Supporting Information

High strength and rapid self-healing daidzein-based polyhydroxyurethanes for high temperature-resistant adhesives

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Total number of pages: 16 (S1-S16)

Total number of figures: 18 (Figure S1-Figure S18)

Total number of tables: 5 (Table S1-Table S5)

1. Synthetic Procedures

1.1 Characterization and measurements

The DZ-PHUs were characterized by Fourier transform infrared (FTIR), which was measured on a Thermo Nicolet 20DXB spectrometer in attenuated total reflection mode. The spectra were collected through 32 scans with a spectral resolution of 2 cm^{-1} for a spectral range from 400 to 4000 cm^{-1}. Hydrogen nuclear magnetic resonance (^{1}H NMR) and carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance II 400 MHz and Varian DLG 400 MHz NMR spectrometer. Mass spectrometric (MS) data was carried out using LTQ Orbit rap XL instruments. Gel fractions were obtained by swelling DZ-PHUs (m_0, 50-100 mg) in DMF (10 mL) for at least 48 hours, then removing the swollen DZ-PHUs and drying to constant weight by heating at 80°C under 20 mTorr vacuum, typically for 48 h, and the final mass measured (m_1). Thermogravimetric analysis (TGA) was performed on TA Q500 thermogravimetric instrument. Samples were heated under a nitrogen atmosphere at a rate of 10°C/min from 40 to 800°C. $T_{5\%}$, 5% mass loss of samples, were determined by TGA. Differential scanning calorimetry (DSC) was performed on a TA instrument Q2000 Differential Scanning Calorimeter. Samples were heated at a rate of 10°C/min from room temperature to 150°C to erase thermal history, cooled to -150°C at 10°C/min, and then heated to 150°C at 10°C/min. Dynamic mechanical thermal analysis (DMTA) was performed on TA-Q800 DMA Instrument using dog-bone-shaped samples (T×W×L=0.5 mm × 2 mm × 35 mm and a gauge length of 12.5 mm). The strain amplitude and frequency were fixed at 0.1% and 1 Hz, respectively. The temperature was varied from -20 to 120°C, and the temperature rise rate was 3°C/min. The mechanical properties were measured on a universal testing machine (Instron 5567AR265) using dog-bone-shaped samples (T×W×L=0.5 mm × 2 mm × 35 mm and a gauge length of 12.5 mm). The stress-strain experiments were carried out at a rate of 5 mm/min at room temperature. Reported values are the averages and standard deviations of at least five replicates. The samples were aged for 2 h at 150°C in oven before testing. Stress relaxation analysis (SRA) was performed on TA-Q800 DMA Instrument using dog-bone-shaped samples (T×W×L=0.5 mm × 2 mm × 35 mm and a gauge length of 12.5 mm). The transducer was set to controlled force mode at a specified temperature (130-160°C). The stress decay was monitored until the stress relaxation modulus had relaxed to at least 37% (1/e) of its initial value. The time for the sample to relax stress to 1/e of the initial stress is defined as the relaxation time (τ) according to the Maxwell model. This was performed three times for each sample. The activation energy (E_a) was determined using the methodology in the literature[1]. Contact angle measurements of DZ-PHUs were performed on the JCD2000D2W apparatus in the sessile drop configuration by deposition of a 5 μL droplet of Milli-Q water. The mean contact angle values were determined from at least 6 measurements realized at different locations of the sample surface.

The self-healing efficiency was calculated using the following equation:

$$Self\ healing\ efficiency = \frac{Stress_{self-healing}}{Stress_{initial}}$$

Reprocessed procedure: To reprocess the materials, the networks were clipped into small pieces, and placed into a mold (T×W×L=0.5 mm × 2 mm × 35 mm) between two tetrafluoro flakes. This material was placed in a PHI 30-ton manual press preheated to the desired temperature (140°C) and allowed to thermally equilibrate for 10 minutes. The material was compressed at 3 MPa of pressure for 1 h, and cut into strips for tensile strength analysis.

Chemical recycling process of DZ-PHUs: To study the chemical recyclability of DZ-PHUs, 3 g of shredded samples and 60 mL of anhydrous ethanol were added to an autoclave. Then, the reaction continued for 24 h after the temperature increased to 140 °C. The degraded mixture was filtered, and the filter residue was weighed after drying. The filtered liquor was concentrated by distillation, and the resulting viscous liquid was poured into a PTFE mold. After curing in an oven at 150 °C for 24 h, a new film was obtained and subjected to a tensile test.

The degradation degree (Dd) can be calculated according to equation:

$$degradation\ degree(\%) = \left(1 - \frac{W_1}{W_0}\right) \times 100\%$$

where W_1 is the mass of the insoluble film after degradation, and W_0 is the initial mass of the film before degradation.

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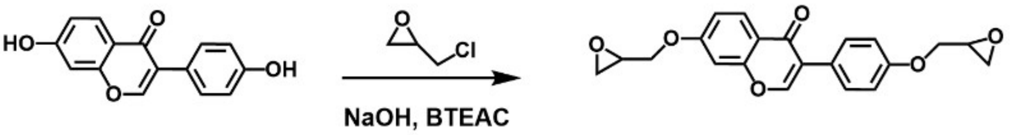
Application of adhesives: The adhesives performance of DZ-PHUs adhesives was studied by the lap shear strength according to the ASTM D1002 standard. Woods and glasses were selected as the bonding plates. 0.1 g DZ-PHUs adhesives were placed between two plates with an overlap area of 25 mm ×12.5 mm. Then these single lap shear joints were hot-pressed under a pressure of 0.5 MPa at 160°C for 1 h. After hot-pressing, the samples were cooled to room temperature for 12 h. The materials were immersed in water at 20°C and 60°C for 24 hours, and then the surfaces were wiped and conducted in tensile shear tests. The lap shear strength was tested using a universal testing machine (Instron 5567AR265) at a rate of 10 mm/min at room temperature with a load cell of 30 kN.

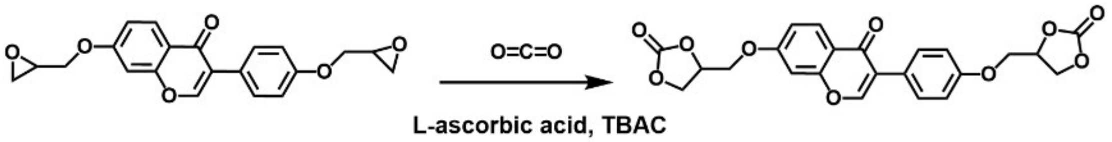
1.2 Synthesis of daidzein-based five-membered cyclic carbonate (DZ-BCC).

Scheme S1. Synthesis of diglycidyl ether of daidzein (DZ-EP).



