

Supporting Information

Tailoring the hard–soft interface with dynamic diels-alder linkages in polyurethanes: toward superior mechanical properties and healability at mild temperature

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1. Materials

Poly(ϵ -caprolactone) diol (CAPA 2403D, manufactured with butanediol as initiator, $M_n = 4000 \text{ g mol}^{-1}$, $M_n \text{ } ^1\text{H NMR} = 4090 \text{ g mol}^{-1}$, Perstorp UK Ltd) and poly(ϵ -caprolactone) diol (CAPA 2803, $M_n = 8000 \text{ g mol}^{-1}$, Perstorp UK Ltd) were azeotropically dried with toluene before use. Allyl glycidyl ether (AGE, 99+%, TCI Chemicals–Japan) was dried over molecular sieves and distilled under vacuum before use. Dichloromethane (99.9%, Fisher Chemicals) was dried over CaH_2 and distilled. Tetrafluoroboric acid diethyl ether complex ($\text{HBF}_4 \cdot \text{Et}_2\text{O}$, 90+%, Sigma–Aldrich), furfuryl mercaptan (FM, 97+%, Sigma–Aldrich), 2-mercaptoethanol (99+%, Sigma–Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Sigma–Aldrich), calcium oxide (96%, Fisher Chemicals), triphenylphosphine (TPP, 99%, Sigma–Aldrich) and 1,1-(Methylenedi-4,1-phenylene)bismaleimide (bismaleimide, 95%, Sigma–Aldrich) were used as received. 3-Maleimido-1-propanol was synthesized according to the previously reported procedure.^[1] Zirconium(IV) acetylacetonate was purchased from Merck. Hexamethylene diisocyanate isocyanurate trimer (HDI-trimer, tradename Desmodur® N 3600) was kindly provided by Bayer (Vietnam Ltd.). 2,5-Bis-(hydroxymethyl)furan (99%+) was purchased Polyscience Inc.

2. Characterization methods and instruments

^1H NMR spectra were recorded in deuterated chloroform (CDCl_3) 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. 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 $10 \text{ }^\circ\text{C}/\text{min}$, from 0 to $170 \text{ }^\circ\text{C}$. Mechanical properties were measured with a Tensilon RTC-1210A tensile testing machine, making use of a 1000 N load cell. The dog bone shaped samples had an effective gauge length of 11 mm, a width of 2 mm, and a thickness of $\pm 1.5 \text{ mm}$ (meeting the requirements of ASTM D638-type IV but the dimensions were scaled down). At least four specimens were tested for each composition. Scanning electron microscope (SEM) images were obtained on a HITACHI S-4800 microscope, operating at 5 kV. Optical microscopic images were recorded on an Olympus GX51F microscope. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a SI 1280B Solartron. The measuring frequency range was from $2 \times 10^4 \text{ Hz}$ to 01 Hz ,

and the impedance spectra were obtained at open circuit potential with a 10 mV sine perturbation. Wide-angle powder X-ray diffraction (XRD) patterns were recorded at room temperature on a Bruker AXS D8 Avance diffractometer using Cu K α radiation ($\lambda = 0.15406$ nm), at a scanning rate of 0.050 s⁻¹. The data were analyzed using DIFRAC plus Evaluation Package (EVA) software. The d-spacings were calculated from peak positions using Cu K α radiation and Bragg's law.

3. Assessment methods of healing efficiency

The tested sample was subjected to damage, followed by healing via heating at 65 °C for either 30 min or 24 h. The healing efficiency was determined as the ratio of the tensile property (i.e. stress of break, Young's modulus, or strain of break) of the healed sample to the reference sample. The reference sample (sample of the same composition and not damaged) was also heated and stabilized under the sample conditions with the healed sample.

3.1. By tensile measurements

a) Healing assessment of cut-in-half and respliced samples:

The dog bone shaped samples were cut through the middle using a razor blade, and the halves were then put back together and placed between two glass slides in an oven at 65 °C under ambient pressure. After heating, the samples were kept at room temperature for 8 h to stabilize before tensile measurements.

b) Healing assessment of samples after large tensile deformation:

The dog bone shaped samples were subjected to large tensile deformations with a strain of 75% of the strain of break. After a minimal instantaneous elastic recovery when releasing the load, the sample was heated in an oven at 65 °C. The original sample shape was almost recovered after 5 min at 65 °C (above the PCL melting transition, i.e. the T_{trans} for the shape-memory effect) and fully recovered after 30 min at 65°C. Besides the shape recovery effect during heating, the healing process via Diels-Alder reaction also occurred. After heating, the samples were kept at room temperature for 8 h to stabilize before tensile measurements.

3.2. By EIS measurements

a) DA-PU films coated on steel panels:

DA-PU films of approximately 150 μm thickness (measured by an Elcometer A456 gauge) were coated on SUS304 stainless steel panels. For the EIS test, a scratch of ~ 0.7 cm length (in the middle of the tested area of 1 cm diameter) was made by pushing a razor blade perpendicularly to the surface into the coating. Full penetration of the organic coating, exposing the underlying steel, was confirmed by

optical microscopy. EIS measurements were carried out using a three-electrode cell in which the sample was placed horizontally. The coated samples under study (exposed surface area of 0.785 cm²) were used as the working electrode and the surface. A saturated Ag/AgCl electrode ($E = 0.197 \text{ V vs SHE}$) as reference and a platinum counter electrode were employed. The samples were immersed in 0.05 M sodium chloride (NaCl) solution and were left for 15–30 min until a stable open circuit was reached.

b) Free-standing DA-PU films:

For EIS tests, both surfaces of a DA-PU free-standing film (of about 200 μm thickness) were spray-coated with a conductive silver paste (YH-A001 (YiHui, Hongkong), viscosity of 35 Pa s at 25 °C and volume resistivity of $1 \times 10^{-5} \Omega \text{ cm}$) as the external electrodes. The silver layers were removed by acetone after each EIS measurement. A cut-through scratch of $\sim 0.7 \text{ cm}$ length was made by a razor blade. Healing was performed at 65 °C for 30 min and 24 h. The exposed surface area was 1 cm².

4. Synthesis of allyl-PCL diol, furan-PCL diol and ref-PCL polyol

The furan end-block functionalized PCLs (furan-PCL diol) and ref-PCL polyol were synthesized according to a previously reported two-step procedure^[2] (Scheme S1).

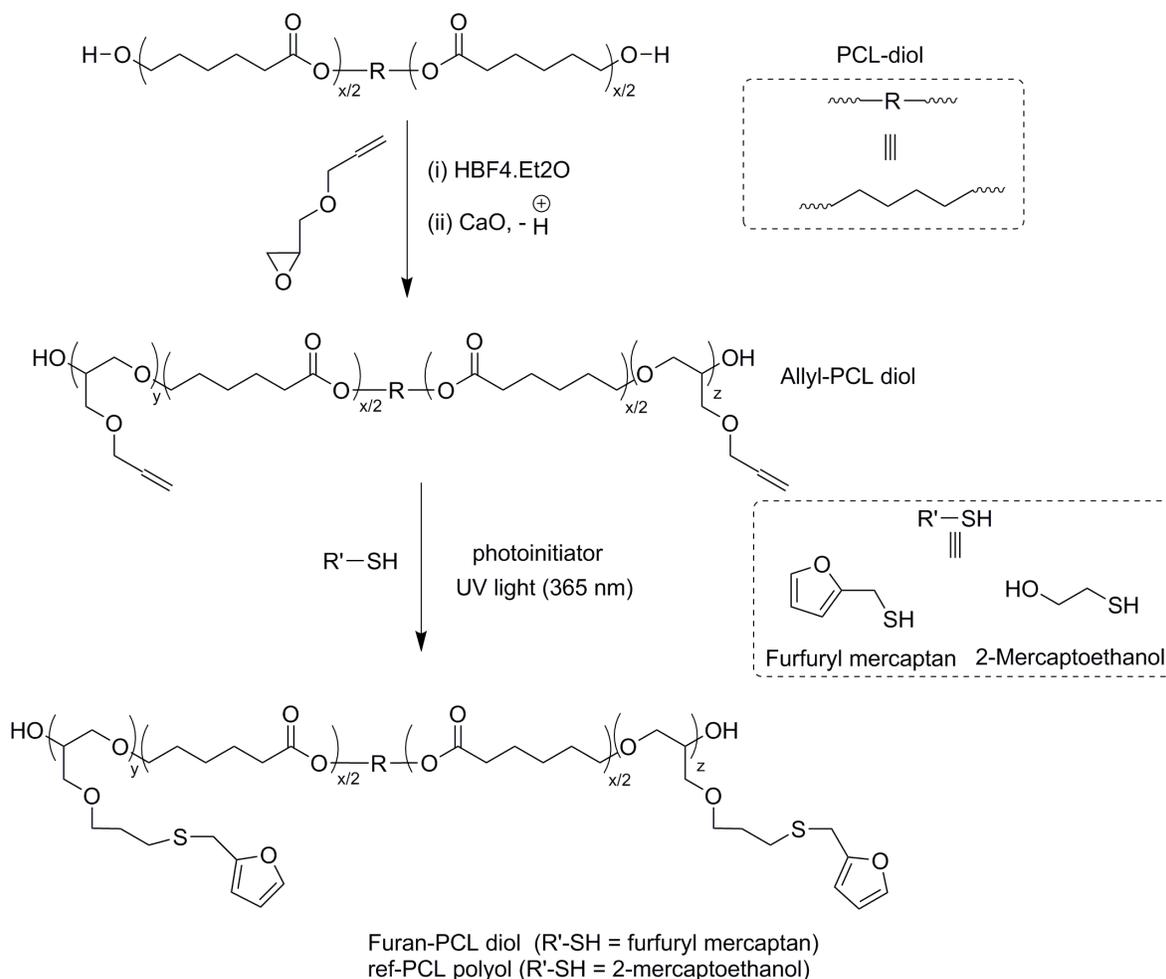
4.1. Allyl-PCL diol:

The accurate M_n values of the PCL-diol (CAPA 2403D) was previously determined by ¹H NMR^[2] to be 4090 g mol⁻¹. Commercial PCL diol (CAPA 2403D) with $M_n = 4090 \text{ g mol}^{-1}$ (3.45 g, 1.69 mmol of –OH groups) was dissolved in 17.5 mL of dichloromethane in a round-bottom flask. To this solution, 0.017 mL (0.12 mmol) of HBF₄·Et₂O was added. Then, a nitrogen flow was passed over the mixture and the flask was closed with a rubber septum. 0.31 mL (4.22 mmol) of AGE was slowly introduced with a syringe during 6 h. The reaction mixture was kept at room temperature for 24 h, and, after that, the acid catalyst was neutralized with solid CaO. After filtration of CaO, the solution was concentrated and the product was isolated by precipitation three times in methanol (dichloromethane/ methanol = 1/5, v/v), washed three times with methanol, filtered and dried on vacuum line. Yields: 80%.

From the ¹H NMR analysis of the product (Figure S1), by comparing the intensity of signals corresponding to the alkene group (5.27–5.04 ppm) with that of the separate signal assigned to repeating CL units (2.55–2.05 ppm) and taking into account the degree of polymerization of the starting PCL-diol, the total number of attached AGE units per polymer chain could be calculated. The total number of attached AGE units per polymer chain was determined to be 3.

4.2. Thiol–ene addition reaction of allyl-PCL diol with furfuryl mercaptan/2-mercaptoethanol:

In a flask containing a stirring bar and closed with a rubber septum, allyl-PCL-diol was melted at 55 °C under stirring. After stopping heating, it remained as a clear liquid and a minimum amount of tetrahydrofuran was added to maintain the polymer in the liquid state at room temperature. Then, DMPA (10 mol% with respect to allyl groups), triphenylphosphine (TPP) and the thiol compound (either furfuryl mercaptan or 2-mercaptoethanol) were added in succession. The allyl : thiol: TPP molar ratio used was 1: 2 : 20. The reaction mixture was degassed and was purged with nitrogen through a needle using vacuum/nitrogen line. After an overnight exposure to UV light (wavelength of 365 nm, with twelve lamps of 9 W circularly oriented), the product was collected by precipitation three times in diethyl ether and was further dried under vacuum (10^{-3} torr) at 60 °C to remove any left unreacted thiol. From the ^1H NMR analysis of the products (Figure S2 for the reaction with furfuryl mercaptan and Figure S3 for the reaction with 2-mercaptoethanol), by comparing the signal intensities before and after coupling reactions, using a separate signal corresponding to the polymer backbone as the reference, both the conversion of allyl groups and the number of attached thiol molecules per allyl group could be determined. Full conversions of the thiol–ene coupling of the allyl-PCL diol with furfuryl mercaptan and 2-mercaptoethanol were obtained.



