene and dichloromethane (DCM) were purchased from XiLong Scientific Co., Ltd.

2.2. Synthesis of Typical HTPB-Based PU Vitrimer Network. The preparation of HTPB-based PU vitrimer networks is shown in Figure 1. HTPB (3.000 g, 1 mmol) and HDI (0.168 g, 1 mmol) were dissolved in THF, and then, a certain amount of BDB, which was synthesized in a reported work,\textsuperscript{31} was added and stirred for 10 min before the reaction mixture was transferred to a release paper mold. The temperature was increased to 140 °C with a 20 °C/6 h program to obtain HTPB-PUv networks. BDB contents were 30, 35, 40, 45, 50, 55, and 60 wt % relative to HTPB, and the abbreviation x%-HTPB-PUv refers to cured PU with x being the wt % of BDB.

2.3. Self-Healing, Welding, Shape Memory, and Reprocessing. A blade-made scratch in the 55%-HTPB-PUv strip was used for the self-healing test. The sample with the scratch was placed in an oven at 130 °C for 3 h. Polarizing optical microscopy (POM) equipped with a heating stage and a UCMOS05100KPA (P/N: TP605100A) microscope camera was utilized to observe the scratch and record its sizes.

Two pieces of 55%-HTPB-PUv samples (30.0 mm × 8.0 mm × 1.0 mm) were held together with a superimposed length of 10 mm at 130 °C with a holding time of 30, 60, or 120 min for the welding treatment. To evaluate the welding efficiencies, mechanical properties were determined by conducting a uniaxial tensile test, and it was quantified by the ratio of the tensile strength or elongation at break of the welded sample to the one of the pristine sample.

The 55%-HTPB-PUv spline for checking the shape memory capability was heated at 130 °C, bent into different shapes with external force, and then cooled to room temperature; finally, the deformed spline was heated at 130 °C to observe the recovery of the spline shape.

A hydraulic plate vulcanizer (ZS-406B-30-300, Dongguan Zhuosheng Machinery Equipment Co., Ltd.) was used as the reprocessing equipment, and the 55%-HTPB-PUv sample was ground into powder and added into the mold for reprocessing, under 5 MPa pressure. The reprocessing was carried out at 130 °C for 1, 2, or 3 h, and the samples were repeated three generations.

2.4. Characterizations. Fourier transform infrared (FTIR) spectrometry data were recorded on a Nicolet 205 FTIR spectrometer between 500 and 4000 cm\(^{-1}\) by the KBr tablet method, and a resolution of 4 cm\(^{-1}\) and a scanning number of 32 times were employed during the measurements. The thermal decomposition behavior of the HTPB-PUv series was examined by means of thermogravimetry analysis (TGA) at a heating rate of 10 K/min in a nitrogen atmosphere from 35 to 800 °C on a TA Q500. Differential scanning calorimetry (DSC 204, NETZSCH, Germany) was performed at a heating rate of 5 °C/min from 25 to 300 °C in a nitrogen gas atmosphere. Using a TA Q800 instrument for dynamic mechanical analysis (DMA), stress relaxation experiments were conducted by monitoring the stress decay at a constant strain of 5% after equilibrating at required temperatures for 20 min. A TA Q800 instrument was used for dynamic mechanical analysis (DMA) and stress relaxation experiments. The 55%-HTPB-PUv (20.0 mm × 5.0 mm × 1.0 mm) was measured by a TA Q800 from 25 to 200 °C (heating rate = 3 °C/min) with a frequency of 1 Hz. The glass-transition temperature (\(T_g\)) was obtained from the first inflection point of the curve. The mechanical performance test employed the UTM4503S-LXY universal tensile testing machine of Shenzhen Sansi aspect Technology Co., Ltd., with a 5 mm/min tensile rate. The width and thickness of the specimens were 8.0 and 1.5 mm, respectively.

Toughness, elongation at break, and tensile strength were obtained from the stress–strain curves. Scanning electron microscopy (SEM) was performed with a field emission scanning electron microanalyzer (HITACHI, S-4800) at an acceleration voltage of 10 kV. The samples were frozen by liquid nitrogen and then fractured in the middle. Before observation, the fracture surfaces were gold-sputtered for 20 s.