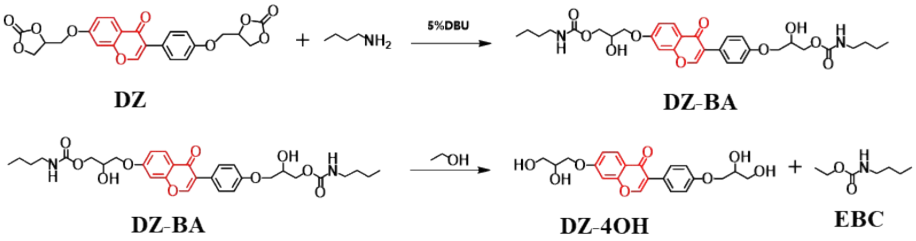
The DZ-EP was prepared according to the literature[2] with some modifications. Daidzein (50 g, 0.197mol) was dissolved in epichlorohydrin (182.3g, 1.97mol) with benzyltriethylammonium chloride (4.48g, 0.0197mol) under stirring at 100℃ for 2 h. After stirring, the mixture was cooled down to room temperature. 40 wt% aqueous sodium hydroxide solution (38.75mL, 0.493mol) was added dropwise into the flask and further reacted for another 2 h. Finally, the mixture was washed with deionized water three times. The organic phase was dried by anhydrous $MgSO_4$ and concentrated in vacuum to remove residual epichlorohydrin. The obtained white solid product DZ-EP was dried at 60°C for 24 h in a vacuum oven. Yield: (67g, 93%). The structure of the product was determined by ^{1}H NMR, and the spectrum was presented in Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 8.22 (d, 2H), 7.92 (s, 1H), 7.50 (d, 2H), 6.99 (m, 3H), 6.88 (s, 1H), 4.36 (d, 1H), 4.24 (d, 1H), 4.00 (m, 2H), 3.38 (m, 2H), 2.93 (m, 2H), 2.78 (m, 2H).

Scheme S2. Synthesis of DZ-BCC.



DZ-BCC was prepared according to the literature[3] with some modifications. DZ-EP (17g, 460 mmol), TBAC (1.032g, 3.714 mmol) and L-ascorbic acid (0.327g, 1.857 mmol) were dissolved in N-Methylpyrrolidone (170 mL). The mixture was charged into a 250 mL pressure reactor. The reactor was immediately sealed and CO_2 was introduced at an initial pressure of 2 MPa. The reaction was carried out at 80°C for 48 h with stirring. A dark green solution was obtained after CO_2 in the reactor was slowly released. The solution was poured into deionized water, and collected the precipitate. The product was washed with deionized water three times, and dried in freeze-drying process to collect pure DZ-BCC with a white solid. Yield:19.2g (91%). The structure of the product was determined by ^{1}H NMR, and spectrum was presented in Figure S2. ^{1}H NMR (400 MHz, DMSO-d6, δ in ppm): 8.46 (s, 1H), 8.05 (d, 1H), 7.54 (d,2H), 7.24 (s, 1H), 7.13 (d, 2H), 7.05 (d, 2H), 5.19 (m, 2H), 4.65 (dd, 2H), 4.28-4.47 (m, 6H).

1.3 Model reaction.



Model compound (DZ-BA): By mixing DZ-BCC (1 eq), butylamine (3 eq), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 0.05 eq), and anhydrous DMF (0.5 M) in a round bottom flask at 80°C overnight, a colorless and transparent solution was obtained. The solution was concentrated under reduced pressure. The crude material was dissolved in a suitable amount of CH_2Cl_2 and filtered through a column chromatography, eluting with ethyl acetate. The filtrate was then concentrated using a rotary evaporator.

Degradation of DZ-BA: By mixing DZ-BA and ethanol in a 100 mL pressure reactor at 140°C for 12 h, a degraded solution was obtained. The excess ethanol was removed by rotary evaporation. The crude material was dissolved in a suitable amount of CH_2Cl_2 and filtered through a column chromatography (gradient 100% ethyl acetate to 100:1 ethyl acetate/methanol). The filtrate was then concentrated using a rotary evaporator to obtain DZ-4OH and EBC.

1.4 Equation

Equation S1:

$$\upsilon_e = E^{'}/3RT \tag{1}$$

where E', R and T represent the storage modulus at T_g + 50°C (T_g is the glass transition temperature), gas constant and absolute temperature, respectively.

Equation S2:

$$\tau^*(T) = \tau_0 e^{E_a/RT} \tag{2}$$

where E_a is the activation energy of bond exchange, T is the experiment temperature, τ_0 is the characteristic relaxation time, and R is 8.314 J mol^{-1} K^{-1}.

2. Characterization Tables and Figures

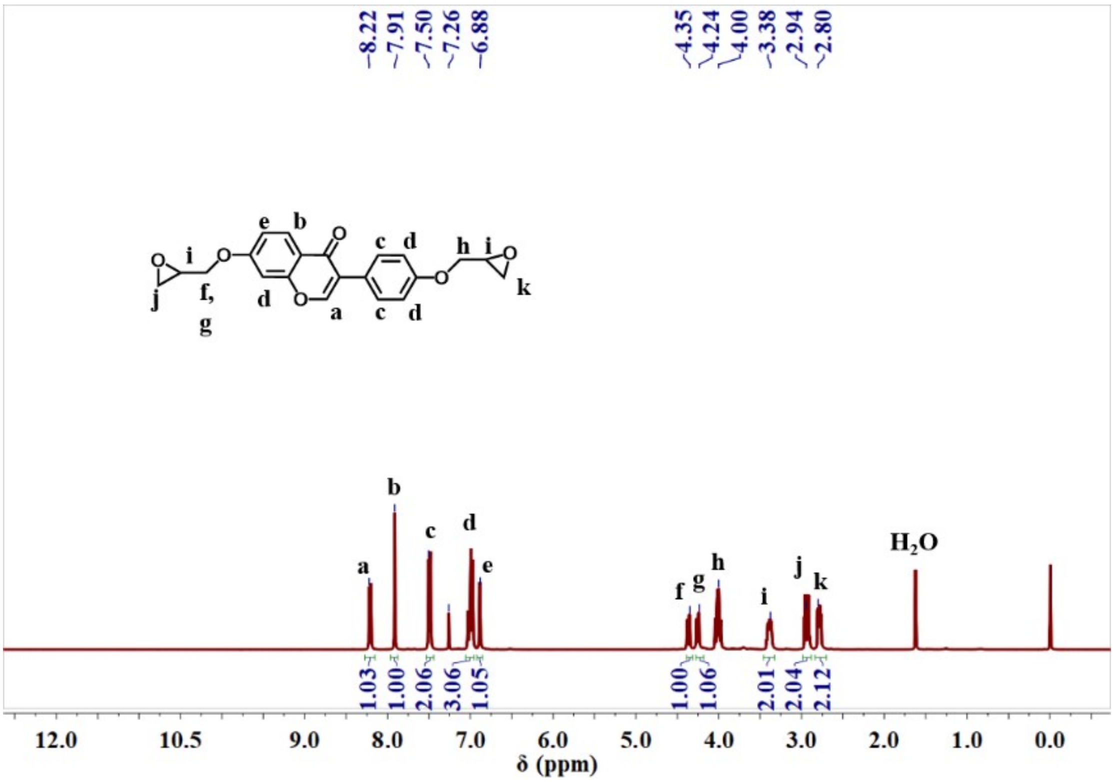


Figure S1. ^{1}H NMR spectra of DZ-EP.