Scheme S1. Synthesis of furan-PCL diol via two steps: (i) Cationic activated monomer oligomerization of allyl glycidyl ether (AGE) initiated by a commercial PCL-diol ($M_n = 4090 \text{ g mol}^{-1}$) to give allyl-PCL diol; (ii) UV-initiated radical thiol-ene reaction of allyl-PCL diol with either furfuryl mercaptan or ethanol mercaptan in the presence of 2,2-dimethoxy-2-phenylacetophenone as photoinitiator and triphenylphosphine as disulfide reducing agent.

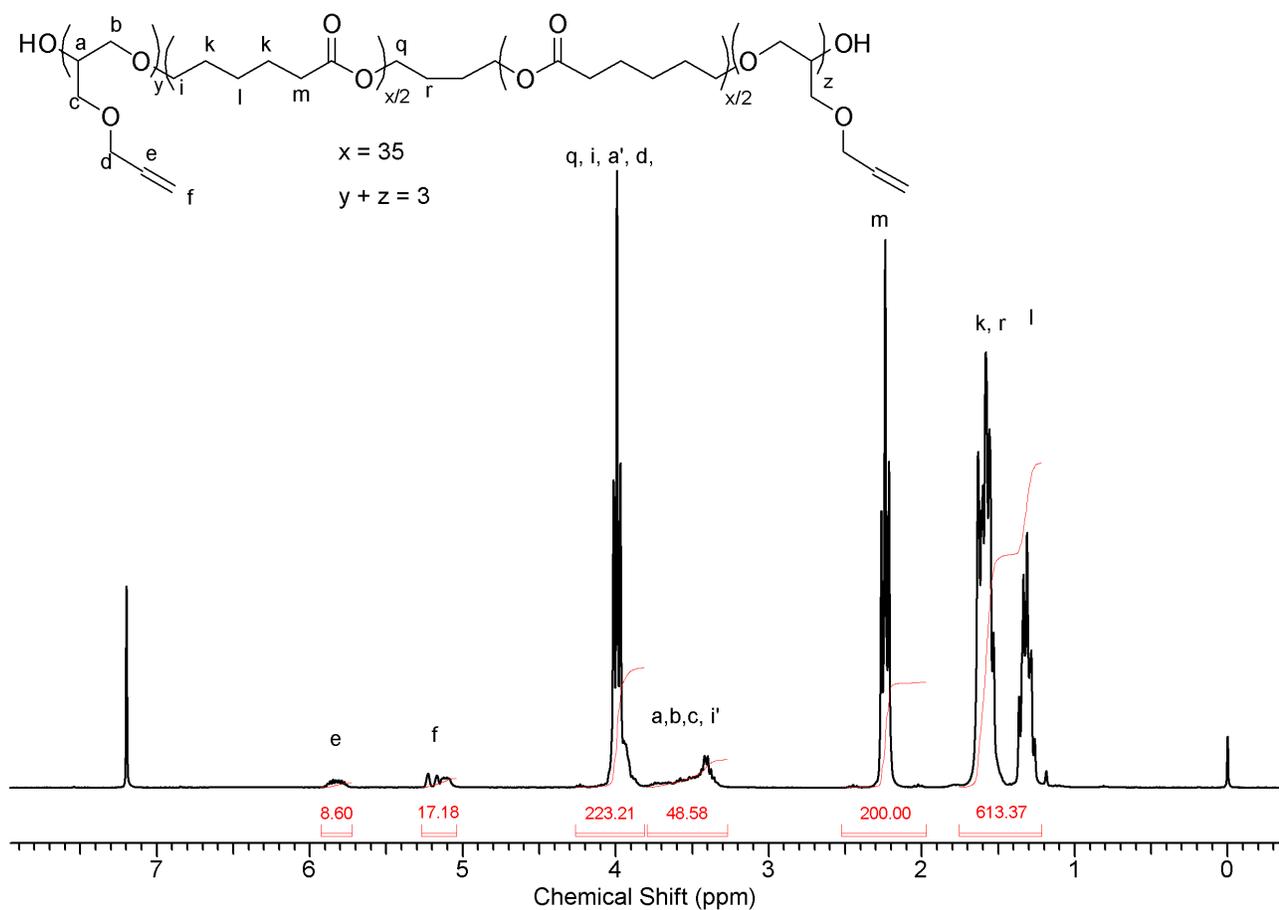


Figure S1. ¹H NMR spectrum of allyl-PCL diol. The signal denoted as a' corresponds to the methine protons of HO-CH(R)- groups of terminal HO-AGE units. The signal denoted as i' corresponds to the methylene protons of -(AGE)_y-CH₂(R)- groups of CL units next to AGE units.

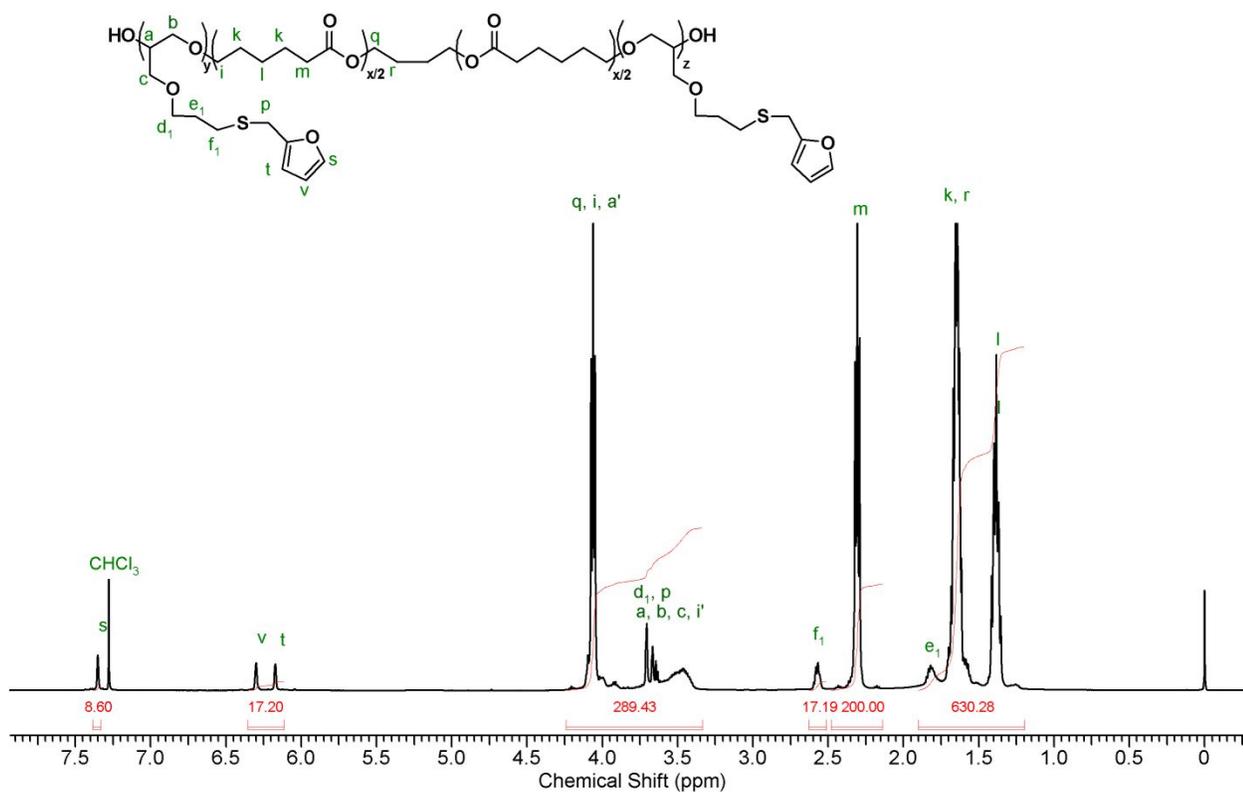


Figure S2. ¹H NMR spectrum of furan-PCL diol (obtained via the thiol-ene reaction of allyl-PCL diol with furfuryl mercaptan). The signal denoted as a' corresponds to the protons of HO-CH(R)- groups of terminal HO-AGE units. The signal denoted as i' corresponds to the methylene protons of -(AGE)y-CH₂(R)- groups of CL units next to AGE units.

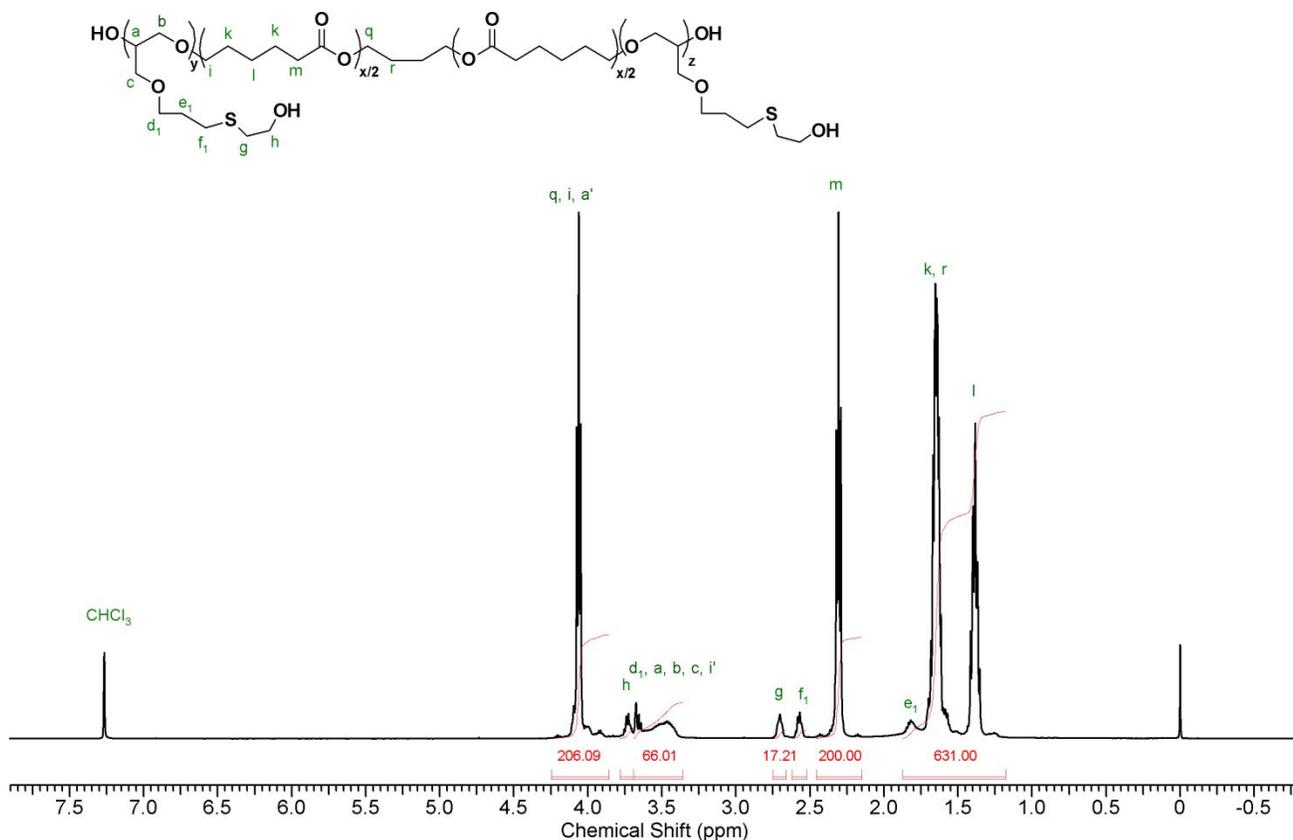


Figure S3. ^1H NMR spectrum of ref-PCL polyol (obtained via the thiol-ene reaction of allyl-PCL diol with 2-mercaptoethanol). The signal denoted as a' corresponds to the protons of HO-CH(R)- groups of terminal HO-AGE units. The signal denoted as i' corresponds to the methylene protons of -(AGE)_y-CH₂(R)- groups of CL units next to AGE units.