Equilibrium swelling experiments were employed to determine the sol fraction and the swelling ratio according to

![Figure 1](https://doi.org/10.1021/acsomega.1c06416)
the Flory–Rehner equation as shown in eqs 1 and 2. The vulcanizate was immersed in toluene, THF, or DCM refluxing for 12 h; then, the solvent was wiped with a filter paper, and the samples were weighed immediately and dried in a vacuum oven at 60 °C until constant weight. Three specimens were measured for each sample. The initial mass was assumed as \( m_0 \), the mass after swelling was \( m_1 \), and the mass after drying was \( m_2 \).

swelling ratio was defined as: \[
\frac{m_1 - m_2}{m_2}
\] (1)

sol fraction was determined as: \[
\frac{m_0 - m_1}{m_0} \times 100\%
\] (2)

Moreover, equilibrium swelling methods were used to determine the cross-linking density \( C_d \) of the obtained polymer, where THF was used as the solvent. One polymer strip was cut into five samples (20 mm × 10 mm × 0.5 mm), weighed, and immersed in separate bottles containing 50 mL of THF for 5 days. After reaching the equilibrium swelling, the sample strips were taken out and the surface solvent was absorbed by a filter paper with the mass weighed; then, the samples were placed in a 60 °C oven to dry and weighed again. The \( C_d \) of the HTPB-PUV series was calculated by the Flory–Rehner formula 3.32,33

\[
C_d = \frac{-\ln[(1 - V_c) + V_c + \chi V_c^2]}{V_c(1/3 - V_c/2)}
\] (3)

\[
V_r = \frac{m_0/\rho_0}{m_1/\rho_1 + (m_1 - m_0)/\rho_c}
\] (4)

\[
\chi = 0.487 + 0.228V_r
\] (5)

where \( m_0 \) is the initial mass of the sample, \( m_1 \) is mass of the sample after the swelling equilibrium, \( \rho_1 \) is the density of the THF, \( \rho_c \) is the density of the polymer, \( V_c \) is the volume fraction of the polymer, \( \chi \) is the interaction parameter between the solvent and the polymer, and \( V_r \) is the molar volume of the solvent.

### 3. RESULTS AND DISCUSSION

#### 3.1. Covalent Cross-Linking of HTPB-PUV

The HTPB-PUV networks with boronic ester bonds are fabricated based on the chemical reactions between \(-\text{SH}\) of BDB and \(-\text{Si}=\text{O}\) of HTPB and \(-\text{OH}\) of HTPB, with BDB as the curing agent. The facts are confirmed explicitly by FTIR spectra in Figure 2. In the spectrum of HTPB, the absorptions at 2915, 2844, 966, and 911 cm\(^{-1}\) correspond to the out-of-plane bending vibration of \(\text{C}−\text{H} \) from the trans-butadiene component.35 In the BDB spectrum, the peak at 2568 cm\(^{-1}\) corresponds to the stretching vibrations of \(-\text{SH}\).36 In the case of HDI, the absorption peak at 2275 cm\(^{-1}\) results from the \(-\text{N}=\text{C}=\text{O}\) group.37 Meanwhile, in the typical spectrum of 55%-HTPB-PUV, the new peaks at 1700 and 1639 cm\(^{-1}\) are assigned to free \(\text{C}=\text{O}\) and H-bonded \(\text{C}=\text{O}\), respectively, indicating the occurrence of a reaction between \(-\text{N}=\text{C}=\text{O}\) and \(-\text{OH}\) to give the formation of \(\text{NHCOO−}\) and the hydrogen bond (NH···O=C), and the absorption at 1517 cm\(^{-1}\) is attributed to the distortion vibrations of \(\text{N}−\text{H}\). Compared with the spectra of BDB/HDI and 55%-HTPB-PUV, the absorption related to \(-\text{SH}/−\text{N}=\text{C}=\text{O}\) in the 55%-HTPB-PUV spectrum completely disappeared, implying that all of the \(-\text{SH}\) and \(-\text{N}=\text{C}=\text{O}\) groups react with HTPB. The peaks at 2915, 2844, 966, and 911 cm\(^{-1}\) appear in the spectrum of 55%-HTPB-PUV, implying the framework of HTPB present in the 55%-HTPB-PUV. Besides, the strong absorption of the \(-\text{OH}\) group in the spectrum of 55%-HTPB-PUV probably comes from water in the sample and the atmosphere, rather than \(-\text{OH}\) in HTPB. The above observations suggest that the HTPB-PUV networks are successfully prepared. Moreover, the covalently cross-linked architecture of the HTPB-PUV can be further confirmed by the fact that it is insoluble in common organic solvents.