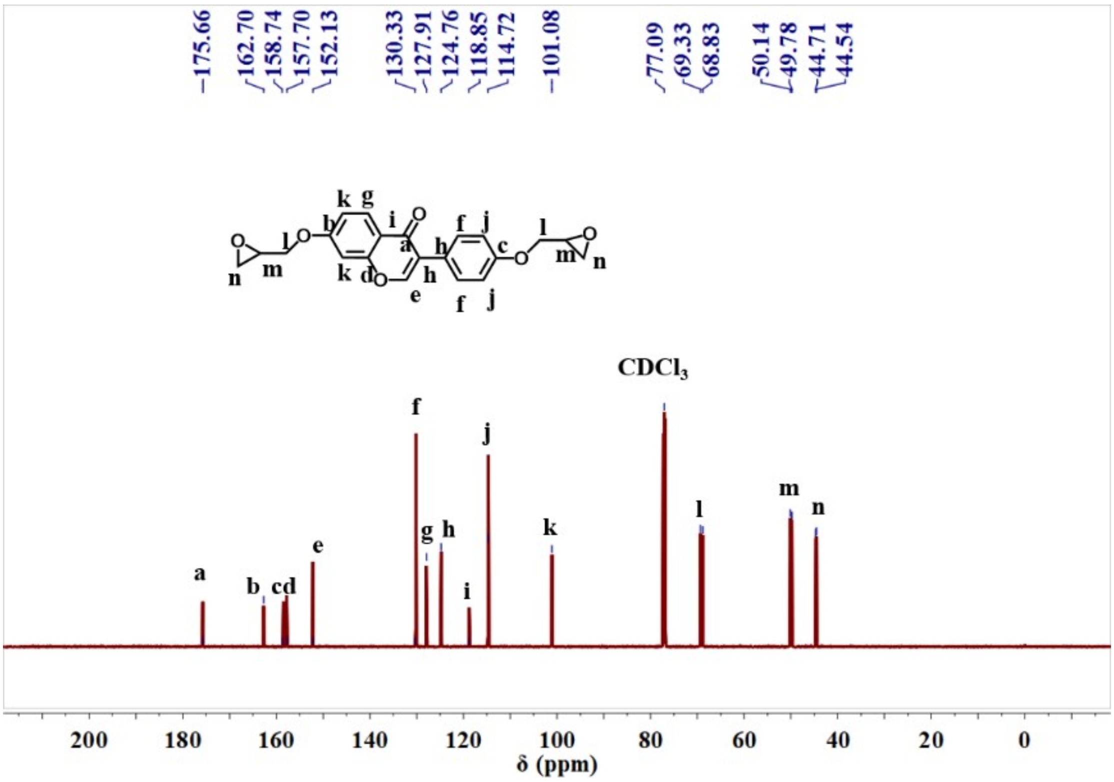


Figure S2. ^{13}C NMR spectra of DZ-EP.

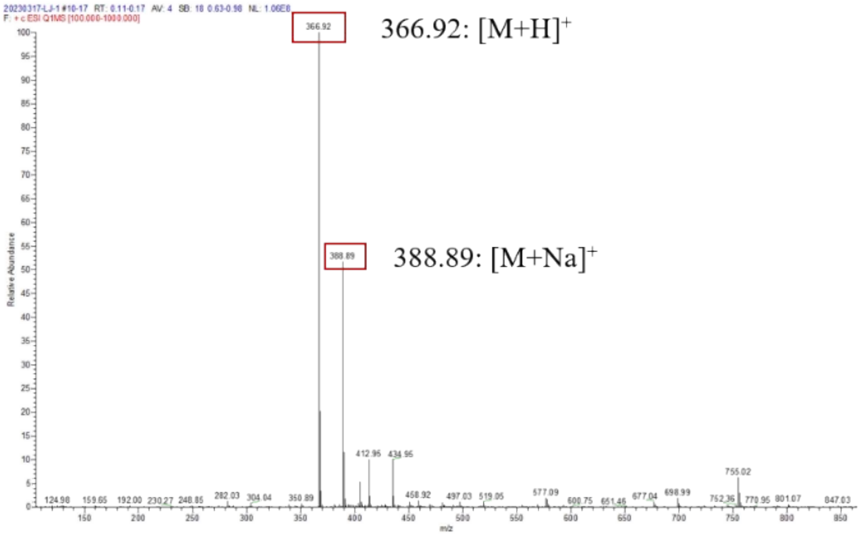


Figure S3. Mass spectra of DZ-EP.

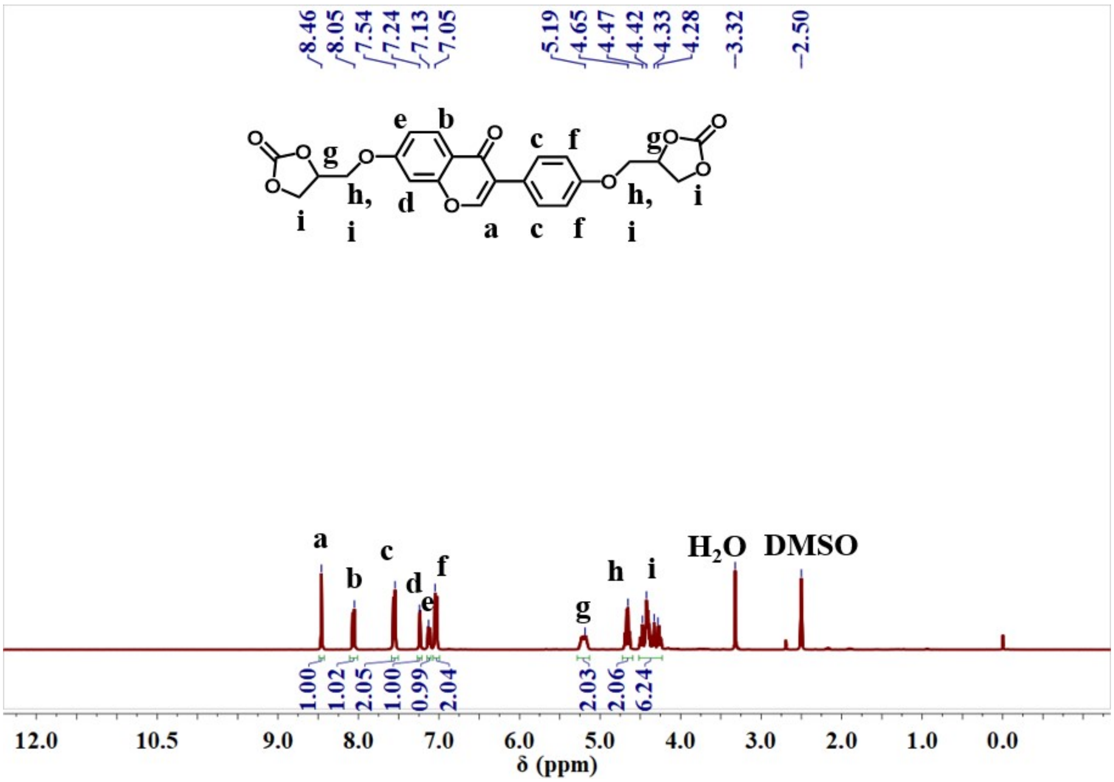


Figure S4. ^{1}H NMR spectra of DZ-BCC.