5. Synthesis of DA-PCL polyol

DA-PCL polyol was synthesized by the DA reaction between a furan end-functionalized PCL diol and 3-maleimido-1-propanol (in tetrahydrofuran, at a maleimide to furan molar ratio of 1), which was effective at 30–60 °C with a conversion of ~ 97% after 24 h.

Figure S4 shows a comparison of the transmission FT-IR spectra of DA-PCL polyol, furan-PCL diol and 3-maleimido-1-propanol. The disappearance of the typical maleimide absorption bands at 696 and 829 cm^{-1} and furan “ring breathing” signal at 1010 cm^{-1} , as well as the appearance of the band at 862 cm^{-1} ascribed to the furan-maleimide cycloadduct, confirms the successful occurrence of the DA reaction.

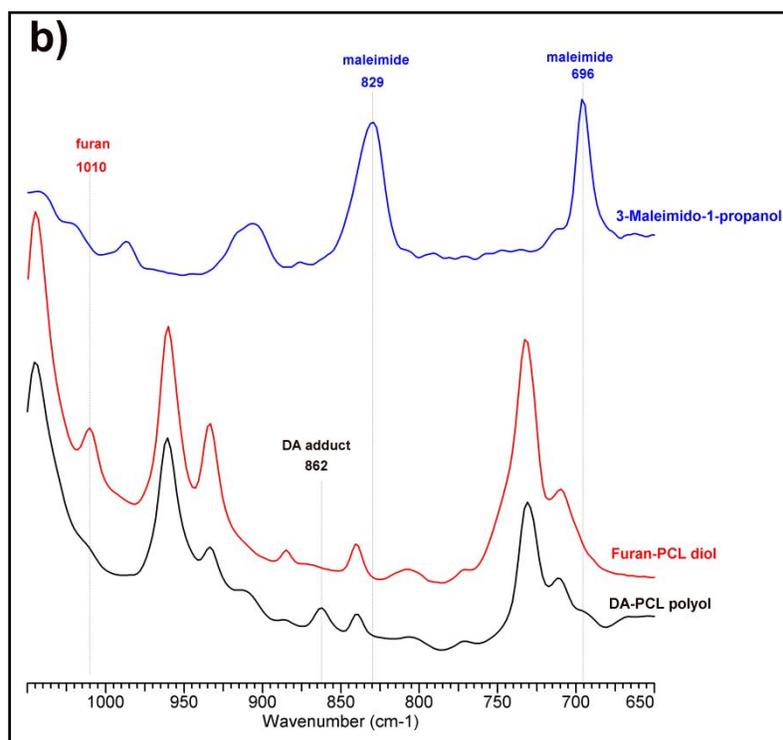
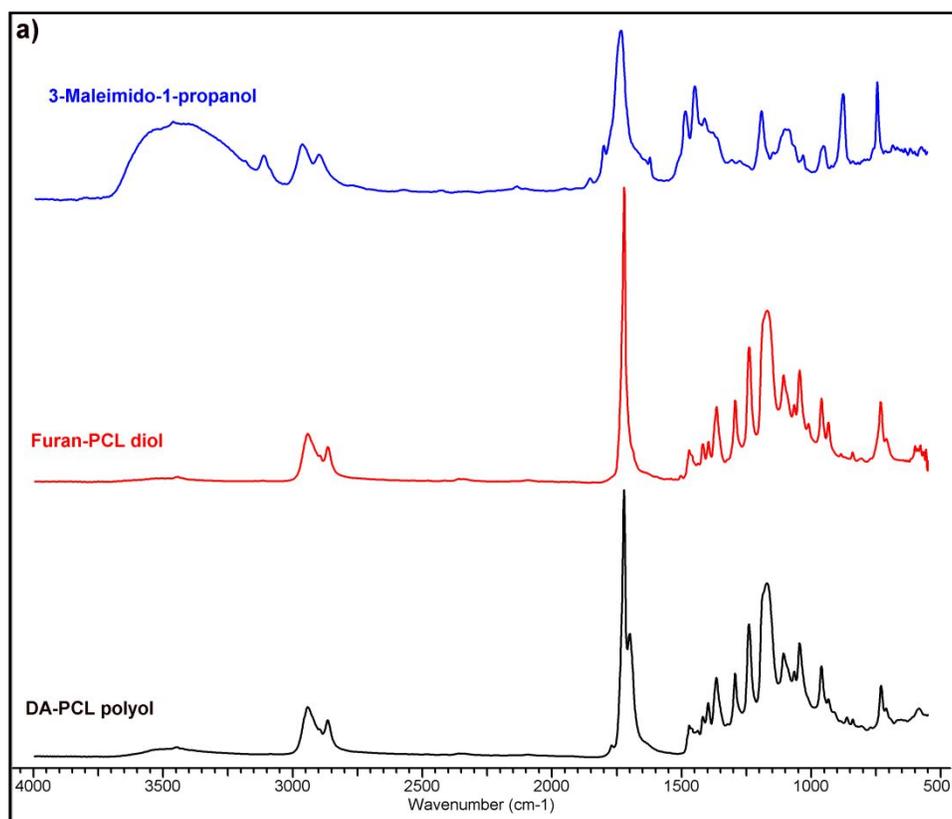


Figure S4. A comparison of the transmission FT-IR spectra of DA-PCL polyol, furan-PCL diol and 3-maleimido-1-propanol: a) full spectra; b) in the range of 1050-650 cm⁻¹.

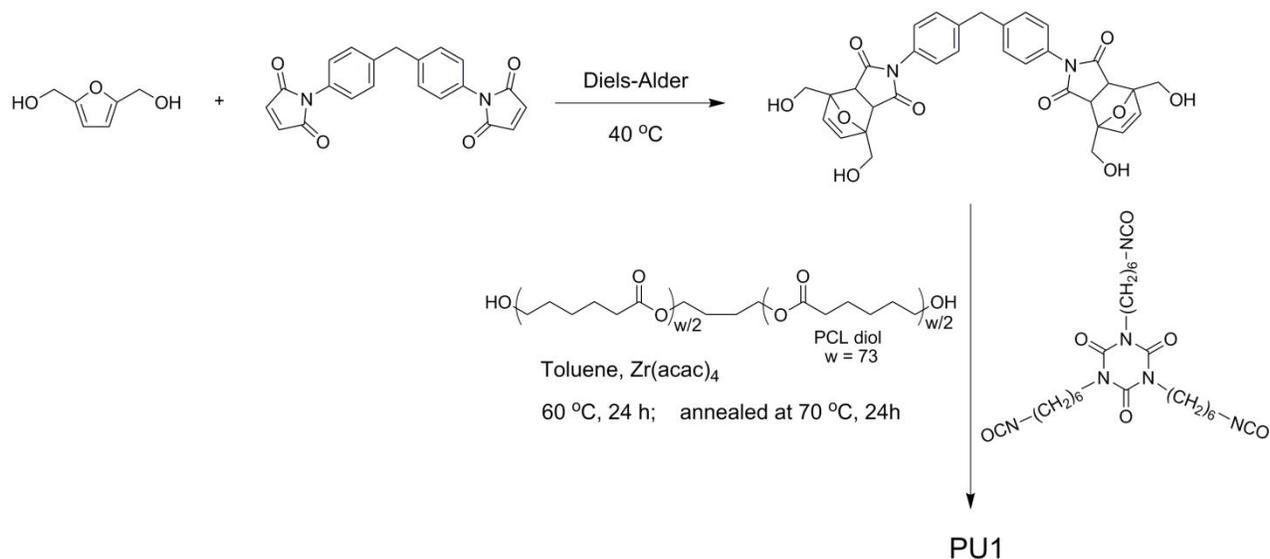
6. Polyurethane (PU) preparation and characterization

a) Synthesis of DA-PUs and ref-PU

All reactants and glasswork were previously dried. PCL (either PCL-diol, DA-PCL polyol or ref-PCL polyol, vacuum dried before use) was dissolved in toluene at 50 °C. The catalyst (zirconium acteylacetonate, 1 mol% with respect to the NCO groups) and the HDI-trimer were incorporated to initiate the polyurethane formation. The ratio of –NCO/–OH functional groups was fixed to 1.05 in all cases. Vacuum and stirring were maintained to avoid undesirable side reactions with water and to ensure a homogeneous system, until the liquid mixture was injected in molds. Samples were cured at 60 °C for 24 h. After opening the molds, the polyurethanes were washed by a Soxhlet extraction in acetone at 60 °C. The sample was dried and annealed at 70 °C for 24 h.

b) Synthesis of PU1

PU1 was synthesized following a previously reported procedure^[3] (Scheme S2). 1,1-(Methylenedi-4,1-phenylene)bismaleimide was first reacted with 2,5-bis-(hydroxymethyl)furan at a maleimide to furan molar ratio of 1 in tetrahydrofuran at 50 °C. The reaction conversion was ~ 96% after 24 h as indicated by ¹H NMR^[11]. The obtained DA adduct-tetraol was combined with PCL-diol to react with HDI-trimer to give PU1, using the PU preparation procedure previously reported.^[3]



Scheme S2. Synthesis of PU1.

c) Characterization of the prepared PUs

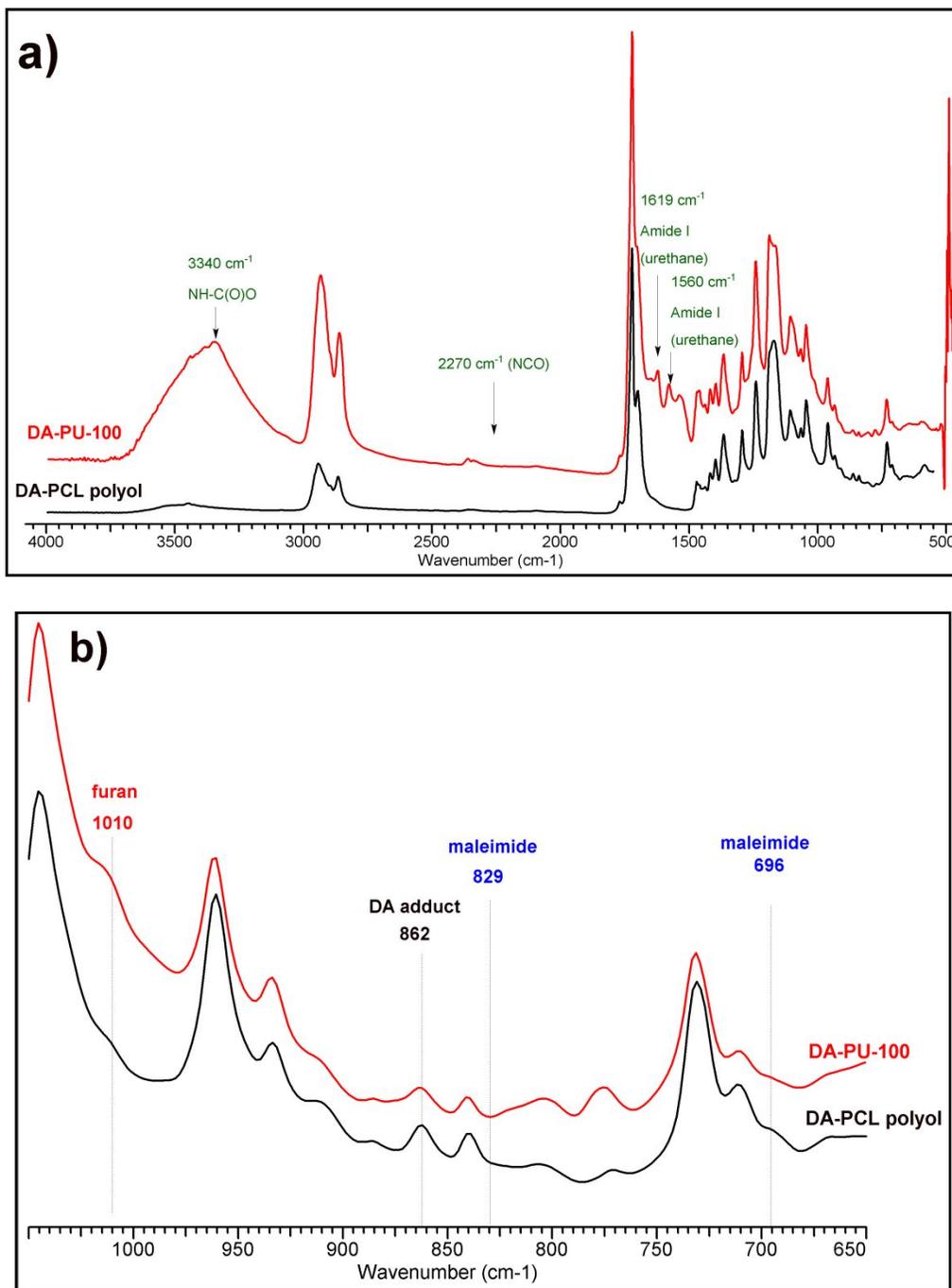


Figure S5. ATR FT-IR spectrum of **DA-PU-100**, in comparison with that of the corresponding precursor DA-PCL polyol: a) full spectra; b) in the range of 1050-650 cm^{-1} .

