Supporting Information

High Strength and Self-Healing Polyurethane Composites via Diels-Alder Dynamic Bonds for Sustainable Thermal Management Materials

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S1. Experimental Section.

S1.1. Synthesis of diols containing DA bonds (DABF)

BMI (3.58 g, 0.01 mol) and FA (1.98 g, 0.02 mol) were dissolved in DMF (10 mL) and added into a 100 mL three-necked flask equipped with magnetic stirring and condensation reflux. The system was heated to 65 ℃ and stirred for 24 h under a nitrogen atmosphere. The crude product was extracted three times with the mixed solution of dichloromethane and water. The organic phase was evaporated to remove dichloromethane, and then dried in 40 ℃ vacuum oven for 24 h. The yield of DABF was about 85 %. Synthesis process, ^{1}H NMR and FT-IR spectra of DABF were shown in **Figure S1**.

S1.2. Sample preparation for lap shear tests

The DRPUs were cut into rectangles (25 mm × 25 mm × 0.1 mm) and placed between

two identical substrates (100 mm × 25 mm × 2 mm) with an overlap area of 25 mm × 25 mm. Two dovetail clips were used to hold the substrate and film together. The substrates with DRPUs were cured in oven at 110 ℃ for 30 min and then at 65 ℃ for 24 h. The lap shear test was performed by using a universal testing machine (MTS E44.304 tensile testing machine) at a strain rate of 10 mm min^{-1} at room temperature. Three specimens were tested per sample and the averaged results were reported. For the self-healing test, the broken DRPUs and corresponding substrates after the first lap shear test were attached again and repaired at 110 ℃ for 30 min and at 65 ℃ for 24 h. The repaired DRPU-bonded plates were subjected to the lap shear test again according to the above procedure.

S1.3. Measurement of gel content

Gel content of DRPUs was determined via solvent extraction with hot ethanol. Pre-dried DRPU samples (1-2 g) were subjected to Soxhlet extraction for 24 h to remove soluble polymers, and then the insoluble gel fraction was dried to constant mass at 50 °C in a vacuum oven. The gel content was calculated as the mass percentage of the dried insoluble residue relative to the initial dried sample mass, with three parallel tests conducted for each sample to ensure data reliability.

S1.4. scratch tests of DRPUs

DRPU films (1 mm thick) were prepared by hot pressing, and a linear scratch with a length of 5 mm and a depth of 0.3 mm was made on the film surface using the scratch tester (KY-3201-A20T, Donghua, China). Then, the scratched samples were subjected to thermal healing treatment (110 °C for 10 min, then 65 °C for 12/24 h). Polarized optical microscope (BX53, Olympus, Japan) (with a magnification of 200×) was used to observe the healing morphology

of the scratch regions after different healing times. The mechanical properties of the healed samples were tested by tensile testing machine to calculate the self-healing efficiency.

S2. Supporting Results

Table S1. Contents of main components used in the synthesis of DRPU with different contents of hard segments.

Sample	Molar Ratio of IPDI:PTMEG:DABF:TEA	IPDI (g)	PTMEG (g)	DABF (g)	TEA (g)	Hard Segment Content (wt%)
$DRPU_{0.41}$	18:9:5:3		9.00	2.49		41
$DRPU_{0.45}$	18:8:6:3		8.10	2.99		45
$DRPU_{0.52}$	18:7:7:3	4.00	6.75	3.74	0.45	52
$DRPU_{0.59}$	18:6:8:3		5.40	4.49		59
$DRPU_{0.64}$	18:5:9:3		4.50	4.99		64

Table S2. Molecular weights of DRPUs.

Sample	M_n (g/mol, × 10^4)	M_w (g/mol, × 10^4)	PDI
$DRPU_{0.41}$	14.0	19.0	1.41
$DRPU_{0.45}$	9.6	18.0	1.94
$DRPU_{0.52}$	6.5	11.0	1.75
$DRPU_{0.59}$	5.5	9.2	1.66
$DRPU_{0.64}$	3.8	5.5	1.43

Table S3. Comparison of reported PUs containing DA bonds.