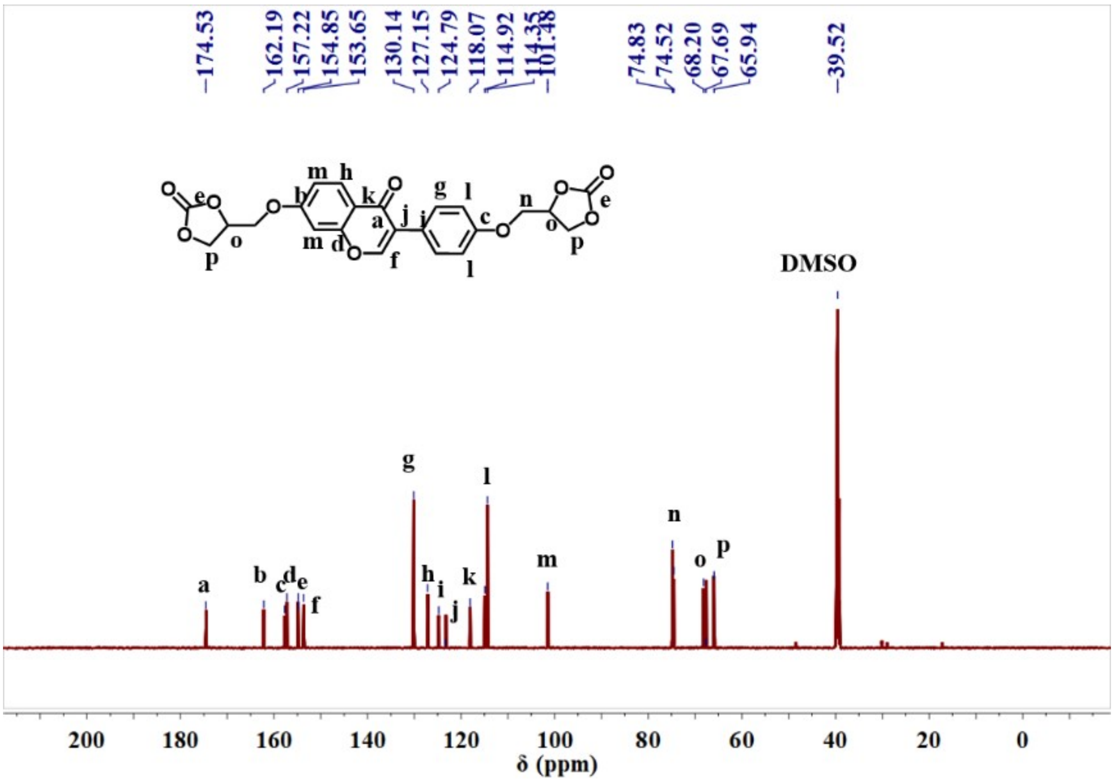


Figure S5. ^{13}C NMR spectra of DZ-BCC.

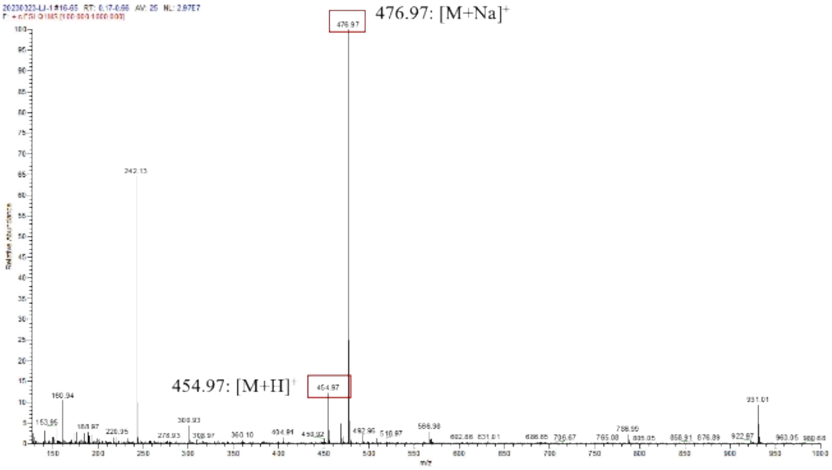


Figure S6. Mass spectra of DZ-BCC.

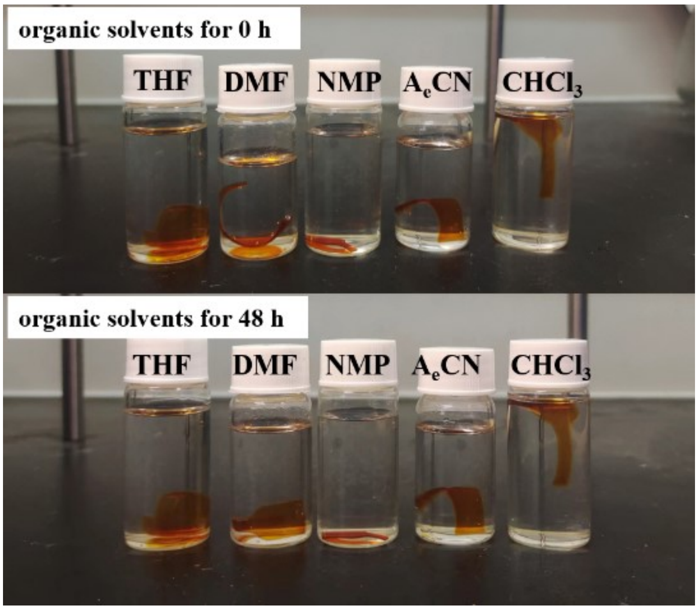


Figure S7. Gel content of DZ-PHU-10% for 0 h and 48 h in different organic solvents at room temperature.

Table S1. The Gel content of DZ-PHU-10%.

Sample	**solvents**	**G(%)**
DZ-PHU-10%	THF	98.1
	DMF	97.1
	NMP	98.8
	A_eCN	96.5
	$CHCl_3$	88.3

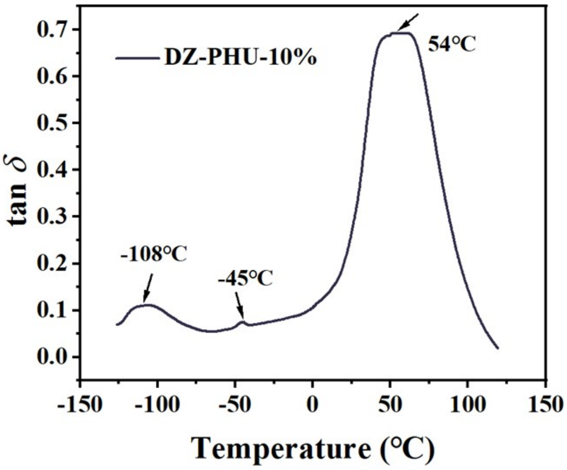


Figure S8. DMA curve of DZ-PHU-10% from -150°C to 120°C.

Table S2. Mechanical and thermal properties of the as-sythesized and reprocessed DZ-PHUs.

