Supporting Information

Healable shape-memory (thio)urethane thermosets

Le-Thu T. Nguyen,*† Thuy Thu Truong,† Ha Tran Nguyen,†‡ Lam Le,†‡ Viet Quoc Nguyen,* Thang Van Le,*‡ Anh Tuan Luu†

†Faculty of Materials Technology, Ho Chi Minh City University of Technology (HCMUT), Vietnam National University, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Vietnam.
‡Materials Technology Key Laboratory (Mtlab), Ho Chi Minh City University of Technology, Vietnam National University, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Vietnam.
§National Key Laboratory of Polymer and Composite Materials- Ho Chi Minh City University of Technology, Vietnam National University, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Vietnam.

* Corresponding author. E-mail address: nguyenthilethu@hcmut.edu.vn

1. Methods

¹H NMR spectra were recorded in deuterated chloroform (CDCl₃) with TMS as an internal reference, on a Bruker Avance 300 at 300 MHz. Transmission Fourier transform infrared (FT-IR) spectra, collected as the average of 128 scans with a resolution of 4 cm⁻¹, were recorded from KBr disk on the FT-IR Bruker Tensor 27. Attenuated total reflectance (ATR) FT-IR spectra were collected as the average of 128 scans with a resolution of 4 cm⁻¹ on a FT-IR Tensor 27 spectrometer equipped with a Pike MIRacle ATR accessory with a diamond/ZnSe element. Size exclusion chromatography (SEC) measurements were performed on a Polymer PL-GPC 50 gel permeation chromatograph system equipped with an RI detector, with either tetrahydrofuran or chloroform as the eluent at a flow rate of 1.0 mL/min. Molecular weight and molecular weight distribution were calculated with reference to polyethylene glycol standards. Differential scanning calorimetry (DSC) measurements were carried out with a DSC Q20 V24.4 Build 116 calorimeter under nitrogen flow, at a heating rate of 10 °C/min, from -40 to 170 °C. The samples were quenched rapidly from 170 °C using liquid nitrogen before each DSC heating scan. Thermogravimetric analysis (TGA) measurements were performed under nitrogen flow using a NETZSCH STA 409 PC Instruments with a heating rate of 10 °C/min from ambient temperature to 900 °C. Hardness measurements were performed on Teclock Durometer GS-709N (Shore A) ASTM D2240A. Tensile tests were measured using a Tensilon RTC-1210A tensile testing machine, making use of a 1000 N load cell. The rectangular specimens met the
requirements of ASTM D882 but the dimensions were scaled down. The specimens were rectangular strips of film with a thickness of approximately 0.1 mm, a length of 40 mm and width of 3 mm. The tensile tests were run at a speed of 0.05 mm/min. At least three specimens were tested for each material. Controlled macro-scratches (>2 cm) were performed by sliding a razor or scalpel blade oriented at 45° to the sample surface, with a motorized constant rate and an applied normal force of 1 N. Optical microscopic images were recorded on an Olympus GX51F microscope.

2. Materials

All materials were used as received, without further purification. Solvents for the synthesis were dried according to standard laboratory procedures prior to use.

1,1′-(Methylenedi-4,1-phenylene)bismaleimide (bismaleimide, 95%), were purchased from Sigma-Aldrich. 3-Amino-1-propanol (99%), 2-furfurylthiol (97%), triethylamine (99%), tetrahydrofuran (99.5%), methanol (99.9%) and poly(caprolactone) diol (average Mn 2000, Mn ¹H NMR = 2112 g/mol) were purchased from Acros. n-Heptane (99+%), chloroform (99+%), dichloromethane (99.5%), diethyl ether (99+%) and toluene (99+%) were purchased from Fisher Chemicals. Exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (98+%) was purchased from TCI Chemicals (Japan). Zirconium(IV) acetylacetonate was purchased from Merck. Poly(caprolactone) diol (Capa™ 2201A Mn ¹NMR = 2100g/mol) was kindly provided by Perstorp Chemicals Asia Pte Ltd. Hexamethylene diisocyanate isocyanurate trimer (HDI-trimer, tradename Desmodur® N 3390 BA, 90 % in n-butyl acetate, NCO content by ¹H NMR = 0.00366 mol/g) was kindly provided by Bayer Vietnam Ltd.

3. Monomer synthesis

3.1. Thiourethane-trisfuran (TUF₃)

A triethylamine-catalyzed thiol-isocyanate reaction took place between HDI-trimer and 2-furfurylthiol in tetrahydrofuran (THF), under ambient conditions. 42.513 g (155.6 mmol of NCO groups) of Desmodur N3390 BA was mixed with 20 mL (198.3 mmol) of 2-furfurylthiol in 110 mL of THF. Triethylamine (277 µL) was then added and the reaction was stirred at room temperature overnight. The product was precipitated into n-heptane, filtered and dried under vacuum to give a brown solid. Yield: 92%.
Fig. S1. Synthetic scheme of TUF$_3$ by the thiol-isocyanate reaction between hexamethylene diisocyanate isocyanurate trimer with 2-furfurylthiol and the corresponding $^1$H NMR spectra.
Fig. S2. Overlay of the transmission FT-IR spectra of hexamethylene diisocyanate isocyanurate trimer and TUF$_3$.