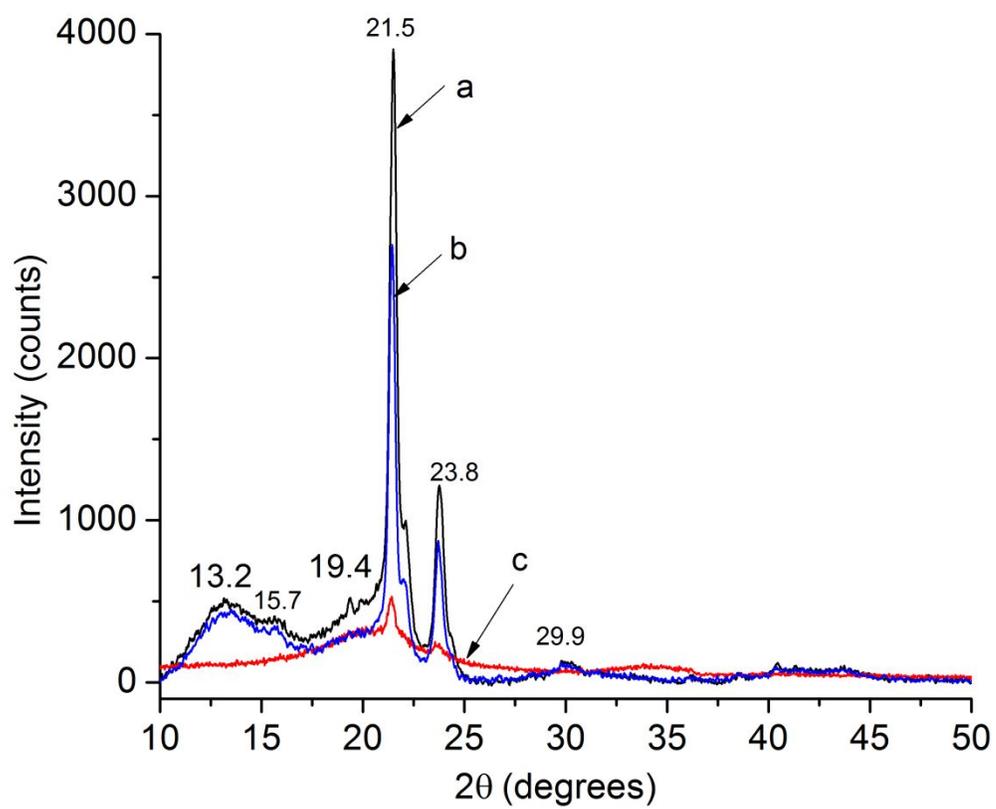


Figure S6. XRD patterns of PU1, DA-PU-70 and DA-PU-100 (a, b, and c, respectively)

7. Demonstration of PU shape-memory

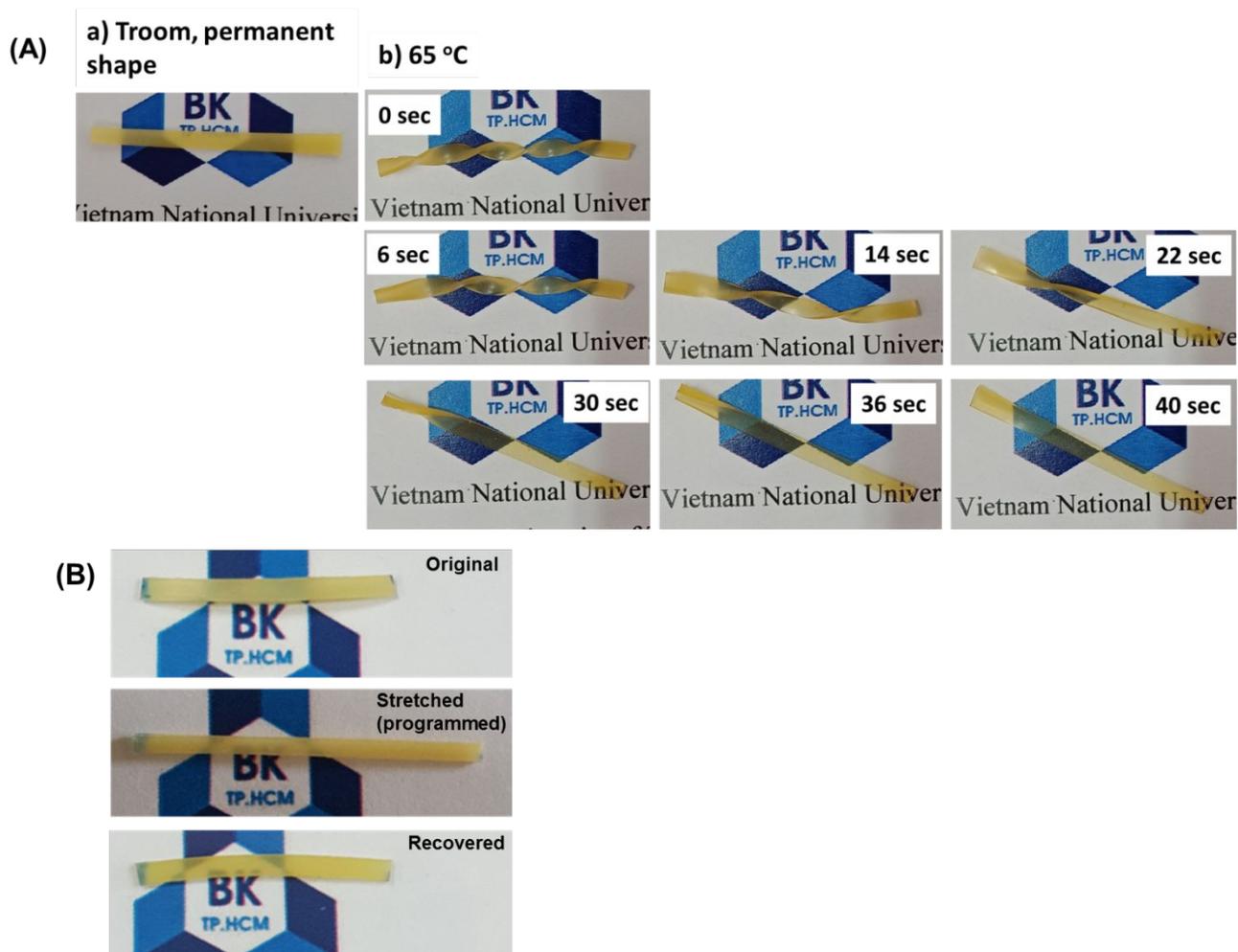


Figure S7. Demonstration of shape-memory behavior of the **DA-PU-70**. Temporary spirial (A) and stretched strip (B) shapes were programmed by twisted and stretched the samples at 75 °C, followed by cooling down to room temperature to fix the temporary shapes. The original permanent shape was recovered by heating the samples at 65 °C. The logo of Ho Chi Minh City University of Technology (HCMUT), Vietnam National University–Ho Chi Minh City (VNU-HCM), also named as Bach Khoa University, is used with permission from the HCMUT, VNU-HCM.

8. Healing assessment

8.1. Healing of scratches

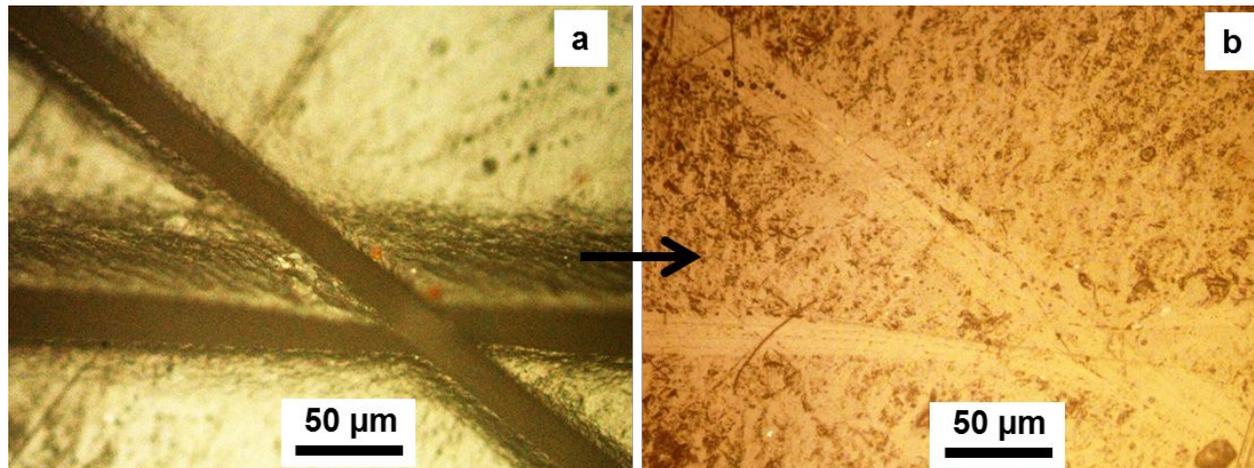


Figure S8. Optical microscopy (OM) images of a cut in sample **DA-PU-50** before (a) and after (b) healing at 65 °C for 24 h.

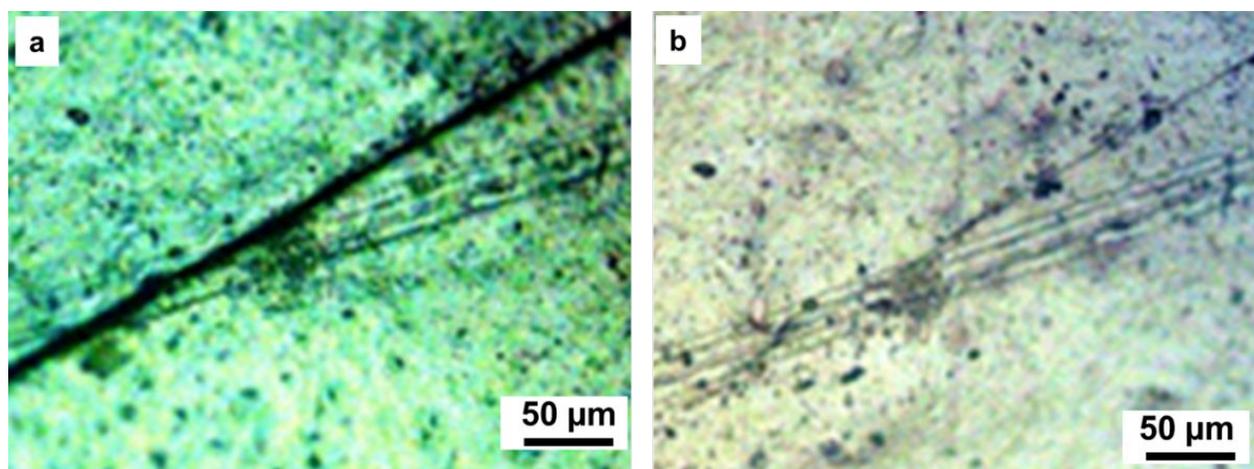


Figure S9. Optical microscopy (OM) images of a cut in sample **DA-PU-100** before (a) and after (b) healing at 65 °C for 24 h.