Sample	*G* (%, DMF)	T_g (°C，DSC)		Tensile strength (MPa)		Elongation at break (%)	
		As-Synthesized	Reprocessed	As-Synthesized	Reprocessed	As-Synthesized	Reprocessed
DZ-PHU-10%	97.1	33	35	6.2±0.8	6.1±1.0	250±2	241±3
DZ-PHU-30%	98.6	40	40	8.0±1.0	7.9±0.8	83±2	82±2
DZ-PHU-50%	98.9	46	48	22.2±0.7	21.6±0.5	55±3	34±3
DZ-PHU-70%	99.5	52	53	28.3±1.1	28.2±0.8	29±1	16±1

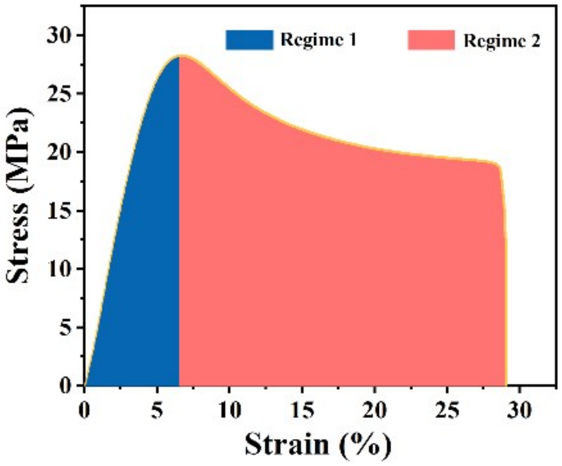


Figure S9. The stretching process of DZ-PHU-70%.

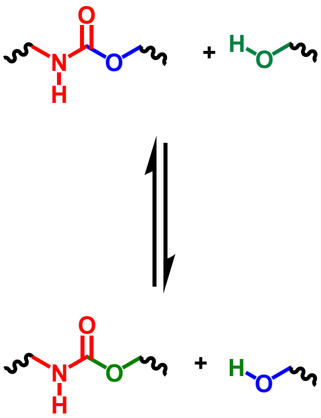


Figure S10. The exchange reaction of transcarbamoylation.

Table S3. The detailed data of DZ-PHU-70% and other reported PHUs in mechanical and dynamic properties.

Serial number	**Tensile stress (MPa)**	**Stress relaxation temperature (℃)**	**Stress relaxation time (min)**	***E*$_a$ (kJ/mol)**
1[3]	2.2	160	60	74
2[4]	11.5	110	40	/
3[5]	34.9	160	66.2	108
4[6]	2.5	140	3	74
5[7]	1.0	160	12	117
This work	28.3	160	16	73

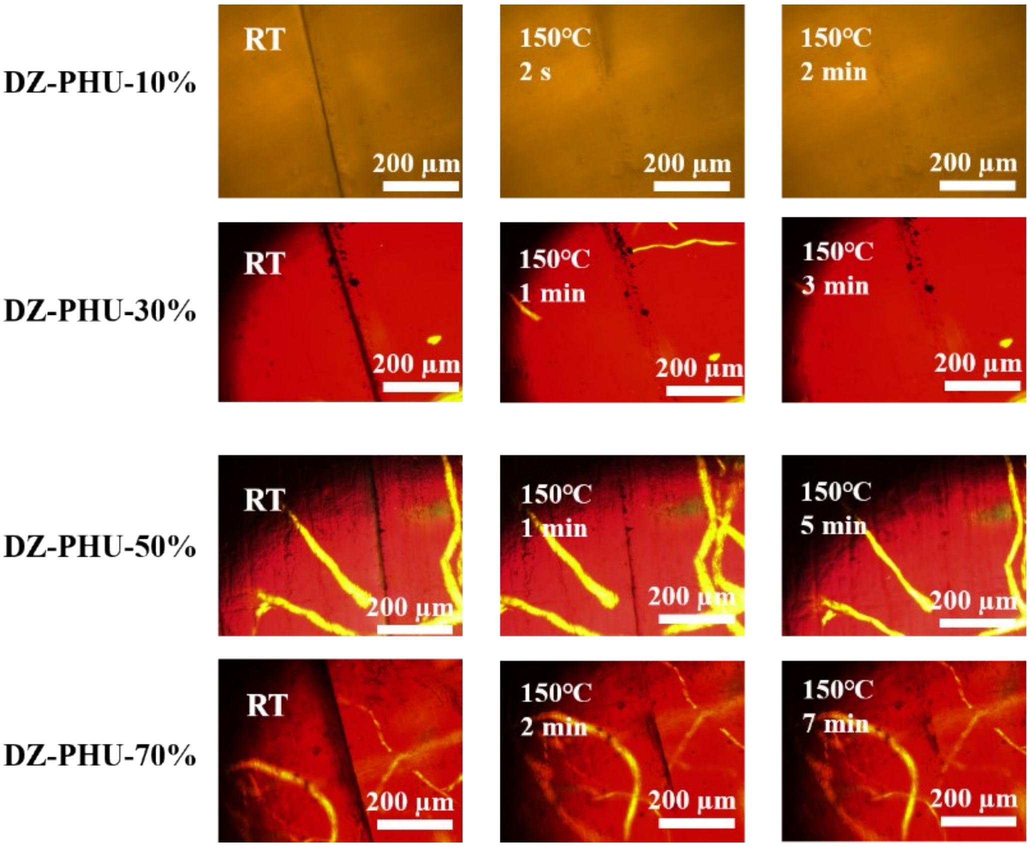


Figure S11. Optical microscopy images of the scratch on the DZ-PHUs film.

Table S4. Formula of the DZ-PHU-50%-HDA.

Samples	DZ-BCC	T403	HDA	[C=O]:[NH_2]	T403:HDA
DZ-PHU-50%	700.0 mg,1.54mmol	225.7 mg,0.513 mmol	89.5 mg,0.770 mmol	1:1	50:50

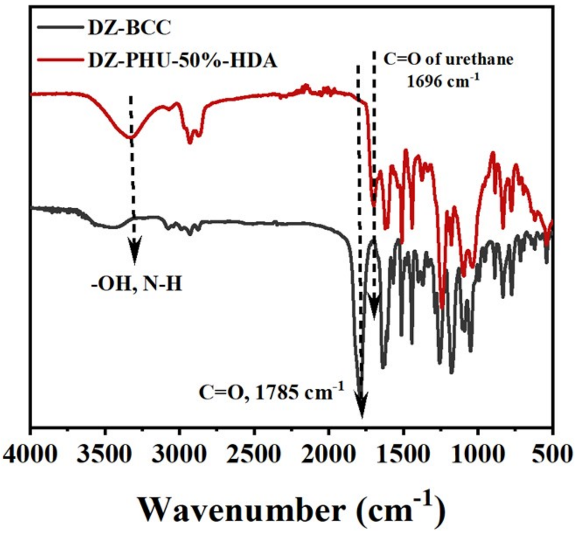


Figure S12. FTIR spectra of DZ-BCC and DZ-PHU-50%-HDA.

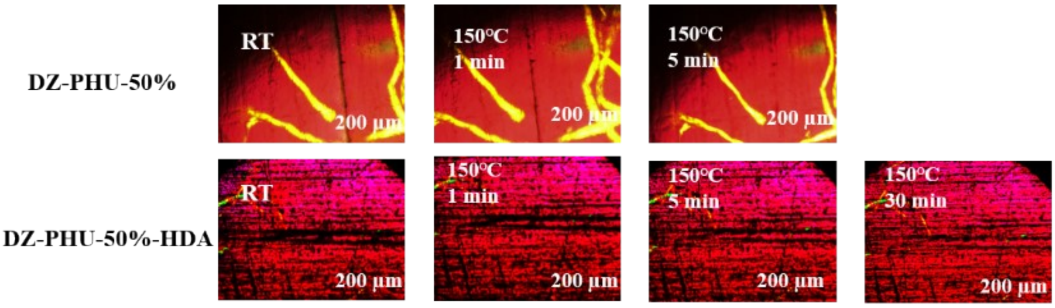


Figure S13. Optical microscopy images of the scratch on the DZ-PHU-50% and DZ-PHU-50%-HDA.