### 3.2. 3-Maleimido-1-propanol

3-Maleimido-1-propanol was prepared according the previously reported procedure.$^1$ 3-Amino-1-propanol (2.04 g, 27.1 mmol) in 20 mL of methanol was added dropwise to a suspension of exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (8) (4.5 g, 27.1 mmol) in methanol (180 mL) at 0 °C. The mixture was stirred at 0 °C for another 5 min and at room temperature for 30 min. The mixture was then refluxed at at 62 °C for 3 days and concentrated to give a clear oil. This oil was purified by column chromatography using methanol/dichloromethane (1: 15) as eluent to give an intermediate product (DA adduct of furan and 3-maleimido-1-propanol). This intermediate product was refluxed in toluene at 110 °C for 8 h to yield 3-maleimido-1-propanol as a yellowish oil. Yield: 63%.
Fig. S3. Synthetic scheme and the $^1$H NMR spectrum of 3-maleimido-1-propanol.

Fig. S4. Transmission FT-IR spectrum of 3-maleimido-1-propanol.
3.3. Bismaleimide terminated PCL (PCLM₂)

HDI (2.0 mL, 12.4 mmol), freshly azeotropically dried PCL (Acros product, $M_n$ 1H NMR = 2112 g/mol, 13.15 g, 6.2 mmol) and zirconium(IV) acetylacetonate (121 mg, 1 mol% per OH group) were dissolved in 160 mL of dry chloroform under nitrogen atmosphere. The reaction was refluxed for 6 h. After the mixture was cooled down, 3-maleimido-1-propanol (1.93 g, 12.4 mmol) was added and the mixture was again refluxed. After 2 h, the reaction was kept at room temperature overnight under nitrogen atmosphere to assure that all –NCO groups were consumed. After the reaction, chloroform was removed. The product was re-dissolved in THF and precipitated into distilled water. The precipitate was washed with diethyl ether and dried under vacuum. Yield: 80%. $M_n$ (estimated by $^1$H NMR) = 2942 g/mol. SEC (THF as eluent): $M_n = 3750$ g/mol; $D = 1.33$.

Fig. S5. $^1$H NMR spectrum of PCLM₂.
3.4. Bisfuranic terminated PCL (PCLF$_2$)

HDI (15.0 mL, 93.4 mmol), freshly azeotropically dried PCL (Capa™ 2201A, 98.05 g, 46.7 mmol) and zirconium(IV) acetylacetonate (0.91 g, 1 mol% per OH group) were dissolved in 600 mL of dry chloroform under nitrogen atmosphere. The reaction was refluxed at 65 °C under nitrogen for 2 h. After the mixture was cooled down, 2-furfurylthiol (11.3 mL, 112.1 mmol) and triethylamine (26 µL) were added and the mixture was stirred at room temperature under nitrogen atmosphere overnight. After the reaction, the solution was concentrated and the product was precipitated from chloroform to $n$-heptane for 3 times. The precipitate was dried under vacuum. Yield: 85%. $M_n$ (estimated by $^1$H NMR) = 2846 g/mol. SEC (chloroform as eluent): $M_n = 5025$ g/mol; $D = 1.52$. 

Fig. S6. Transmission FT-IR spectrum of PCLM$_2$. 

![Transmission FT-IR spectrum of PCLM$_2$.](image-url)
Fig. S7. $^1$H NMR spectrum of PCLF$_2$.

Fig. S8. Transmission FT-IR spectrum of PCLF$_2$. 
3.5. Urethane-trismaleimide (UM₃)

Under nitrogen atmosphere, the mixture of Desmodur N3390 BA (2.35 g, 8.6 mmol of NCO groups), 3-maleimido-1-propanol (2 g, 12.9 mmol) and zirconium(IV) acetylacetonate (41.9 mg) in 150 mL of dry chloroform was refluxed at 65 °C for 5 h, and was then stirred at room temperature overnight. After the reaction, the solution was concentrated and the product was precipitated from chloroform to n-heptane. The product was further purified to remove excess 3-maleimido-1-propanol by thorough washing with distilled water for many times until a pure product was obtained as indicated by thin layer chromatography. Yield: 82%.

Fig. S9. Synthetic scheme of UM₃ and the corresponding ¹H NMR spectra.
4. Synthesis of DA cross-linked networks

To prepare DA cross-linked thio(urethane) networks, a mixture of multi-maleimide and multi-furan compounds in a 1:1 furan to maleimide equivalent ratio in tetrahydrofuran was cast in a glass petri disk at 40 °C for 48 h, followed by vacuum dried at 60 °C for 24 h.

Fig. S11-14 compare the ATR FT-IR spectra of the maleimide and furan monomers and corresponding (thio)urethane networks 1-4, respectively. The occurrence of the DA crosslinking reaction was proven by the nearly complete disappearance of the furan (1011 cm⁻¹, as a shoulder) and maleimide (696 and 828 cm⁻¹) bands in the resulting materials.