Table S1. Scratch widths observed by optical microscopy of PU materials before and after healing

Sample	Scratch width (μm)			
	Surface cut by a razor blade		Surface cut by a scalpel blade	
	Before healing	After healing	Before healing	After healing
DA-PU-100	4-5	~ 1	9-10	~ 1-2
DA-PU-85	12-13	~ 1-2	20-22	~ 1-2
DA-PU-70	13-14	~ 0	23-29	~ 0
DA-PU-50	15-16	~ 0	32-35	~ 0-1
Ref-PU	15-16	~ 4-5	30-33	~ 5-11

8.2. Healing of punctures

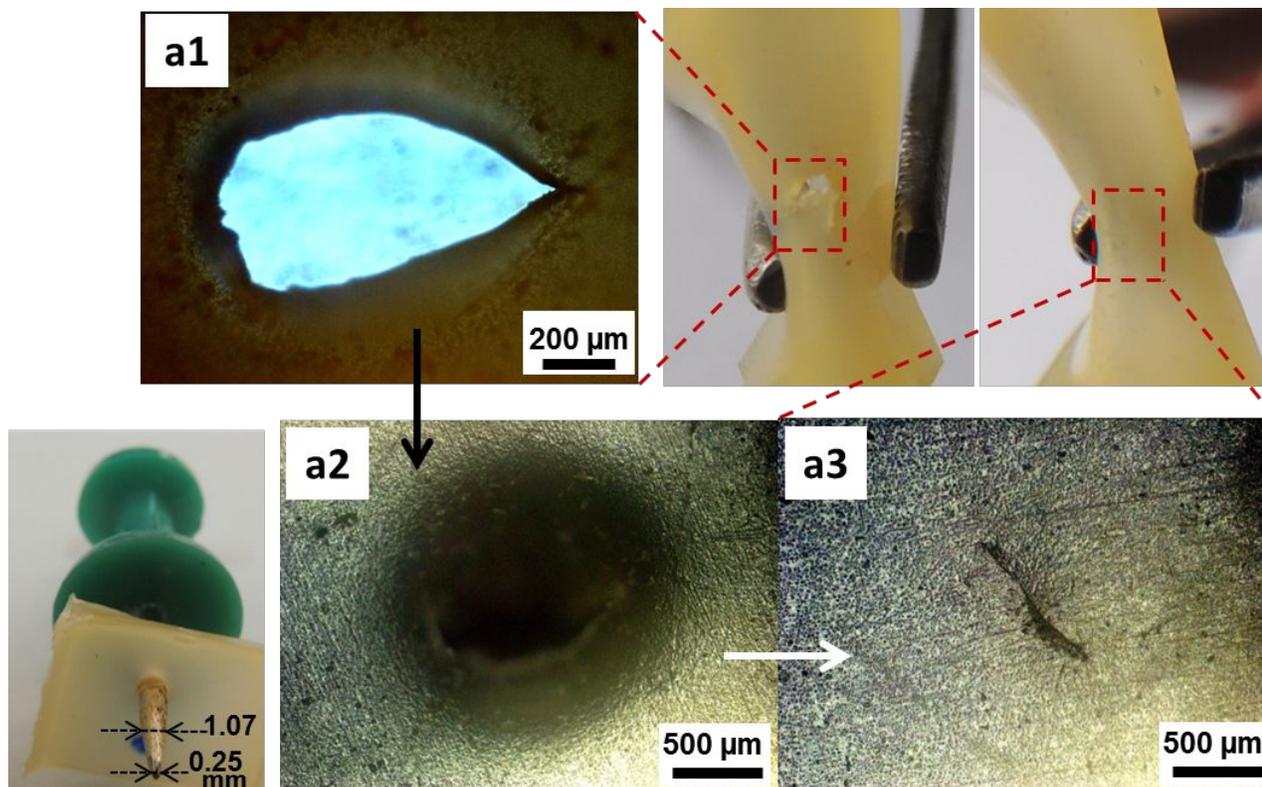


Figure S10. Optical microscopy (OM) images of a puncture by a paper pin on sample **DA-PU-50** before (a1) and after healing at 65 °C for 30 min (a2) and 24 h (a3). Corresponding photographs are also shown. The puncture is healed completely.

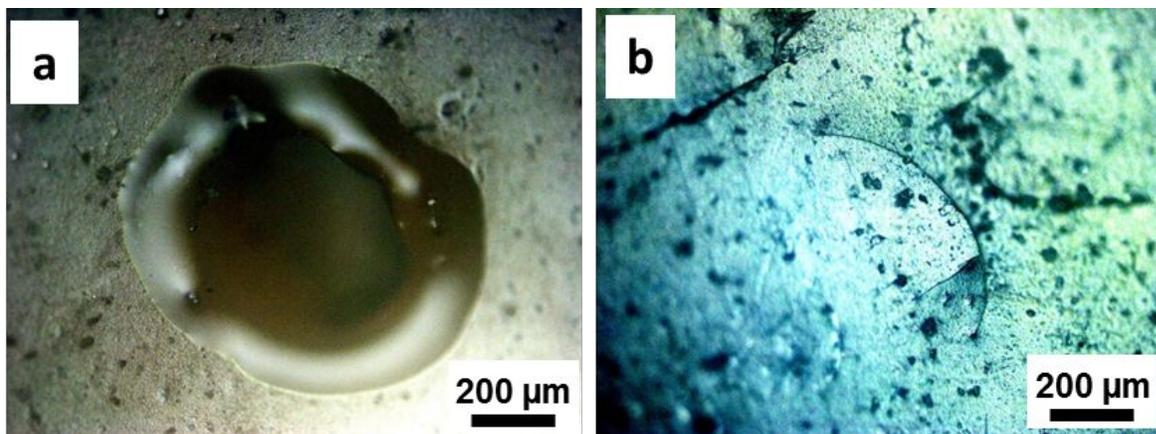


Figure S11. Optical microscopy (OM) images of a puncture by a paper pin on sample **DA-PU-85** before (a) and after (b) healing at 65 °C for 24 h. The puncture is closed but not completely healed.

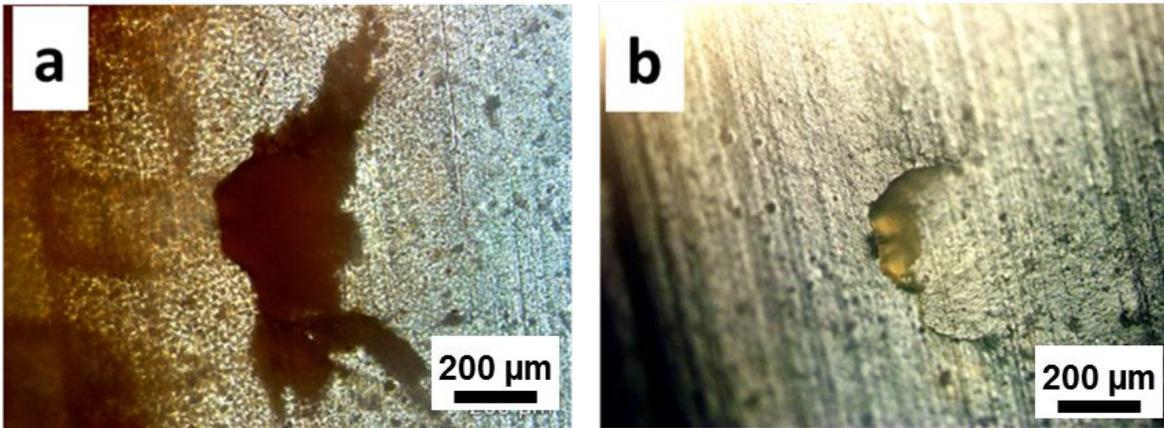


Figure S12. Optical microscopy (OM) images of a puncture by a paper pin on sample **DA-PU-100** before (a) and after (b) heating at 65 °C for 24 h. The puncture is closed but not completely healed.

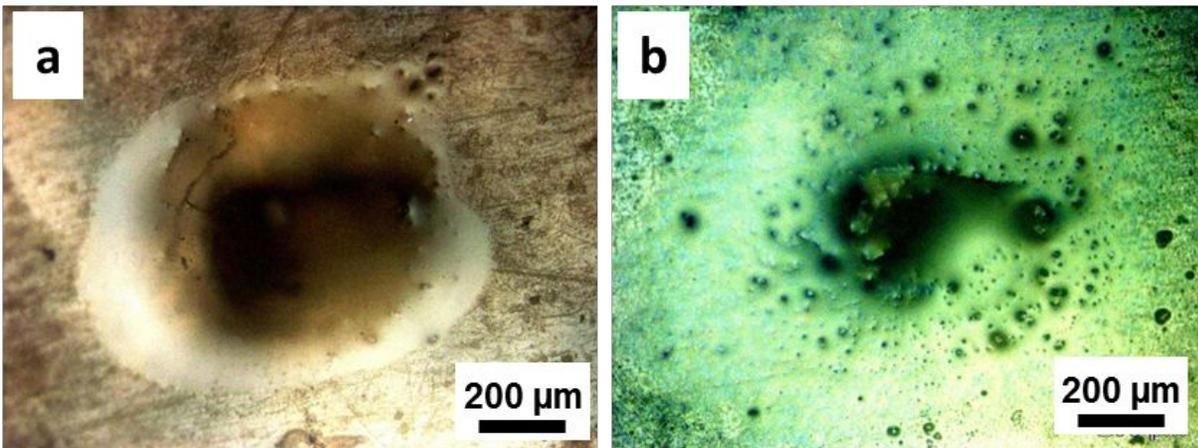


Figure S13. Optical microscopy (OM) images of a puncture by a paper pin on sample **ref-PU** before (a) and after (b) heating at 65 °C for 24 h. The puncture is closed but not healed.

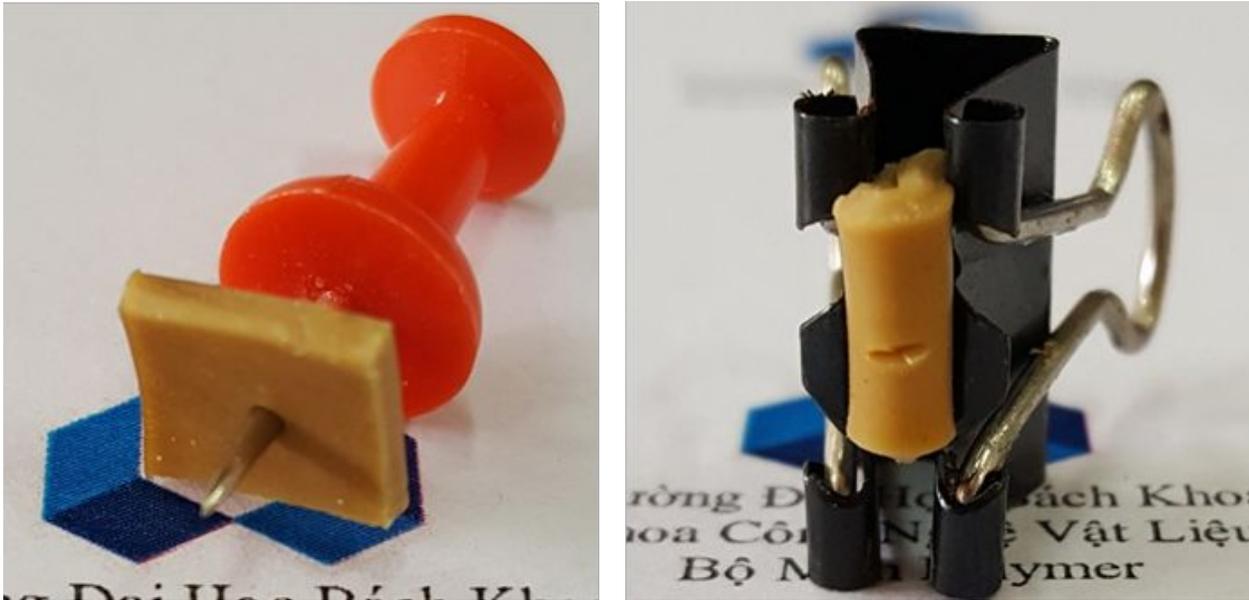


Figure S14. Photographs of a puncture by a paper pin on a cured natural rubber material before (left) and after (right) healing at 65 °C for 24 h. After thermal treatment, the sample was bended showing that the puncture is not healed. The logo of Ho Chi Minh City University of Technology (HCMUT), Vietnam National University–Ho Chi Minh City (VNU-HCM), also named as Bach Khoa University, is used with permission from the HCMUT, VNU-HCM.