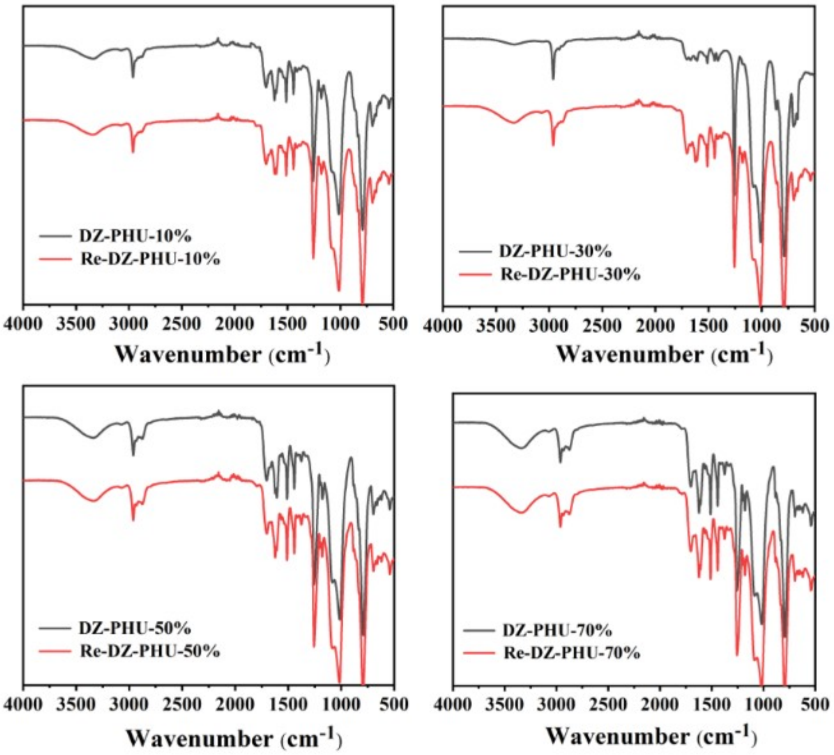


Figure S14. FTIR spectra of the as-synthesized and reprocessed DZ-PHUs.

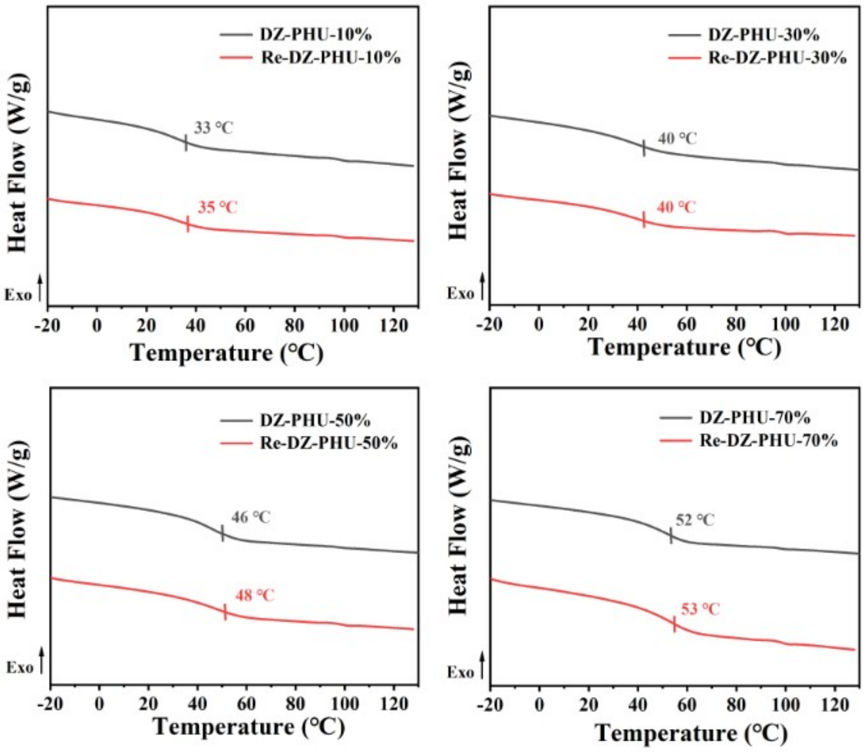


Figure S15. DSC curves of the as-synthesized and reprocessed DZ-PHUs.

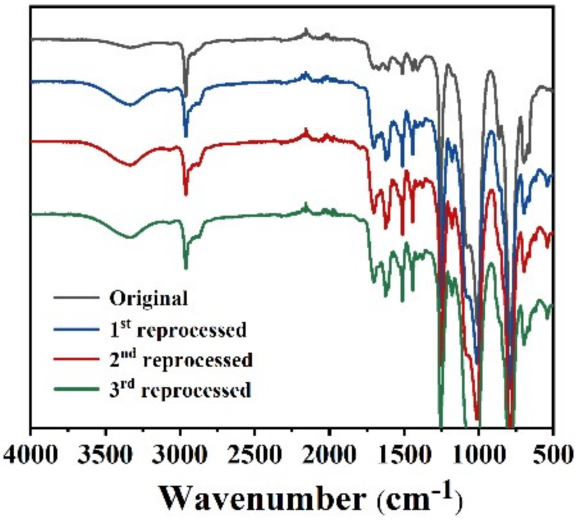


Figure S16. FTIR spectra of the as-synthesized and reprocessed DZ-PHU-30%.

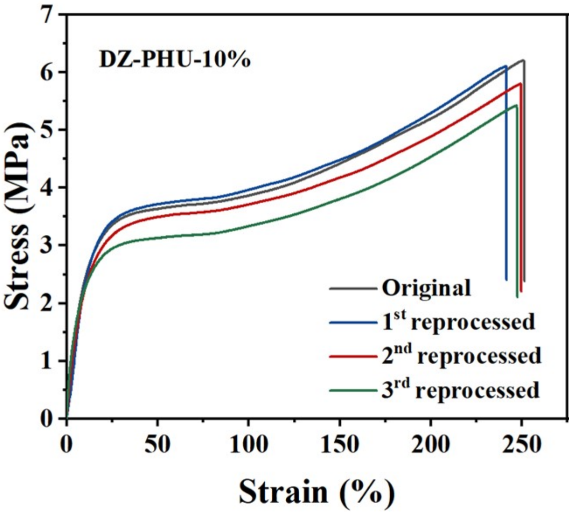


Figure S17. Stress-strain curves of original and reprocessed DZ-PHU-10% for three cycles.

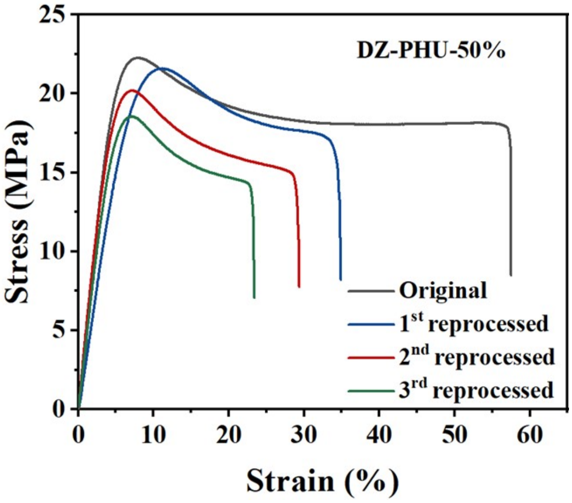


Figure S18. Stress-strain curves of original and reprocessed DZ-PHU-50% for three cycles.