Fig. S10. Transmission FT-IR spectrum of UM₃.
Fig. S11. ATR FT-IR spectra of PCLM₂, TUF3 and Network 1 (TUF₃-PCLM₂).

Fig. S12. ATR FT-IR spectra of TUF₃, M₂ and Network 2 (TUF₃-M₂).
Fig. S13. ATR FT-IR spectra of TUF$_3$, UM$_3$ and Network 3 (TUF$_3$-UM$_3$).

Fig. S14. ATR FT-IR spectra of PCLF$_2$, UM$_3$ and Network 4 (UM$_3$-PCLF$_2$).
5. TGA analysis of (thio)urethane networks

![TGA thermograms](image)

Fig. S15. Comparative TGA thermograms under N₂ of (thio)urethane networks of different structures.

6. Shape memory behavior

![Shape memory behavior](image)

Fig. S16. Photographs showing the sequential recovery from the temporary shape (spiral) to the permanent shape (strip) of Network 1 at 60 °C.
Fig. S17. Photographs showing the sequential recovery from the temporary shape (spiral) to the permanent shape (strip) of Network 4 at 60 °C.

Fig. S18. Photographs of Network 2 film: a) permanent shape, b) temporary shape after deforming at 85 °C and fixing at room temperature, c) shape recovery after heating at 85 °C for 60 sec.

Fig. S19. Shape recovery rate at 60 °C of (thio)urethane networks.
Table S1. Strain fixity ($R_{f}$) and recovery ($R_{r}$) rates

<table>
<thead>
<tr>
<th>cycle</th>
<th>Network 1</th>
<th>Network 3</th>
<th>Network 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (exp. 1)</td>
<td>$S_t$ (%)</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>$R_{f,4}$ (%)</td>
<td>99.5</td>
<td>96.6</td>
</tr>
<tr>
<td></td>
<td>$R_{f,30}$ (%)</td>
<td>99.5</td>
<td>75.9</td>
</tr>
<tr>
<td></td>
<td>$R_r$ (%)</td>
<td>100</td>
<td>98.9</td>
</tr>
<tr>
<td>I (exp. 2)</td>
<td>$S_t$ (%)</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>$R_{f,4}$ (%)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>$R_{f,30}$ (%)</td>
<td>100</td>
<td>96.3</td>
</tr>
<tr>
<td></td>
<td>$R_r$ (%)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>II (exp. 2)</td>
<td>$S_t$ (%)</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>$R_{f,4}$ (%)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>$R_{f,30}$ (%)</td>
<td>100</td>
<td>95.5</td>
</tr>
<tr>
<td></td>
<td>$R_r$ (%)</td>
<td>100</td>
<td>98.9</td>
</tr>
<tr>
<td>III (exp. 2)</td>
<td>$S_t$ (%)</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>$R_{f,4}$ (%)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>$R_{f,30}$ (%)</td>
<td>100</td>
<td>92.8</td>
</tr>
<tr>
<td></td>
<td>$R_r$ (%)</td>
<td>100</td>
<td>97.2</td>
</tr>
</tbody>
</table>

*The cast films were stretched with a strain of $S_t$% by external stress at 60 °C, and the stretched films were kept at either 4 °C for 10 min or at room temperature (30 °C) for 15 min (corresponding to the $R_{f,4}$ and $R_{f,30}$ parameters, respectively).

7. Study of the reversibility of the DA crosslinking reaction by ATR FT-IR

The networks were heated up to 100 °C for 1 h, and the rDA reaction was checked by the fast recovery of typical maleimide (696 and 828 cm⁻¹) absorption bands in the ATR FT-IR spectra. Then, a mild heating at 60 °C for 3 days reformed the DA cross-linkers. These results were evidenced in Fig. S20-22 for Network 1-4, respectively.
Fig. S20. ATR FT-IR spectra of Network 1 (TUF$_3$-PCLM$_2$) showing the evolution of the 696 cm$^{-1}$ maleimide band upon the rDA reaction at 110 °C and the DA reaction at 60 °C.

Fig. S21. ATR FT-IR spectra of Network 2 (TUF$_3$-M$_2$) showing the evolution of the 696 and 829 cm$^{-1}$ maleimide bands upon the rDA reaction at 110 °C and the DA reaction at 60 °C.
Fig. S22. ATR FT-IR spectra of Network 4 (UM$_3$-PCLF$_2$) showing the evolution of the 696 and 829 cm$^{-1}$ maleimide bands upon the rDA reaction at 110 °C and the DA reaction at 60 °C.

8. Scratch healing

Fig. S23. Optical micrographs of a scratches of the Network 1 sample before (i) and after (ii) healing at 60 °C for 5 min.
Fig. S24. Stress-strain curve of the initial and damaged Network 1 sample after healing.

Fig. S25. Stress-strain curve of the initial and damaged Network 3 sample after healing.
Reference