Samples	Tensile strength (MPa)	Tensile strain (%)	Self-healing efficiency	Lap Shear Strength (MPa)	References
DA-PU (containing DA bond)	16-30	190-445	90%		R1
SLS-printed PUDAM (containing DA bond)	20-35	250-350	98%	-	R2
DSF-PU elastomer (containing disulfide bond and DA bond)	39.5	455	97%	-	R3
PU-DA (containing DA bond)	9.9	57.15	78.8%	-	R4
PU-EDM/rmGO nanocomposites(containing DA bond and GO)	23.8-31.1	569-809	62-90%	-	R5
NIR triggered healing DAPU–PDAP (containing DA bond)	22	1385	96%	-	R6
PU-TREN-Fe (containing DA bond and Fe ion coordination)	6.4	1838	96.6%	-	R7
DRPUs (containing DA bonds)	**35.8**	**714**	**87%**	**3.3**	**This work**

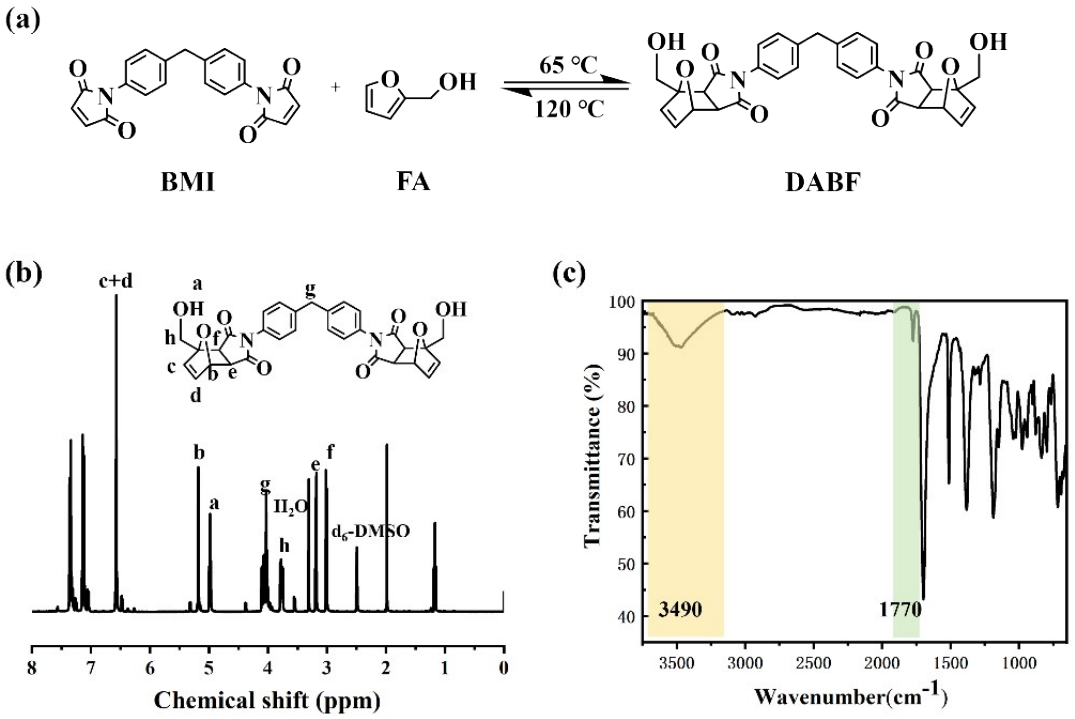

Figure S1. (a) Synthesis of DABF. (b) ^{1}H NMR and (c) FT-IR spectra of DABF.

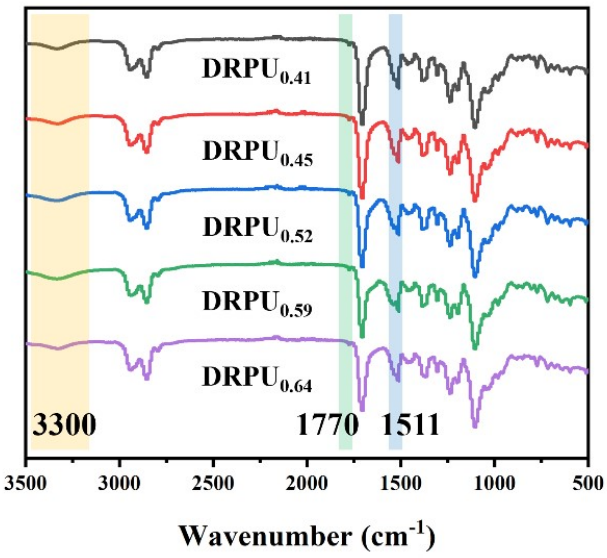

Figure S2. FT-IR spectra of DRPUs with different contents of hard segment.

