Supporting Information

Mechanically Robust, Self-healable and Reprocessable Elastomers Enabled by Dynamic Dual Cross-Links

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1. Characterization of BDB

$^1$H NMR (CDCl$_3$, 600 MHz): BDB-δ 7.83 (s, 4H), 4.74 (m, 2H), 4.49 (dd, J=8 Hz, 7 Hz, 2H), 4.18 (dd, J=13 Hz, 5.5 Hz, 2H), 2.82 (dd, J=7.5 Hz, 5 Hz, 4H), 1.49 ppm (t, J=7.5 Hz, 2H).

Figure S1. $^1$H NMR spectrum of BDB.

$^{13}$C NMR (CDCl$_3$, 600 MHz): BDB-δ 133.1, 76.6, 68.8, 28.6 ppm. Carbon adjacent to boron is not detected.

Figure S2. $^{13}$C NMR spectrum of BDB.


**2. Formation and characterization of cross-linked ENR**

In the FTIR spectrum of BDB, the absorptions at 2560 and 1219 cm\(^{-1}\) are due to stretching vibrations of -SH and B-O, respectively. In the case of neat ENR, the absorption at 874 cm\(^{-1}\) is assigned to the stretching vibration of epoxy groups. \(^1\) Compared with the uncured BE5, the absorption related to -SH completely disappeared after curing.

![Figure S4. FTIR spectra of BDB, neat ENR, uncured BE5 compound and cured BE5 sample.](image)
The cross-linking kinetics can be monitored by measuring the torque value of BEx compounds at 160 °C on a rheometer. The torque value firstly increases and then levels off with time. The increased torque is due to the cross-linking of ENR. It can be seen that the covalent cross-linking reaction is accomplished within 40 min. In addition, the maximum torque value consistently increases with BDB loading, which indicates an increase in the cross-linking density.

**Figure S5.** Photo of BE5 swelling in toluene after 72 h.

**Figure S6.** Evolution of torque for BEx at 160 °C.

**Equilibrium swelling experiments.**

Sol fraction, swelling ratio and cross-linking density was determined by equilibrium swelling experiment in toluene based on Flory-Rehner equation.2-3 Equilibrium swelling
experiments were conducted by immersing vulcanizations in toluene at room temperature for 72 h, and the solvent is replaced with fresh solvent for each 24 h. After swelling, the solvent was wiped off quickly from the sample surface using filter paper, and the samples were immediately weighed and then dried in a vacuum oven at 60 °C until constant weight. Three specimens were measured for each sample.

The swelling ratio is defined as \((m_1 - m_2)/m_2\), and sol fraction is determined as \((m_0 - m_2)/m_0\). The volume fraction of SBR in the swollen gel, \(V_r\), was calculated by the following Equation S1:

\[
V_r = \frac{(m_2 - m_0\varphi)/\rho_r}{(m_2 - m_0\varphi)/\rho_r + (m_1 - m_2)/\rho_s}
\]

where \(m_0\) is the sample mass before swelling, \(m_1\) and \(m_2\) are the weights of the swollen and deswollen sample, respectively; \(\varphi\) is the weight fraction of the insoluble components, \(\rho_r\) and \(\rho_s\) are the densities of the rubber and solvent, respectively.

The elastically active network chain density can be calculated by the well-known Flory-Rehner Equation S2:

\[
V_e = -\frac{\ln (1 - V_r) + V_r + \chi V_r^2}{V_s(V_r^{1/3} - V_r^{1/2})}
\]

where \(\chi\) is the Flory-Huggins polymer solvent interaction parameter (0.341 for ENR and toluene), and \(V_s\) is the molar volume of the solvent (106.5 cm\(^3\).mol\(^{-1}\) for toluene).

![Figure S7](image_url)

**Figure S7.** Cross-linking density, sol fraction and swelling ratio for BEx series.
3. Stress relaxation of BEx samples

Figure S8. Stress relaxation curves for BEx series at 160 °C.

Figure S9. Stress relaxation curves of BE5 and control sample at 140 °C.
Figure S10. Stress relaxation curves for BE5 at different temperatures ranging from 130 to 160 °C.