Equilibrium swelling tests display that the HTPB-PUV series cannot completely dissolve in toluene, THF, or DCM and only swell to some degree due to the nature of covalently cross-linked networks. With the BDB content increasing from 30 to 60%, the swelling ratio and sol fraction consistently decrease from 6.1 to 3.1 and from 45 to 16%, respectively, as shown in Figure 3, resulting in an increase in the cross-link density \((0.35−2.43 \text{ mol/cm}^3\) in Table 1), which reveals a denser network at a higher BDB content.

#### 3.2. Dynamic Property Analysis, Mechanical Properties, and Thermal Performance

To determine the rearrangement of the HTPB-PUV network topology and the rate of exchange reactions, DMA measurements are employed to investigate the time- and temperature-dependent stress relaxation modulus. The normalized relaxation modulus of \(G/ G_0\) of the 55%-HTPB-PUV at different temperatures is shown in Figure 4a. When the temperature is elevated to 60 °C, relaxation the stress become quickly; which is in agreement with the law of temperature rise and stress relaxation time shortened. Following Maxwell’s viscoelastic fluid model, the relaxation time \(\tau\) is defined as the time required for the initial modulus to decrease to 1/e.40 The \(\tau\) of HTPB-PUV is 104 s at 40 °C, 54 s at 60 °C, and 35 s at 80 °C due to the faster exchange rate of dioxaborolane metathesis at higher temperatures. Besides, the activation energy \(E_a\) of dioxaborolane metathesis reactions can be calculated via Arrhenius’ law,41
Figure 3. Swelling ratio, sol fraction, and cross-linking density of the HTPB-PUv series with different BDB contents.

following eq 6, where \( \tau \) is the relaxation time, \( \tau_0 \) is the characteristic relaxation time at infinite temperature, \( T \) is the testing temperature, and \( R \) is the universal gas constant. The Arrhenius relationship of the characteristic relaxation time \( \tau \) versus 1000/\( T \) for 55%-HTPB-PUv is shown in Figure 4b. The \( E_a \) (25 kJ/mol) is calculated, and the value is in the range of 7.7–76.7 kJ/mol for the vitrimer with boronic ester bonds.42,43

\[
\ln \tau = \ln \tau_0 + \frac{E_a}{RT}
\]

The topology freezing transition temperature (\( T_g \)) is an important characteristic parameter for the vitrimer at which the viscosity becomes higher than 1015 Pa·s.44,45 In our system, the \( T_g \) = −105 °C is determined by extrapolating from the Arrhenius’ fitted line, which is similar to the reported boronic ester vitrimer’s \( T_g \) (in Figure 4b) to the relaxation time \( \tau = 4.2 \times 10^8 \) s. When the temperature is above \( T_g \), the 55%-HTPB-PUv network softens and its strain increases sharply due to the more facile occurrence of the exchange reactions. However, below \( T_g \), the network exhibits a similar performance with ordinary thermosets, for the cross-linking network would be frozen due to the low exchange reaction rate. These results illustrate the excellent heat-induced malleability of the 55%-HTPB-PUv. Moreover, the storage modulus and tan \( \delta \) plots of the 55%-HTPB-PUv are shown in Figure 4c. Tan \( \delta \) curves of the 55%-HTPB-PUv show two peaks at 54 and 103 °C, as shown in Figure 4c, due to the network dissociation of soft and hard segments,48 respectively, giving a \( T_g \) of 54 °C. Moreover, a rubber platform (\( E' = 7.15 \) MPa, storage modulus at \( T_g + 30 \) °C) is obtained from the storage modulus plot.

