Dihydrazone-based Dynamic Covalent Epoxy Networks with High Creep Resistance, Command Degradability, and Intrinsic Antibacteria from Bioresources

Xiwei Xu, Songqi Ma, Sheng Wang, Jiahui Wu, Qiong Li, Na Lu, Yanlin liu, Jintao Yang, Jie Feng, Jin Zhu

a Key laboratory of bio-based polymeric materials technology and application of Zhejiang province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China

b School of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China

c University of Chinese Academy of Sciences, Beijing 100049, P. R. China

*Corresponding authors: (Songqi Ma) E-mail masongqi@nimte.ac.cn, Tel 86-0574-87619806

Contents

Fig. S1 Non-isothermal DSC curve of HBP. 2
Fig. S2 Non-isothermal DSC curve of HBE. 2
Fig. S3 Strain recovery as a function of time for a) HBE-D400 and b) HBE-IPDA during the creep tests. 3
Fig. S4 Reprocess of HBE-IPDA at 180 °C for 45 min under 10 MPa pressure. 3
Fig. S5 Representative tensile stress−strain curves of the original and reprocessed HBE-IPDA. 4
Table S1 Tensile properties of the original and reprocessed HBE-IPDA. 4
Fig. S6 Different degradation rate of HBE-IPDA in 0.1 M HCl water/acetone (2/8, v/v) solution at 23 °C and 50 °C. 4
Fig. S7 Degradation rate of HBE-IPDA in 0.1 M HCl water/main solvent (2/8, v/v) solution with different main solvent at 50 °C. 5
Fig. S8 Degradation rate of HBE-IPDA in different acid water/acetone (2/8, v/v) solutions at 50 °C. 5
Fig. S10 The real-time 1H NMR spectra of small-molecule model dihydrazone DBH after degradation at 23 °C for different times. 6
Fig. S11 The real-time 1H NMR spectra of dihydrazone CANs after degradation. 7
Table S2 Contact angle and swelling degree of HEB-IPDA in different solvents at 50 °C. 7
Fig. S1 Non-isothermal DSC curve of HBP.

Fig. S2 Non-isothermal DSC curve of HBE.
Fig. S3 Strain recovery as a function of time for a) HBE-D400 and b) HBE-IPDA during the creep tests.

Fig. S4 Reprocess of HBE-IPDA at 180 °C for 45 min under 10 MPa pressure.
Fig. S5 Representative tensile stress–strain curves of the original and reprocessed HBE-IPDA

Table S1 Tensile properties of the original and reprocessed HBE-IPDA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>1991±34</td>
<td>95±4</td>
<td>8.7±0.5</td>
</tr>
<tr>
<td>1st reprocessed</td>
<td>1965±26</td>
<td>90±3</td>
<td>9.3±0.3</td>
</tr>
<tr>
<td>2nd reprocessed</td>
<td>2044±19</td>
<td>89±2</td>
<td>8.8±0.2</td>
</tr>
<tr>
<td>3rd reprocessed</td>
<td>2093±17</td>
<td>88±2</td>
<td>8.0±0.2</td>
</tr>
</tbody>
</table>
**Fig. S6** Different degradation rate of HBE-IPDA in 0.1 M HCl water/acetone (2/8, v/v) solution at 23 °C and 50 °C.

**Fig. S7** Degradation rate of HBE-IPDA in 0.1 M HCl water/main solvent (2/8, v/v) solution with different main solvent at 50 °C.

**Fig. S8** Degradation rate of HBE-IPDA in different acid water/acetone (2/8, v/v) solutions at 50 °C.
**Fig. S9** Degradation rate of HBE-IPDA in 0.1 M HCl water/acetone solutions with different solvent ratios at 50 °C.

**Fig. S10** The real-time $^1$H NMR spectra of small-molecule model dihydrazone DBH after degradation at 23 °C for different times.
Fig. S11 The real-time 1H NMR spectra of dihydrazone CANs after degradation.

Table S2 Contact angle and swelling degree of HEB-IPDA in different solvents at 50 °C.

<table>
<thead>
<tr>
<th>Main solvent</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>THF</th>
<th>DMSO</th>
<th>DMF</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/Mai</td>
<td>2/8</td>
<td>2/8</td>
<td>2/8</td>
<td>2/8</td>
<td>2/8</td>
<td>2/8</td>
</tr>
<tr>
<td>n solvent,  (v/v)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contact angle (°)</td>
<td>28.3</td>
<td>36.4</td>
<td>20.6</td>
<td>24.1</td>
<td>41.5</td>
<td>83.8</td>
</tr>
<tr>
<td>Swelling degree (%)</td>
<td>25</td>
<td>9</td>
<td>18</td>
<td>21</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

*: Swelling test at 23 °C
**Fig. S12** Digital photographs of static contact angle of HBE-D400.

**Fig. S13** Digital photographs of static contact angle of HBE-IPDA.
Calculation of topology-freezing temperatures ($T_v$) and activation energies ($E_a$).

Topology-freezing temperatures ($T_v$) and activation energies ($E_a$) were determined using the methodology reported in literature\(^1,2\). The measured values of characteristic relaxation times ($\tau^*$s) were plotted versus $1000/T$. The plots were fit to the Arrhenius law in equation (1)

$$\tau^*(T) = \tau_0 e^{E_a/RT} \quad (1)$$

($R$ : universal gas constant; 8.314 J K\(^{-1}\) mol\(^{-1}\) )

Equation (1) can be transformed to equation (2):

$$\ln \tau^*(T) = \ln \tau_0 + E_a/RT \quad (2)$$

For HBE-D400:

$$\frac{1000}{T} E_a/R = 11.458, E_a = 95.26 \text{ kJ mol}^{-1}$$

For HBE-IPDA:

$$\frac{1000}{T} E_a/R = 11.208, E_a = 93.18 \text{ kJ mol}^{-1}$$

$T_v$ is defined to be the temperature at which the material reaches a viscosity of $10^{12}$ Pa. The relation of the viscosity $\eta$ and the $\tau^*$ is known as the Maxwell relation equation (5)

$$\eta = G \times \tau^* = (E'/2 (1 + \nu)) \times \tau^* \quad (5)$$

($G$ : shear modulus, $E'$ : storage modulus, $\nu$ : Poisson's ratio)

Using the Poisson’s ratio ($\nu$) of epoxy resin (0.38),

$$\eta = 0.284 \times E' \times \tau^* \quad (6)$$

The storage modulus of HBE-D400 from 170 °C to 185 °C is 9.3 MPa, and that of HBE-IPDA in the same temperature range is 13.1 MPa. Because $\eta$ is $10^{12}$ Pa at $T_v$, $\tau^*$s at $T_v$ of HBE-D400 and HBE-IPDA are calculated to be $3.9 \times 10^5$ s and $2.7 \times 10^5$ s, respectively. Using these values and equation (3) and (4), $T_v$ was computed to be 109 °C for HBE-D400 and 105 °C for HBE-IPDA.

References