8.4. Demonstration of healing movies

Movie S1 (high resolution):

http://www.mediafire.com/file/kd1cf2co22586n1/Movie_S1.mp4/file

Movie S2 (high resolution):

http://www.mediafire.com/file/zyff1f33byq1fi6/Movie_S2.mp4/file

8.5 Healing of cut-in-half and respliced samples

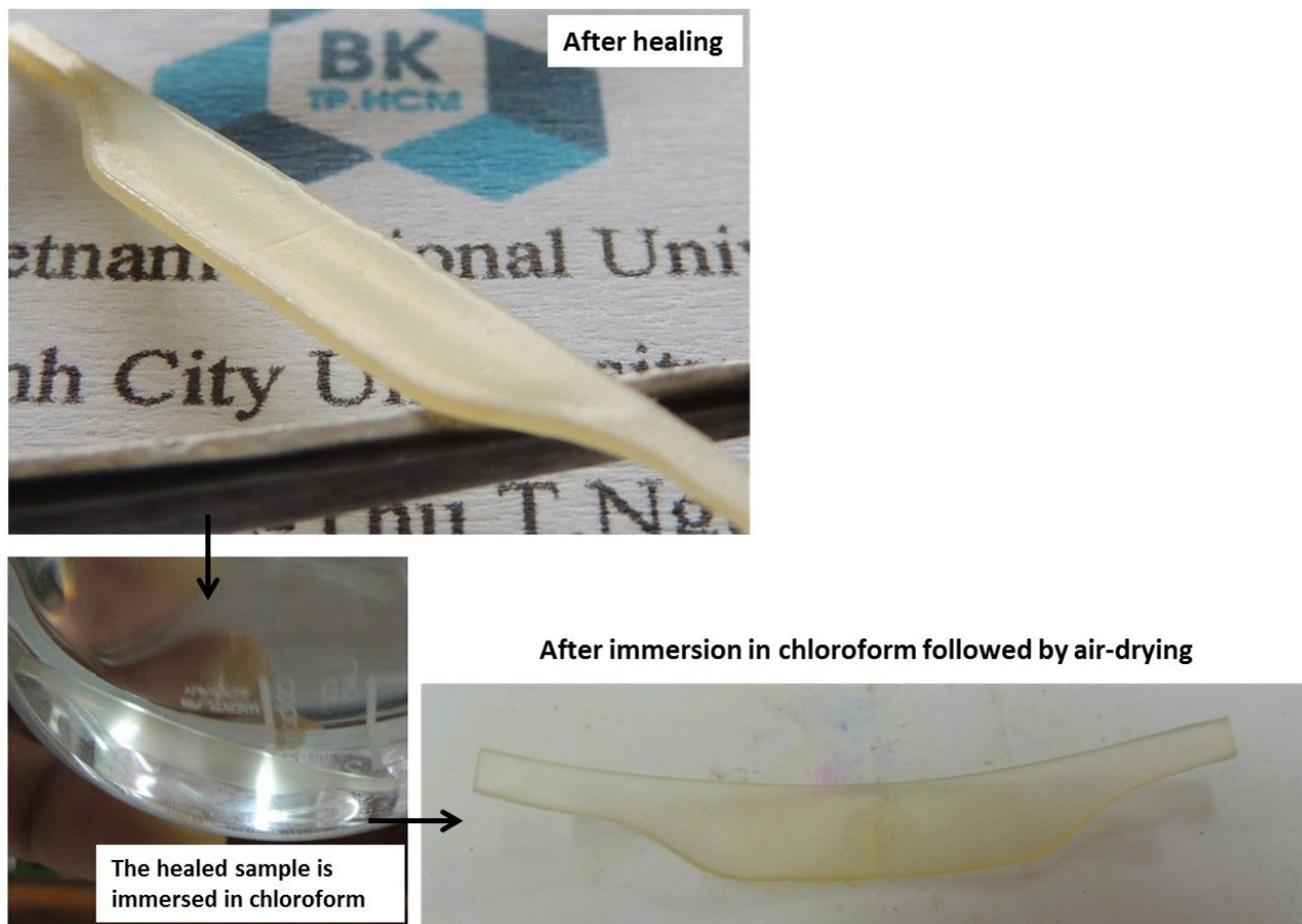
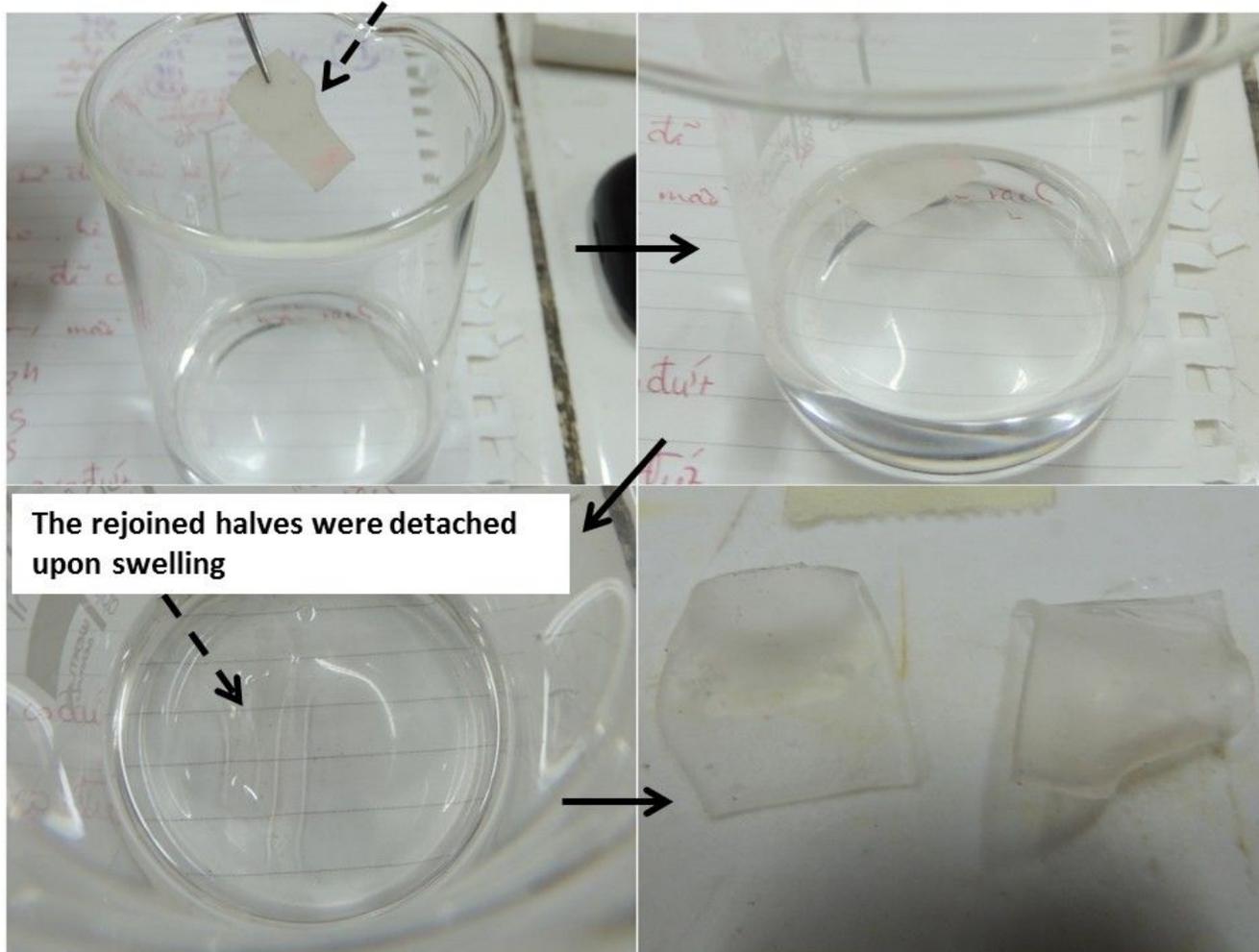


Figure S15. Swelling tests for the cut-in-half and rejoined films of **DA-PU-70** after healing at 65 °C for 24 h. The sample remains intact upon immersion in chloroform. The logo of Ho Chi Minh City University of Technology (HCMUT), Vietnam National University–Ho Chi Minh City (VNU-HCM), also named as Bach Khoa University, is used with permission from the HCMUT, VNU-HCM.

The rejoined sample is immersed in chloroform



The rejoined halves were detached upon swelling

Figure S16. Swelling tests for the cut-in-half and rejoined films of ref-PU after healing at 65 °C for 24 h. The rejoined halves were detached due to swelling upon immersion in chloroform.

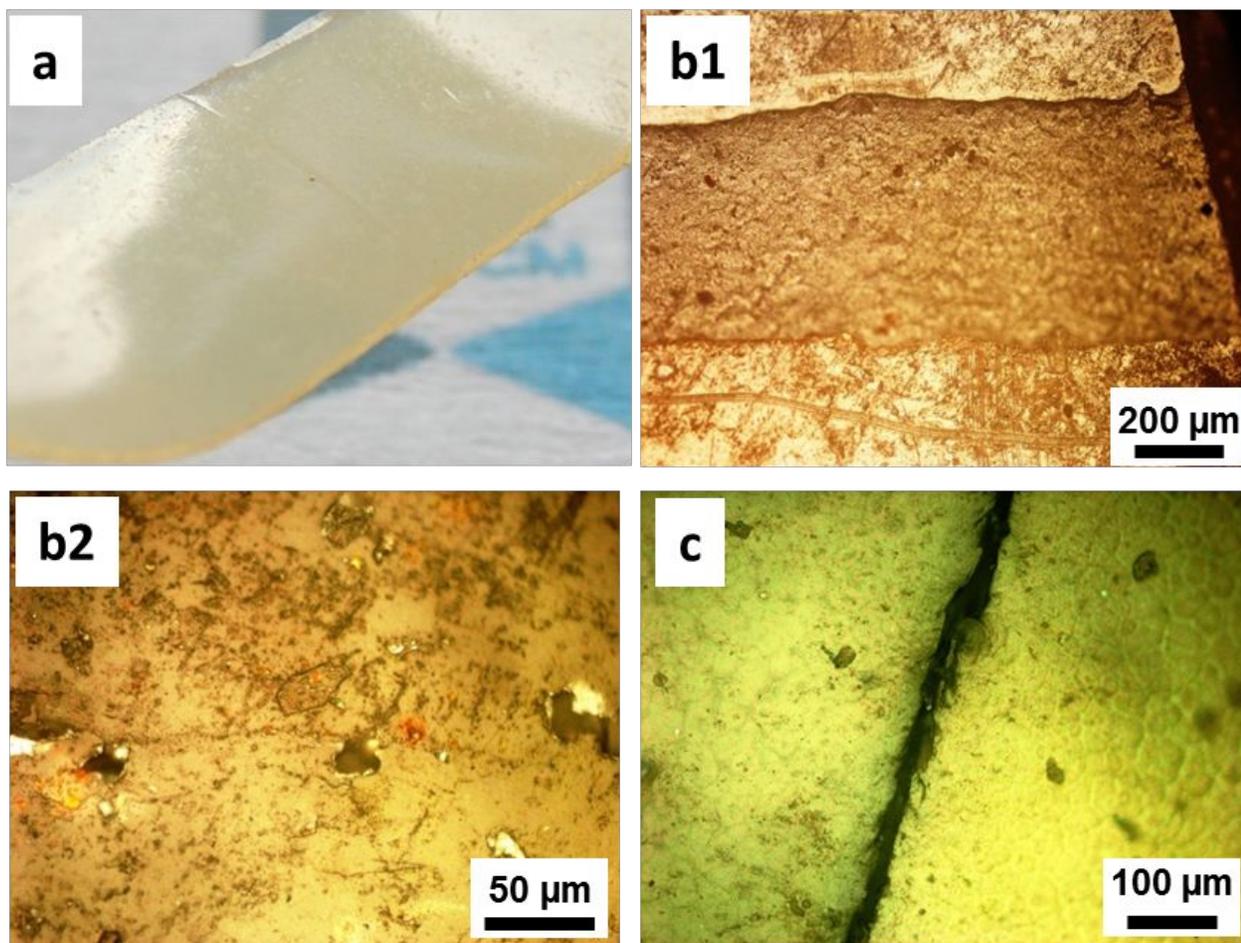


Figure S17. A photograph (a) and OM images of the upper (b1) and bottom (b2) sides of the cut-in-half and rejoined film of **DA-PU-50** after healing. For comparison, an OM image of the respliced film before thermal treatment is shown (c). The logo of Ho Chi Minh City University of Technology (HCMUT), Vietnam National University–Ho Chi Minh City (VNU-HCM), also named as Bach Khoa University, is used with permission from the HCMUT, VNU-HCM.