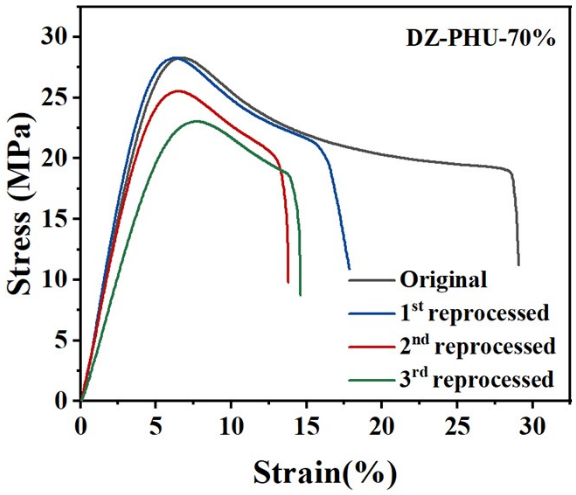


Figure S19. Stress-strain curves of original and reprocessed DZ-PHU-70% for three cycles.

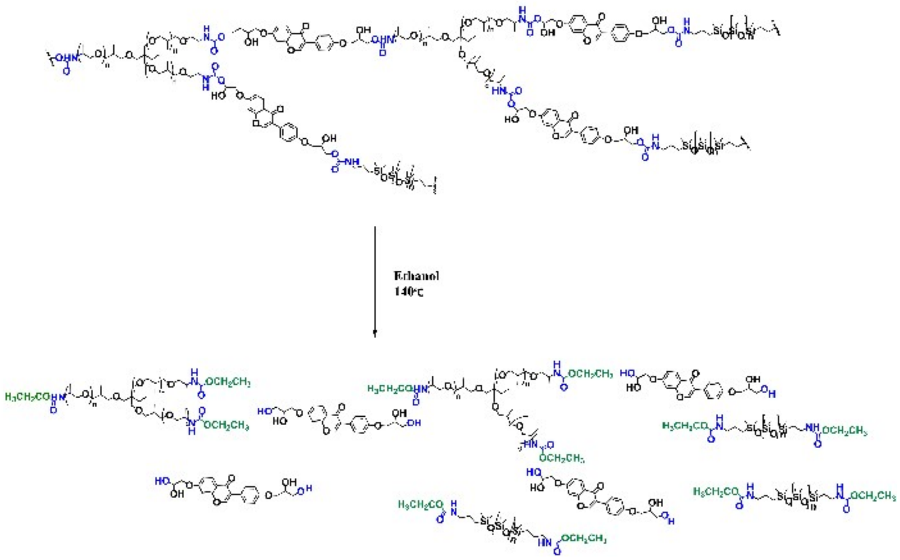


Figure S20. Degradation mechanism of DZ-PHUs in ethanol.

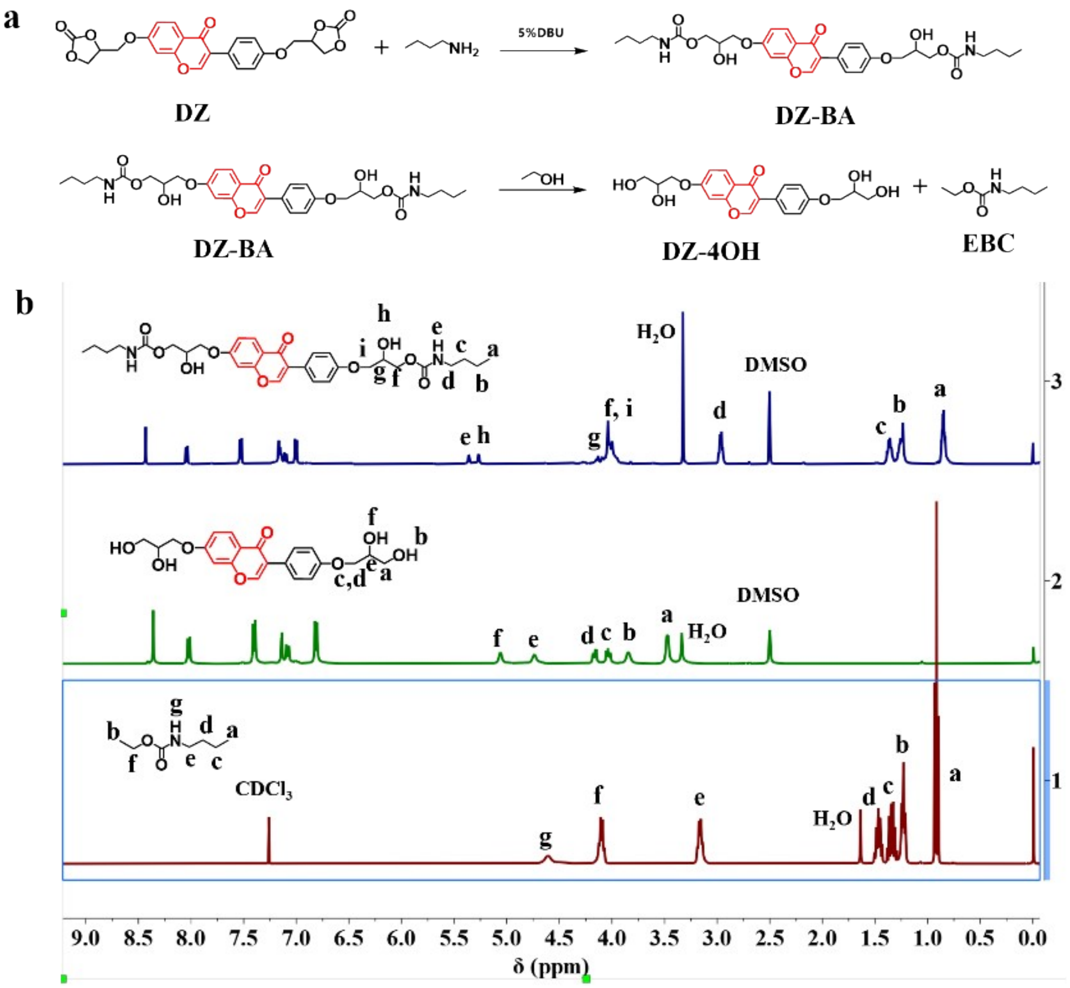


Figure S21. ^{1}H NMR of spectrum of the degraded sample (DZ-PHU-50%).

Figure S22. Photographs of the DZ-PHU-70% adhered between the two woods, supporting a weight of 500 g without rupture.