Figure S11. Fitting of characteristic relaxation time to temperature using the Arrhenius equation.
4. Self-healing properties of BEx samples

**Figure S12.** Network rearrangement of BEx samples via exchange reaction of boronic ester.
Figure S13. Typical stress-strain curves of (a)-(b) BE1, (c)-(d) BE3, (e)-(f) BE7, (g)-(h) BE10 after healing at various temperatures for 24 h and healing at 80 °C for various times.
Figure S14. Stress-strain curves of reference sample before and after healing at 80 °C for 24 h.

5. Reprocessability studies of BEx samples

Figure S15. Stress-strain curves of original and recycled for (a) BE1, (b) BE5, (c) BE7 and (d) BE10.
6. Thermogravimetric stability of BEx samples

TGA experiments show that the samples have an onset degradation temperature around 280 °C and negligible weight loss after keeping them at 160 °C for 2 h.

Figure S16. TGA curves of BEx samples.

Figure S17. Isothermal TGA curve of BE3 under nitrogen atmosphere at 160 °C.
7. Characterization of Zn$^{2+}$-O coordination

To envisage the coordination between Zn$^{2+}$ and epoxy groups and eliminate the confounding influence of BDB, ENR-ZnCl$_2$ model compound was prepared by mixing ENR and ZnCl$_2$ (molar ratio of epoxy group to zinc ion is 3:1) in tetrahydrofuran and then drying to produce a film for FTIR and Raman measurements. In the FTIR spectrum of ENR-ZnCl$_2$ model compound, the absorptions at 874 and 1256 cm$^{-1}$ that are associated with the asymmetric and symmetric vibrations of epoxy ring are drastically decreased, and a newly emerging absorption at 905 cm$^{-1}$ is observed, which can be ascribed to the coordination between Zn$^{2+}$ and oxygen in epoxy groups.$^4$

![Figure S18. FTIR spectra of neat ENR and ENR-ZnCl$_2$ model compound. The spectra are normalized by using the absorption intensity of -CH$_2$- at 1451 cm$^{-1}$ as an internal reference.](image)
When compared to neat ENR, a new band around 300 cm$^{-1}$ is observed in the Raman spectrum of ENR-ZnCl$_2$ model compound although the baseline is lifted due to the existence of fluorescence and noises, providing convincing evidence for the formation of Zn$^{2+}$-O coordination.$^5$

**Figure S19.** Raman spectra of neat ENR and ENR-ZnCl$_2$ mixture.

8. Stress relaxation of BE5-$y$ samples

**Figure S20.** Stress relaxation curves for BE5-$y$ series at 160 °C.
9. Self-healability and reprocessability studies of BE5-\(y\) samples

**Figure S21.** Healing efficiency of BE5-\(y\) with different ZnCl\(_2\) contents after being healed at 80 °C for 24 h.

**Figure S22.** Recover ratio of BE5-\(y\) series after being recycled.
10. Mechanical properties of BE\textsubscript{x} samples and comparison with reported self-healing materials

Table S1. Mechanical properties of BE\textsubscript{x} samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Young’s modulus (MPa)</th>
<th>Stress at 100 % Strain (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE1</td>
<td>1.60 ± 0.06</td>
<td>811 ± 9</td>
<td>0.85 ± 0.09</td>
<td>0.30 ± 0.01</td>
</tr>
<tr>
<td>BE3</td>
<td>6.31 ± 0.25</td>
<td>727 ± 28</td>
<td>1.18 ± 0.13</td>
<td>0.56 ± 0.01</td>
</tr>
<tr>
<td>BE5</td>
<td>9.55 ± 0.13</td>
<td>648 ± 5</td>
<td>1.58 ± 0.14</td>
<td>0.83 ± 0.01</td>
</tr>
<tr>
<td>BE7</td>
<td>12.53 ± 0.72</td>
<td>595 ± 7</td>
<td>2.64 ± 0.14</td>
<td>1.22 ± 0.02</td>
</tr>
<tr>
<td>BE10</td>
<td>14.63 ± 0.56</td>
<td>475 ± 8</td>
<td>4.45 ± 0.12</td>
<td>2.17 ± 0.01</td>
</tr>
</tbody>
</table>