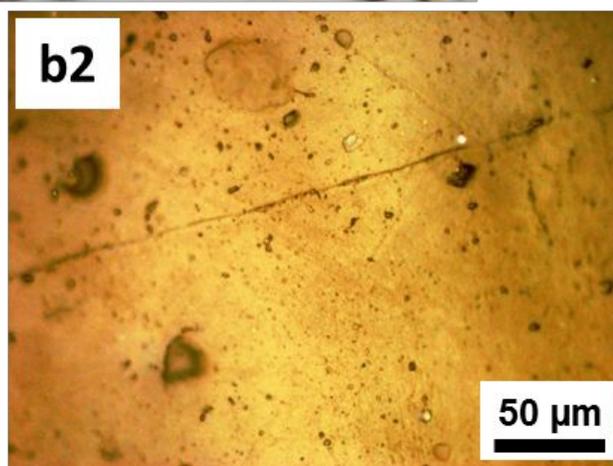
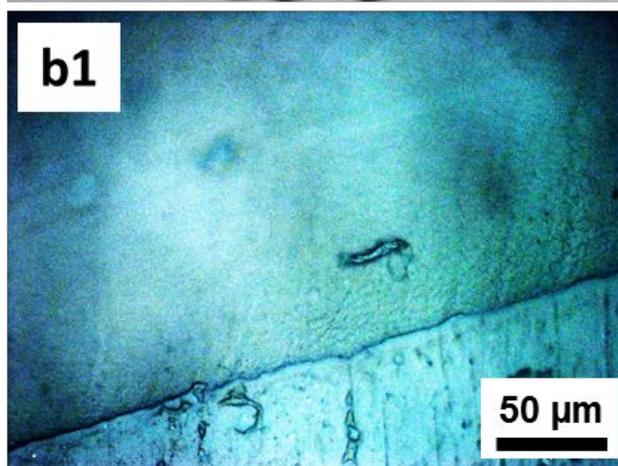
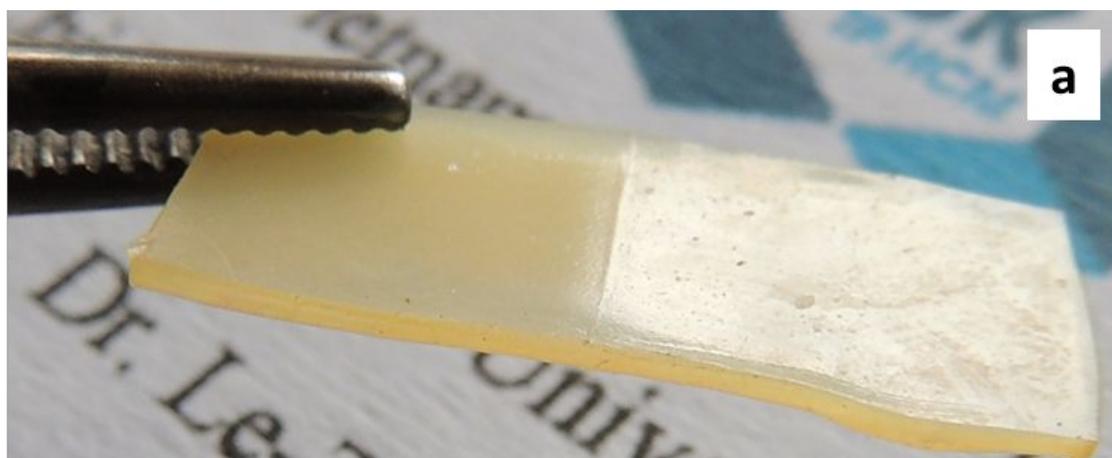


Figure S18. A photograph (a) and OM images of the upper (b1) and bottom (b2) sides of the cut-in-half and rejoined film of **DA-PU-85** after healing. The logo of Ho Chi Minh City University of Technology (HCMUT), Vietnam National University–Ho Chi Minh City (VNU-HCM), also named as Bach Khoa University, is used with permission from the HCMUT, VNU-HCM.

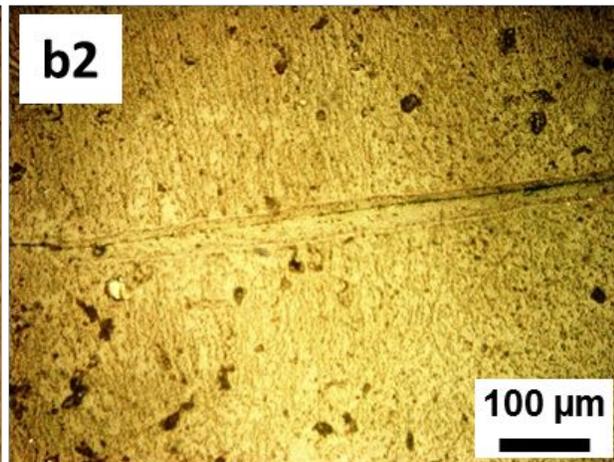
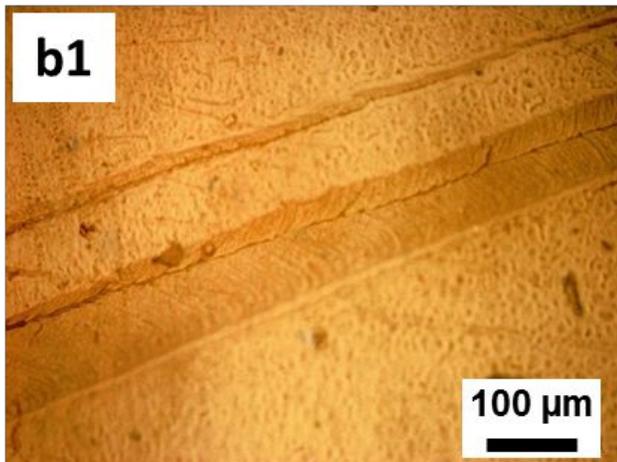


Figure S19. A photograph (a) and OM images of the upper (b1) and bottom (b2) sides of the cut-in-half and rejoined film of **DA-PU-100** after healing. The logo of Ho Chi Minh City University of Technology (HCMUT), Vietnam National University–Ho Chi Minh City (VNU-HCM), also named as Bach Khoa University, is used with permission from the HCMUT, VNU-HCM.

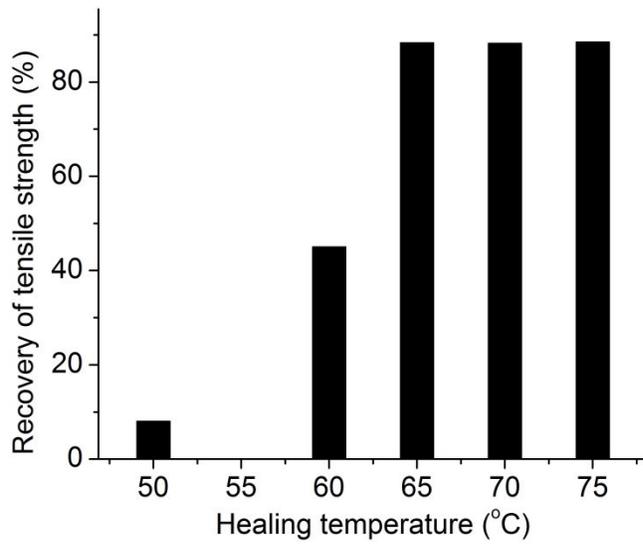


Figure S20. A comparison of the strength recoveries at varying mild healing temperatures for DA-PU-70. The samples were cut-in-half and respliced, followed by keeping in an oven at the investigated healing temperature for 24 h.

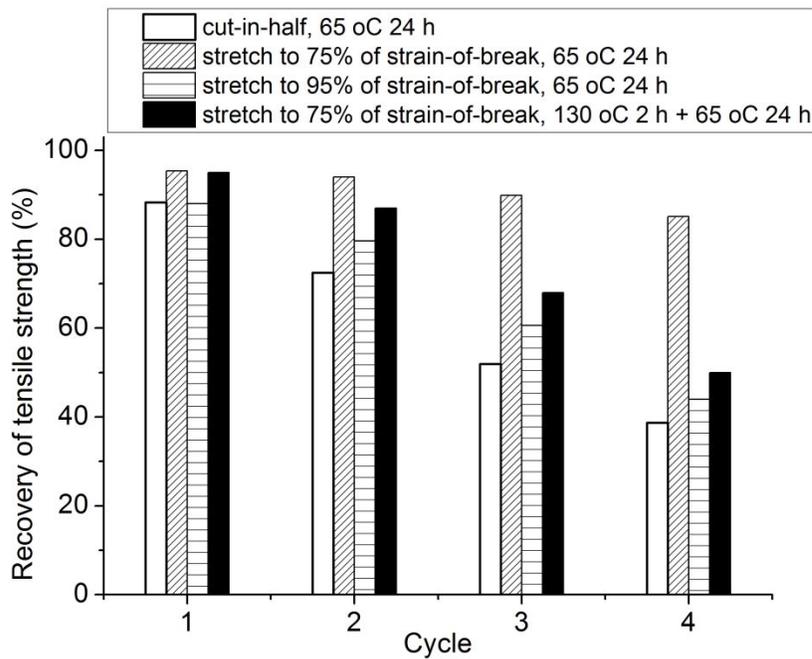


Figure S21. A comparison of the strength recoveries of DA-PU-70 at varying damage and healing programs.