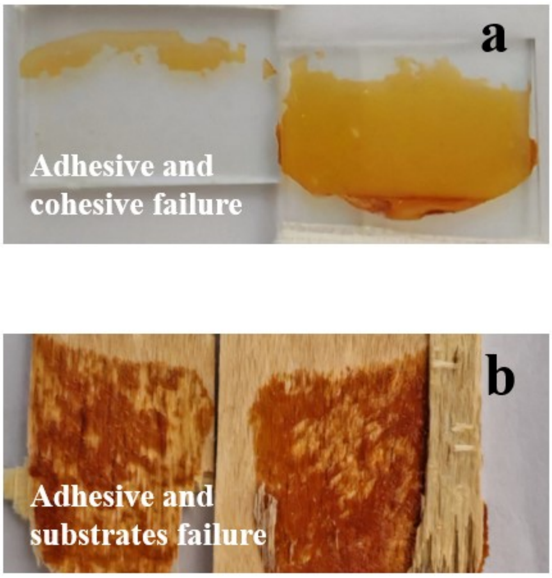


Figure S23. The adhesive failure mode of DZ-PHU-70%.

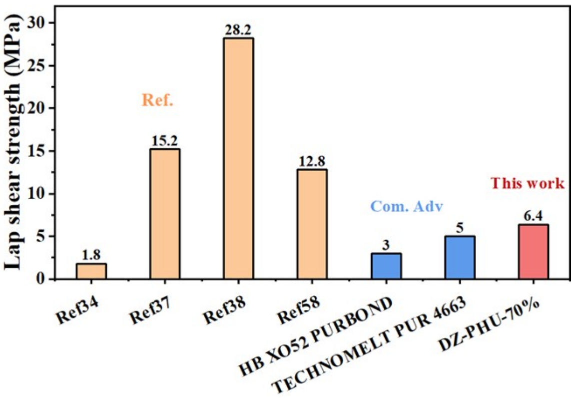


Figure S24. Comparison of lap shear strength of DZ-PHUs and other thermoset PHU and PU adhesives.

Table S5. The detailed data of DZ-PHU-70% and other reported adhesives in bonding wood.

Reference	**Samples**	**Type of wood**	**The thinkness of wood (mm)**	**Lap shear strength (MPa)**
Ref.35	**ECMP-1.0 Polyhydroxyurethanes**	poplar plywood	/	1.8
Ref.38	**TMPTC/ PPOBC640/CBMA**	/	/	15.2
Ref.39	**Catechol-based Polyhydroxyurethanes**	beech	10	28.2
Ref.58	**hybrid-NIPUs**	oak	5	12.8

Commercial PUR	**HB XO52 PURBOND**	/	/	3
Commercial PUR	**PUR 4663**	/	/	5
This work	**PHU**	poplar plywood	2	6.4

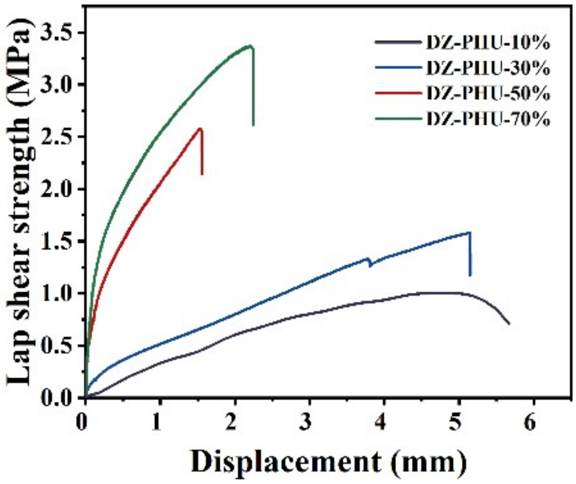


Figure S25. Lap shear strength-displacement curves of various DZ-PHUs bonded with glasses.

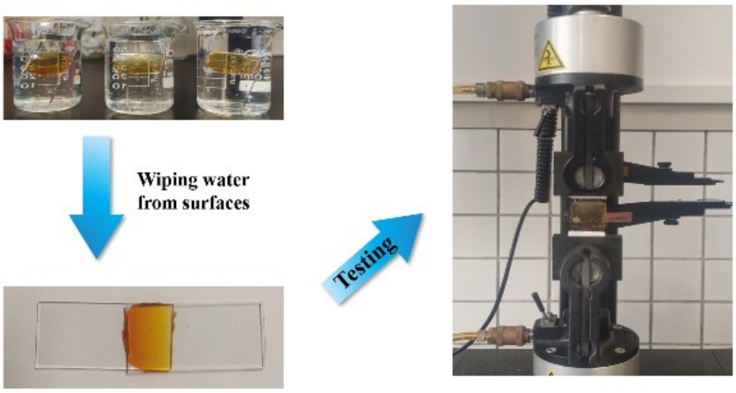


Figure S26. Photographs of soaking two glasses bonded with DZ-PHU based adhesive in water.

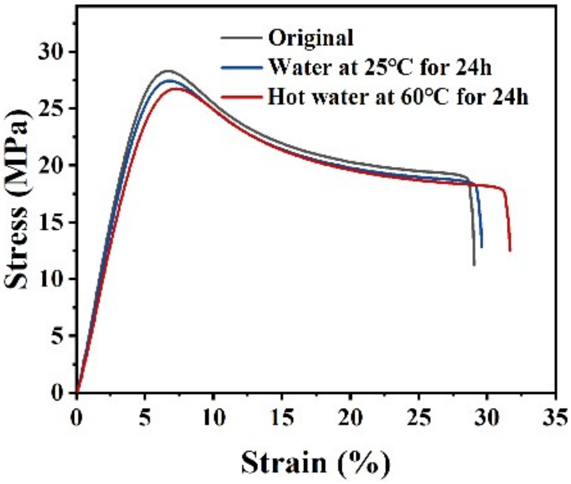


Figure S27. The stress-strain curves of DZ-PHU-70%, DZ-PHU-70% soaked in water at 25°C for 24h, and DZ-PHU-70% soaked in hot water at 60°C for 24h.

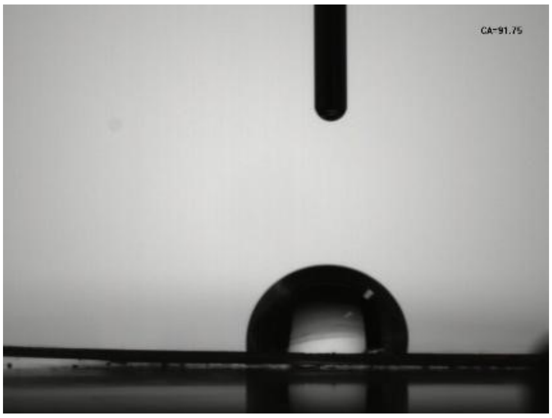


Figure S28. The water contact angle of DZ-PHU-70%.

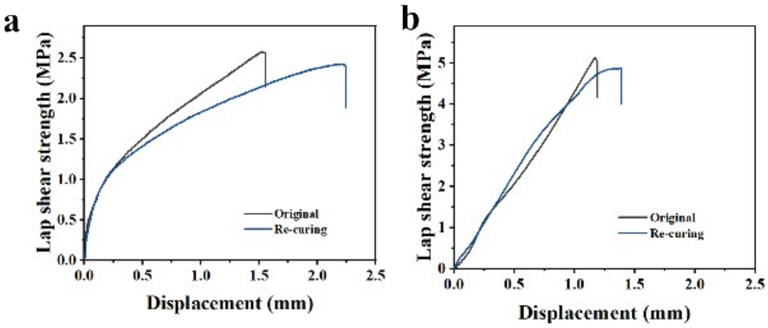


Figure 29. Lap shear strength-displacement curves of DZ-PHU-50%: (a) bonded with glass; (b) bonded with wood.

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