Table S2. Comparison on the mechanical performance between reported self-healing systems and BE\textsubscript{x} samples.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Type of dynamic bond</th>
<th>Strength (MPa)</th>
<th>Breaking strain (%)</th>
<th>Heating condition</th>
<th>Healing efficiency</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>Disulfide and hydrogen bonds</td>
<td>0.87</td>
<td>2745</td>
<td>65 °C for 2 h</td>
<td>97%</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>(\pi)-(\pi) interaction</td>
<td>0.3</td>
<td>1400</td>
<td>80 °C for 1 h</td>
<td>(~100%)</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Diels-Alder reaction</td>
<td>0.61</td>
<td>51</td>
<td>140 °C for 3 h and 80 °C for 24 h</td>
<td>95%</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Metal-ligand bonds</td>
<td>0.35</td>
<td>330</td>
<td>60 °C for 24 h</td>
<td>88%</td>
<td>9</td>
</tr>
<tr>
<td>OLE</td>
<td>Hydrogen bond</td>
<td>0.36</td>
<td>2550</td>
<td>80 °C for 20 h</td>
<td>95%</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.12</td>
<td>560</td>
<td>120 °C for 24 h</td>
<td>70%</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>190</td>
<td>hot-pressing at 160 °C for 10 min</td>
<td>83%</td>
<td>12</td>
</tr>
<tr>
<td>Bond Type</td>
<td>Value</td>
<td>Temperature</td>
<td>Duration</td>
<td>Efficiency</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>-------</td>
<td>-------------</td>
<td>----------</td>
<td>------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boronic ester bonds</td>
<td>2.68</td>
<td>80 °C</td>
<td>24 h</td>
<td>&gt;80%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diels–Alder reaction</td>
<td>3.6</td>
<td>100 °C</td>
<td>5 h</td>
<td>90%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disulfide bonds</td>
<td>3.2</td>
<td>110 °C</td>
<td>12 h</td>
<td>72%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disulfide bonds</td>
<td>11</td>
<td>80 °C</td>
<td>4 h</td>
<td>92%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PU Diels–Alder reaction</td>
<td>5.4</td>
<td>130 °C (5 min)</td>
<td>92%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PU Disulfide bonds</td>
<td>2.62</td>
<td>75 °C</td>
<td>48 h</td>
<td>95%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal-ligand bonds</td>
<td>9.1</td>
<td>60 °C</td>
<td>24 h</td>
<td>~100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPG Alkoxyamine bonds</td>
<td>5.5</td>
<td>80 °C</td>
<td>2.5 h</td>
<td>70%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPG Disulfide and metal-ligand bonds</td>
<td>0.15</td>
<td>80 °C</td>
<td>5 h</td>
<td>76%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR Ionic interaction</td>
<td>1.53</td>
<td>80 °C</td>
<td>3 min</td>
<td>51%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR Ionic interaction</td>
<td>0.63</td>
<td>80 °C</td>
<td>1 min</td>
<td>73%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSU Disulfide bonds</td>
<td>1.02</td>
<td>75 °C</td>
<td>6 h</td>
<td>90%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSU Disulfide bonds</td>
<td>0.5</td>
<td>60 °C</td>
<td>1 h</td>
<td>97%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA Thiol-Michael reaction</td>
<td>0.25</td>
<td>90 °C</td>
<td>16 h</td>
<td>~90%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA Ionic bonds</td>
<td>1.4</td>
<td>80 °C</td>
<td>30 min</td>
<td>~100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ENR β-hydroxyl esters</td>
<td>5.76</td>
<td>160 °C</td>
<td>3 h</td>
<td>83%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ENR Boronic ester bonds</td>
<td>14.63</td>
<td>80 °C</td>
<td>24 h</td>
<td>&gt;90% This work</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PDMS (polydimethylsiloxane), OLE (olefin elastomer), PU (polyurethane), PPG (poly(propylene glycol)), NR (natural rubber), PSU (polysulfide), PA (polyacrylate),

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ENR (epoxidized natural rubber).

REFERENCES


(24) Xu, C.; Cao, L.; Huang, X.; Chen, Y.; Lin, B.; Fu, L. Self-Healing Natural Rubber with Tailorable