8.6. EIS spectra

a) Three-electrode measurements of DA-PU films coated on stainless steel

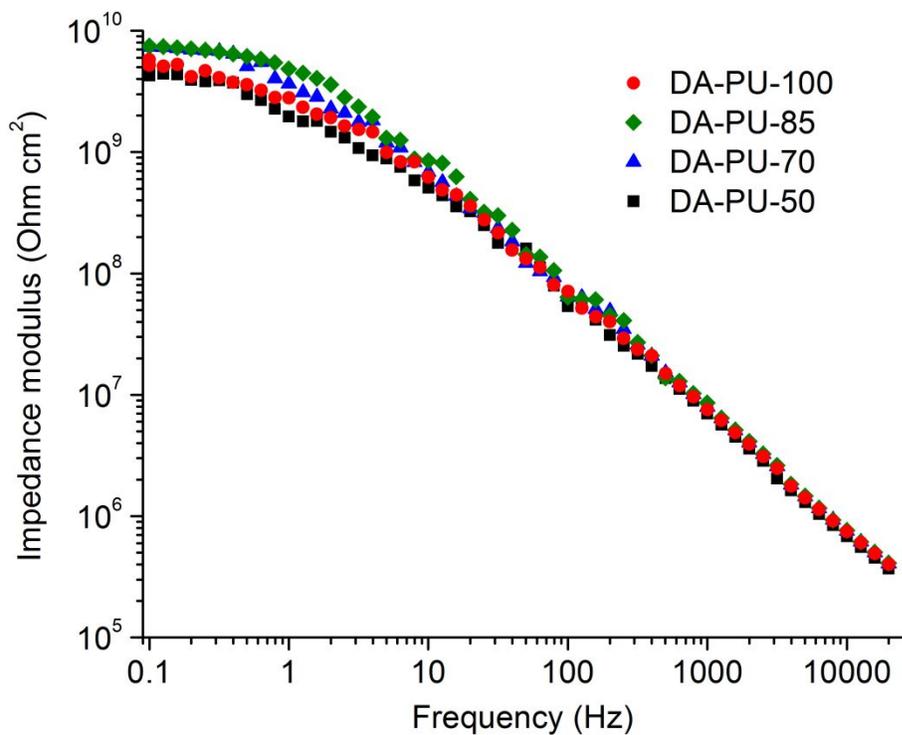


Figure S22. Bode plots of DA-PU films coated on stainless steel

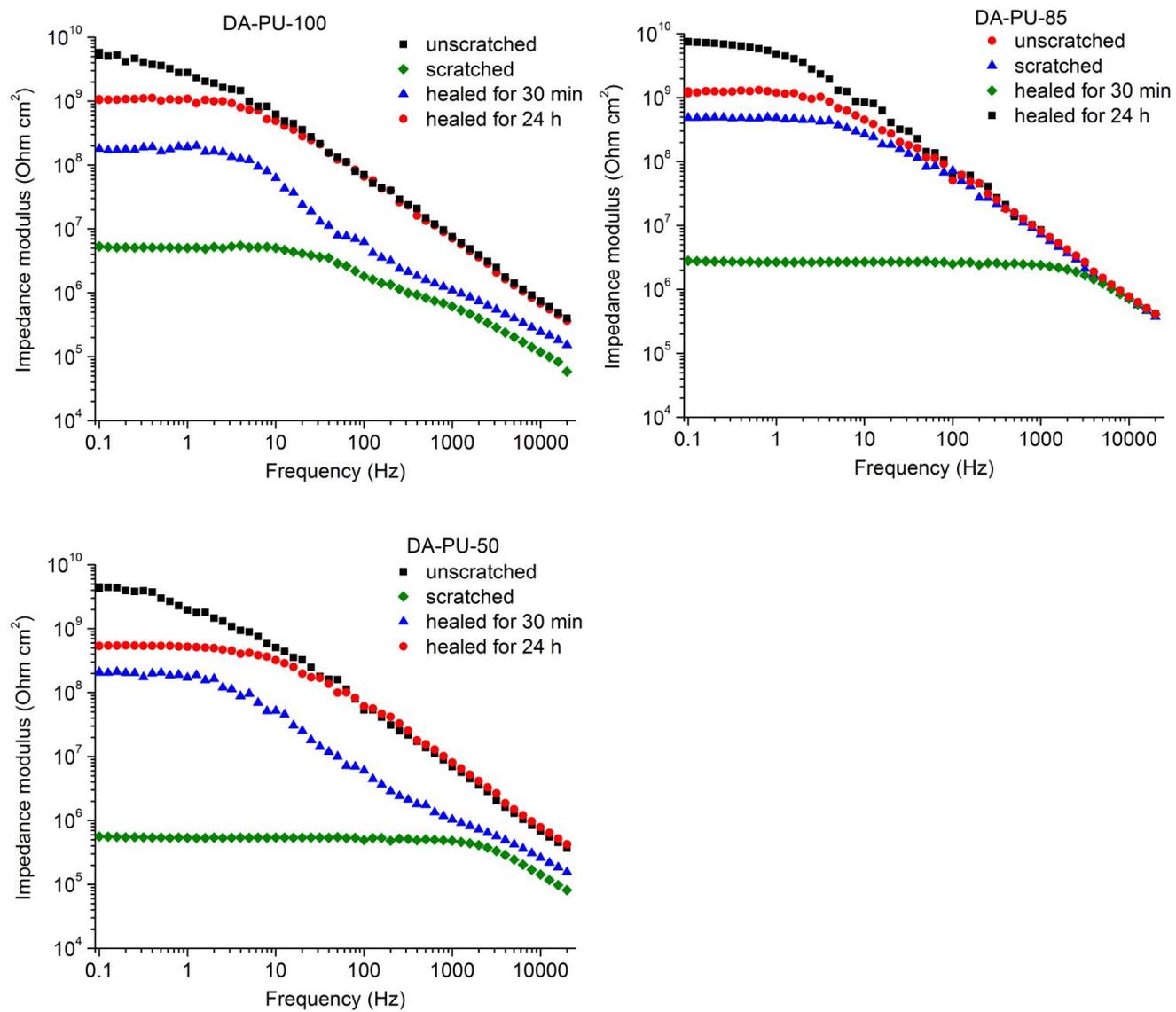


Figure S23. Bode plots of coated DA-PU films before and after scratching and the scratched coatings after healing at 65 °C for 30 min and 24 h.

b) Two-electrode EIS measurements of free-standing DA-PU films:

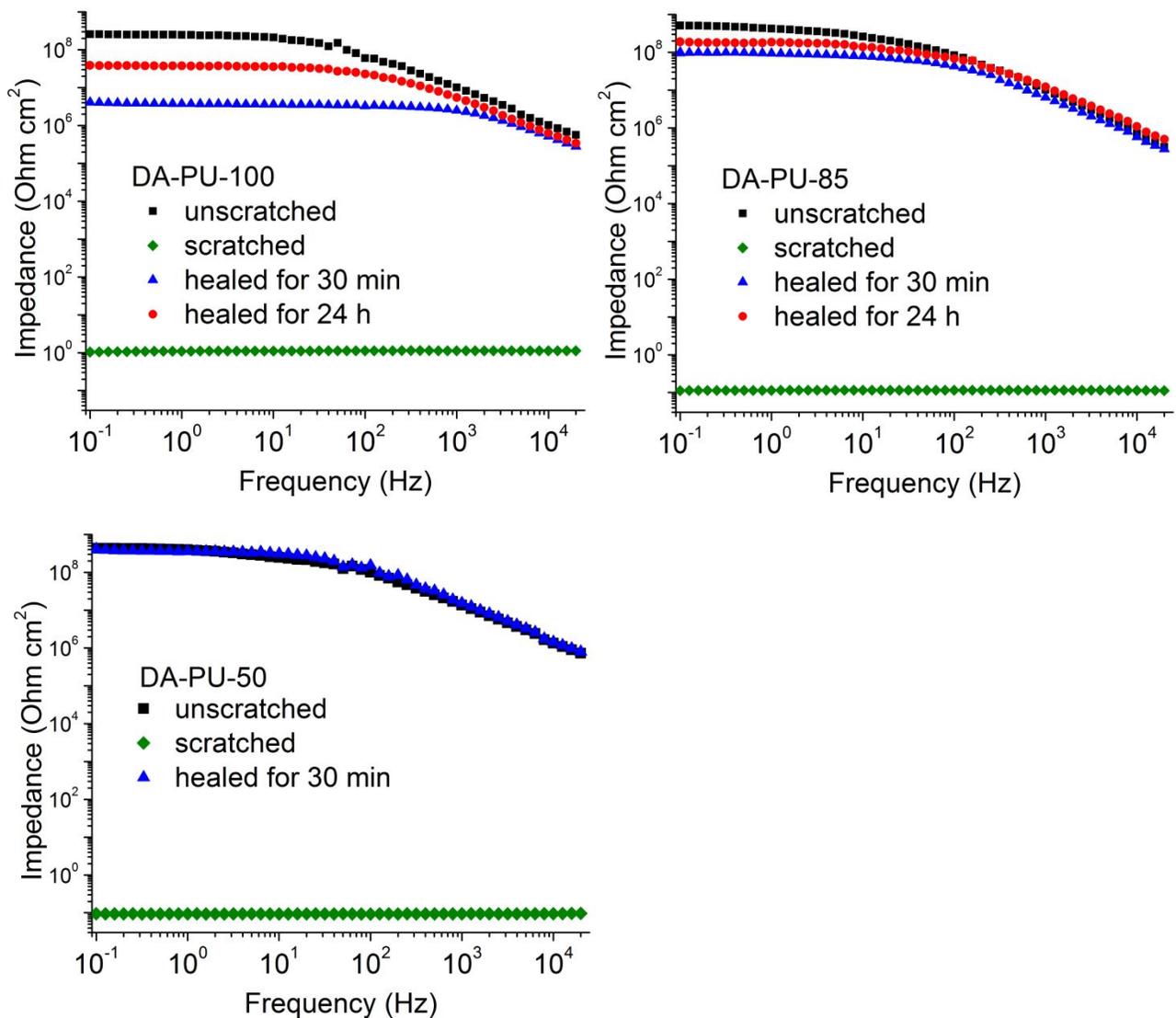


Figure S24. Bode plots of free-standing DA-PU films before and after scratching and the scratched coatings after healing at 65 °C for 30 min and 24 h.

9. Comparison of tensile properties and healing efficiencies of various DA-based healing polyurethanes reported and in this work

Table S2. Estimated ultimate tensile strength, Young's modulus, elongation at break, toughness, and recovery tests of various DA-based healing polyurethanes

Healing motif	Ultimate tensile strength [MPa]	Young's modulus [MPa]	Ultimate tensile strain (%)	Toughness [MJ m ⁻³]	Healing temperature, time	Healing efficiency	Type of damage/Method used to evaluate healing efficiency	Ref.
Healing at mild temperatures (50–70 oC)								
DA at the hard/soft phase interface DA-PU-70	25.4	215.9	344	65	65 °C for 24 h	100%	Scratching by razor blade/Optical microscopy to evaluate the scratch width	This study
						88%	Cut-in-half and respliced sample/ Recovery of tensile strength	
						95%	Elongated deformation/ Recovery of tensile strength	
DA at the hard/soft phase interface DA-PU-50	30.5	226.8	445	96	65 °C for 24 h	100%	Scratching by razor blade/Optical microscopy	This study
						70%	Cut-in-half and respliced sample/Recovery of tensile strength	
						70%	Elongated deformation /Recovery of tensile strength	
DA in the hard phase	33	81	264	-	50°C for 1-7 days	100%	Microscratching by a universal nanomechanical tester	[3]
						>100%	Elongated deformation /Recovery of tensile strength and modulus	
						No healing of complete cuts		
DA in the hard phase	27.1	347.9	19.1	-	60 °C for 3 days	80%	A crack made on the tested film/Recovery of tensile strength	[1]
						No healing of		

						complete cuts		
DA in the hard phase (PU with low mechanical properties)	1.47	28.7	9		60 °C for 24 h	70%	Scratched film/ recovery of tensile strength	[4]
						No healing of complete cuts		

Healing at high temperature (≥ 110 °C)

DA in the hard phase	76.8-87.8	2370-2570	30.5-5.4	-	Multi-step heating (135-70 °C in total 9.5 h): +Heated to 135 °C over 2.5 h +135 °C for 2 h +Cooled to 90 °C over 1 h +90 °C for 1 h +Cooled to 70 °C over 1h +70 °C for 2 h	80-85%	Compact tension test/recovery of failure load	[5]
DA in the hard phase	6.5	4.53	444	-	120 °C for 15 min, followed by 60 °C for 24 h	80%	A crack made on the tested film/Recovery of tensile strength	[6]
DA in the hard phase	46.5	-	250	-	130 °C for 5 min (no healing at 120 °C)	92%	A crack made on the tested film/Recovery of tensile strength	[7]
DA in the hard phase	22-15	-	40-45	-	120 °C for 20 min, followed by 60 °C for 48 h	80-60%	A crack made on the tested film/Recovery of tensile strength	[8]
DA in the hard phase (silver nanowire-PU electrode)	-	-	-	-	Intense pulsed light irradiation to quickly increase the temperature of Ag nanowires to above 100 °C	-	Recovery of conductivity of silver nanowire-PU electrode	[9]
DA in the hard phase (silver nanowire-PU electrode)	-	-	-	-	Heat treatment at 120 °C triggered by electrical power	-	Scratching by a knife cut/observation of the damage by FE-SEM	[10]
DA in the hard phase	22	-	140	-	100-110 °C for 30 min, followed by 30 °C for 24 h	79%	A crack made on the tested film/Recovery of tensile strength	[11]

h							
DA in the hard phase	~ 50	-	300	-	130-180 °C	-	Demonstration of remendability by solubility (at 130 °C in dimethylacetamide) and re-processing (hot compression molding at 160-180 °C for 5-20 min) tests [12]
DA in the hard phase	26.3	-	250	-	130 °C for 10 min, followed by 60 °C for 1 h	69%	Cut-in-half and respliced sample/ Recovery of tensile strength [13]
DA in the hard phase	23.6-28.0	208-292			Ultrasound for 60 min (with an equilibrium sample temperature of 90 °C)	92%	Partially cut sample/Recovery of tensile strength [14]
DA in the hard phase	25	239	138	-	140 °C for 20 min	~100%	Microscratching/ recovery measured by diamond-tip profilometry [15]
					130 °C for 30 min, followed by 50 °C for 24 h	68%	Cut-in-half and respliced sample/ Recovery of tensile strength
DA in the hard phase	-	-	-	-	Multi-step heating (140-70 oC in total 9.5 h): +Heated to 140 °C over 2.5 h +140 oC for 2 h +Cooled to 90 °C over 1 h +90 °C for 2 h +Cooled to 70 oC over 1h +70 oC for 2 h	80%	Compact tension test/recovery of failure load [16]
DA in the hard phase (Polyurethane/polyd opamine composites)	16.3-22.6	216-247	1320-1386		+Ultrafast near-infrared light treatment for 60 s (the temperatures of irradiated PU composites are 100-150 °C) +Thermal healing:	96%	Cut-in-half and respliced sample/ Recovery of tensile strength [17]

					110 °C for 1 h, followed by 80 °C for	76%		
Triazolinedione-indole DA in the hard phase	8.9-18.6	199-48	40-429	-	120 °C for 30 min	~70%	Cut-in-half and respliced sample/ Recovery of tensile strength	[18]

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