Another significant parameter for network movements is the glass-transition temperature (\( T_g \)), below which the network chain is frozen,49 and is determined by DSC analysis. DSC plots of the HTPB-PUv series with different BDB contents are shown in Figure 5. It is found that the \( T_g \) of the HTPB-PUv series gradually increases from 9.0 to 13.5 °C with the BDB contents increasing from 30 to 60% because with the cross-linker BDB content increasing, a higher cross-linking density, which is calculated using eq 3 by the equilibrium swelling measurement approaches.52

Static tensile measurements are employed to study the mechanical properties of the HTPB-PUv series with different BDB contents; the static tensile measurements are conducted at a strain rate of 5 s\(^{-1}\). All of the stress–strain curves are shown in Figure 6a, and the mechanical properties are summarized in Figure 6b and Table 1. It is found that BDB contents have a remarkable effect on the mechanical properties. As the BDB content increases from 30 to 60%, the tensile strength also increases from 0.7 to 2.6 MPa because the tensile strength is closely related to the cross-linking density, as shown in Table 1, consistent with an increasing \( T_g \).53 Meanwhile, both the values of elongation at break and toughness first increase to the maximum and then decrease with BDB contents increasing because a high cross-linking density makes the network hard, leading to a decreased elongation at break and toughness at a high BDB content. The maximum values of elongation at break and toughness are 101.9% and 1.8 MJ/m\(^3\) at BDB contents of 50 and 55%, respectively.

The thermostability of the HTPB-PUv series with different BDB contents is studied by TGA at a heating rate of 10 °C/min under a nitrogen atmosphere, and the TGA and DTG curves are shown in Figure 7. For all of the HTPB-PUv series, the thermal gravimetric profiles are similar with two weight loss stages around 350 and 470 °C. The HTPB-PUv series show excellent thermal stability with the onset decomposition temperature around 300 °C, which is much higher than the thermal processing temperature (∼130 °C), demonstrating thermal stability during thermal processing. The decomposition temperature of the first stage is ∼350 °C, which is attributed to the thermal decomposition of the urethane bond in polyurethane.48,54 The second stage is the main decomposition stage, in which the temperature can reach ∼450 °C.

| sample   | \( T_g \) (°C) | \( C_s \) (mol/cm\(^3\)) | elongation at break (%) | tensile strength (MPa) | toughness (MJ/m\(^3\)) |
|----------|---------------|---------------------------|------------------------|------------------------|------------------------|
| 30%-PUV  | 9.0           | 0.35 × 10\(^{-3}\)       | 79.0 ± 1.8             | 0.7 ± 0.09             | 0.3 ± 0.08             |
| 35%-PUV  | 9.4           | 0.36 × 10\(^{-3}\)       | 78.3 ± 1.4             | 0.9 ± 0.08             | 0.5 ± 0.07             |
| 40%-PUV  | 9.7           | 0.31 × 10\(^{-3}\)       | 83.2 ± 3.1             | 1.1 ± 0.05             | 0.6 ± 0.04             |
| 45%-PUV  | 10.9          | 0.47 × 10\(^{-3}\)       | 93.1 ± 2.7             | 1.3 ± 0.11             | 0.8 ± 0.10             |
| 50%-PUV  | 11.2          | 1.09 × 10\(^{-3}\)       | 101.9 ± 3.0            | 1.4 ± 0.09             | 1.1 ± 0.09             |
| 55%-PUV  | 12.0          | 1.42 × 10\(^{-3}\)       | 86.6 ± 2.7             | 2.5 ± 0.11             | 1.8 ± 0.12             |
| 60%-PUV  | 13.5          | 2.43 × 10\(^{-3}\)       | 61.7 ± 2.5             | 2.6 ± 0.10             | 1.4 ± 0.09             |
due to the collapse of networks. Thermal stability of the HTPB-PUv series is comparable, which is slightly affected by BDB contents.

3.3. Self-Healing, Welding, and Shape Memory. At elevated temperatures, network rearrangement can occur across the interfaces of fractured surfaces; thus, covalent bonding can be re-established at the same place due to the dioxaborolane metathesis reaction between two boronic ester bonds. For proof of the self-healing performance, the 55%-HTPB-PUv strip sample is cut with a thickness of 1.5 mm using a blade. The sample with a width of 96.7 μm scratch is treated with heating at 130 °C for 3 h in an oven for healing. It was considered that the network could be frozen when the temperature decreased below $T_g$; therefore, a temperature higher than $T_g$ was chosen as the reprocessing temperature. Figure 8a displays optical microscope images of the 55%-HTPB-PUv after and before healing. It is found that the scratch after healing almost completely disappears, indicating an excellent self-healing behavior. However, for the HTPB-PUv sample without BDB, it is observed that the width of the scratch after healing at 130 °C for 3 h is only slightly decreased, as shown in Figure 8b. Therefore, the self-healing behavior of the 55%-HTPB-PUv can be mainly attributed to the presence of the dynamic bionic ester bond in the network. Moreover, the schematic illustration of the self-healing mechanism in HTPB-PUv based on the dynamic bionic ester bond is shown in Figure 8c. Due to the dioxaborolane metathesis reaction of boronic ester bonds, covalent bonding can be re-established across the interfaces of fractured surfaces, giving rise to reconstructing of the network topologies, similar to the reported polyurethane vitrimer based on boronic ester bonds.22

Figure 5. DSC plots of the HTPB-PUv series with different BDB contents.
To check the welding ability of the 55%-HTPB-PU_V networks, the specimen is cut into half, and the two parts (30.0 mm × 8.0 mm × 1.0 mm) are overlapped by 10 mm. After holding together for welding at 130 °C for 30, 60, or 120 min, the two parts are welded tightly, as shown in Figure 9a, due to the dioxaborolane metathesis reactions of the boronic ester bond. Lap-shear testing is applied to evaluate the welding efficiency by carrying out tensile tests at 25 °C with a cross-head speed of 5 mm/min. The welding efficiency of the 55%-HTPB-PU_V can be determined as the proportion of the welded sample’s tensile strength or elongation at break with respect to the original one’s. Stress–strain curves of the samples with

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Figure 7. TGA and DTG curves of HTPB-PU_V series with different BDB contents.

Figure 8. (a) Optical microscope images of self-healing behaviors for 55%-HTPB-PU_V at 140 °C. (b) Self-healing performance of the HTPB-PUv sample without BDB at 140 °C. (c) Schematic self-healing mechanism of the dioxaborolane metathesis reaction of boronic ester bonds at 140 °C.
different welding treatment times (30, 60, or 120 min) are shown in Figure 9c. It is observed that the original sample displays a typical ductile fracture, whereas the welded sample exhibits a less ductile fracture, as shown in Figure 9b. Moreover, with the welding time extending, mechanical properties are improved. The best mechanical properties were obtained from the welded sample with 120 min of heating, which shows a tensile strength of 2.9 MPa, elongation at break of 35.7%, and toughness of 0.6 MJ/m³, and the recovery ratio of the tensile strength reaches 120%. The above results demonstrate that the HTPB-PUV network with the dynamic boronic ester bonds possesses an attractive thermal welding capability.55

The typical thermosets are inherently difficult to reshape because of the permanent cross-linking networks. In this work, the boronic ester bonds can undergo dioxaborolane metathesis reactions in the obtained networks, which gives network rearrangements and results in a gradual Arrhenius-like viscosity dependence, leading to a shape memory ability of the network in the solid state. The 55%-HTPB-PUV with dynamic boronic

Figure 9. (a) Optical images of before and after welding of 55%-HTPB-PUV, (b) Fractured specimens of welded (left) and pristine (right) samples after lap-shear testing. (c) Tensile curves and (d) recovery ratios of the mechanical properties of 55%-HTPB-PUV welding at 130 °C for different treating times of 30, 60, and 120 min.

Figure 10. Optical images of shape memory performance of the 55%-HTPB-PUV sample.
Figure 11. (a) Optical images of thermal recycling performance of 55%-HTPB-PUV by hot pressing. (b) Tensile curves and (c) mechanical properties of samples with different treating times at 130 °C. (d) Tensile curves and (e) mechanical properties of the samples with different generations of reprocessing. SEM images of (f) the original, (g) the first generation, (h) the second generation, and (i) the third generation of the 55%-HTPB-PUV.
ester bonds can be healed and welded at elevated temperatures. Similarly, the 55%-HTPB-PUv can undergo dioxaborolane metathesis reactions to achieve topological rearrangements above $T_g$ and $T_v$, giving a shape memory ability.\textsuperscript{40,66} Figure 10 shows the optical images for the shape memory performances. First, the sample is heated to 130 °C, which turns it into an oblique or heart shape, and which could be fixed upon cooling down to room temperature. Subsequently, the temperature is elevated to 130 °C again, and the oblique or heart shape reverts to its original flat state quickly and then recovers by following the same procedure of “heating—cooling”. It is reported that the thermal-responsive shape memory property presenting in the polymer needs chemical or physical cross-linked networks and an appropriate ratio of flexible and stiff segments.\textsuperscript{57} Herein, the networks of the 55%-HTPB-PUv contain chemical cross-linking networks with bionic acid linkage, consistent with FTIR measurements. Besides, boronic ester bonds in the network undergo dioxaborolane metathesis reactions, which result in a gradual memory property presenting in the polymer needs chemical or physical cross-linked networks and an appropriate ratio of flexible and stiff segments.\textsuperscript{57} Herein, the networks of the 55%-HTPB-PUv contain chemical cross-linking networks with bionic acid linkage, consistent with FTIR measurements.

### 3.4. Reprocessing

The most significant reprocessing capability is researched since the HTPB-PUv networks can arrange their topology by the exchange reaction of boronic ester bonds. The dioxaborolane metathesis reaction can take place between boronic ester bonds in the network; thus, the network has rearrangement, leading to reprocessability of the network.\textsuperscript{58} First, the 55%-HTPB-PUv sample is cut into powder and then is reprocessed by hot pressing at 130 °C under 5 MPa with different treating times (1, 2, or 3 h) for three cycles. Homogenous well-shaped samples are obtained as shown in Figure 10, with the generation increasing the color of the recycled sample to become slightly dark. Moreover, the reprocessability of the HTPB-PUv is examined by the mechanical properties’ measurements. Stress—strain curves of the samples with different welding treatment times (1, 2, or 3 h) and generations (1st, 2nd, or 3rd) are shown in Figure 11b,d, and recovery ratios of the mechanical properties for the recycled samples are exhibited in Figure 11c,e. From the stress—strain curves, it can be easily observed that a more rigid network is formed after reprocessing, while the original 55%-HTPB-PUv shows a clear transition of elastic—plastic deformation. The tensile strength of all of the reprocessed samples increases compared with the original one. It is found that the recycled samples show brittle fracture with decreased elongation at break and increased tensile strength in comparison with the original sample. Possibly, because the macroscopic phase separates into soft and hard regions in the pristine PU sample, after high-temperature reprocessing, the phase structure is improved in the cyclic samples.\textsuperscript{31,59—61} Moreover, it is confirmed by SEM images, as shown in Figure 11f—i, that the original 55%-HTPB-PUv shows coarse fracture; however, the recycled samples display more smooth fractures. With treatment times prolonging from 1 to 3 h, the recovery of tensile strength is increased from 112 to 141%. Therefore, different generation samples are obtained from 3 h hot pressing; the mechanical properties reasonably decay for more recycled samples, and the recovery of tensile strength decreases from 140 to 111%. All of the phenomena indicate that the HTPB-PUv networks with dynamic boronic ester bonds possess excellent reprocessability.\textsuperscript{62,63}

### 4. CONCLUSIONS

In this work, HTPB-PUv networks with dynamic boronic ester bonds were successfully synthesized using a facile one-pot reaction approach, with BDB as the cross-linker, which were characterized by FTIR and DMA measurements. The 55%-HTPB-PUv network ($E_a = 25 \text{ kJ/mol}, T_a = -105 \text{ °C}$) possesses superior malleability due to the fast dioxaborolane metathesis reaction of boronic ester bonds. The HTPB-PUv networks exhibit distinct reprocessing, self-healing, welding, and shape memory capabilities. Through hot pressing at 130 °C, for 3 h, the recycled samples display excellent reprocessability because of the introduction of dynamic boronic ester bonds into PU networks. Meanwhile, the tensile strength of reprocessed samples is higher than the original one due to improvement in the phase structure in the recycled samples with reprocessing treatment. The scratches on the healed sample completely disappear. The welded sample shows a welding efficiency of 120%.

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### Notes

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