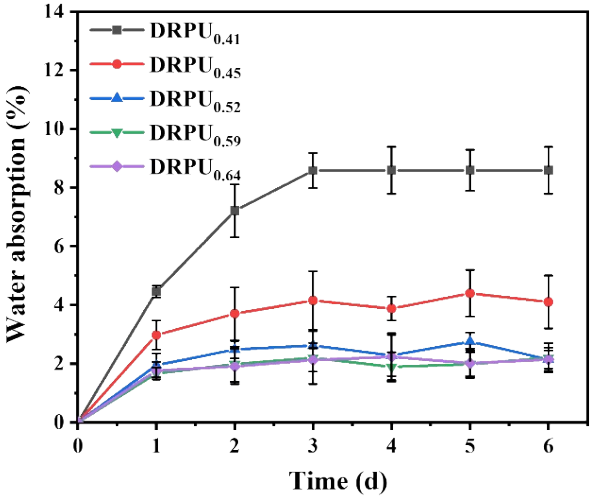

Figure S3. Stability in H_2O of DRPUs.

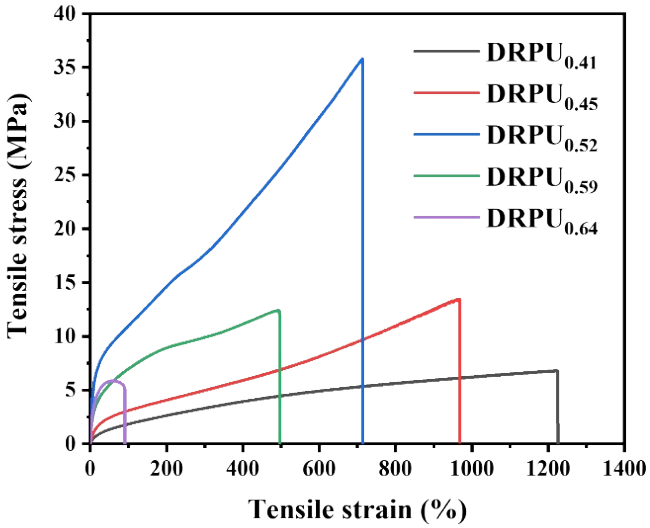

Figure S4. Stress-strain curves of DRPUs.

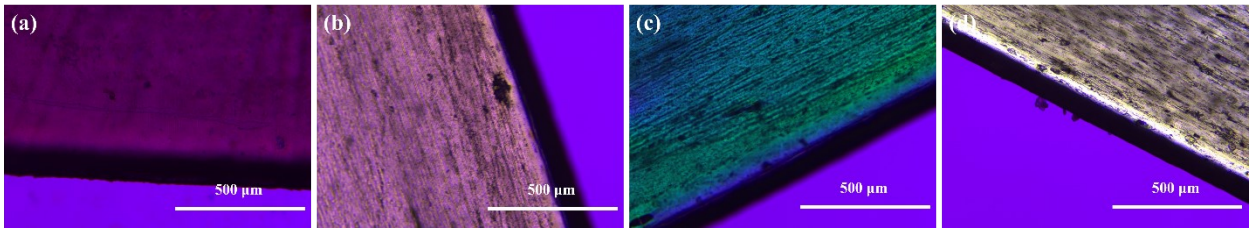

Figure S5. Polarized optical micrographs of (a) original $DRPU_{0.52}$, (b-d) different polarized angles of $DRPU_{0.52}$ after stretching.

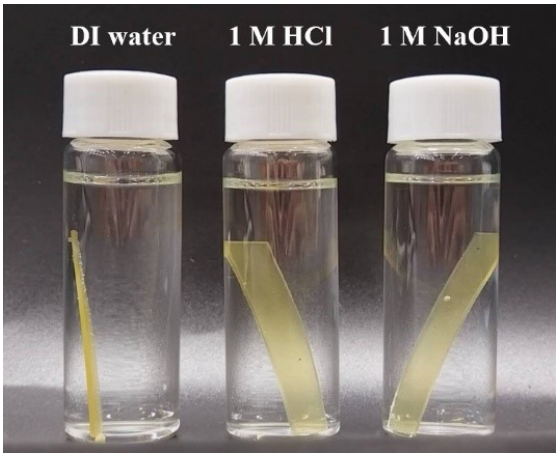

Figure S6. Pictures of $DRPU_{0.52}$ after soaking in DI water, 1 M HCl, 1 M NaOH solution for 7 days.

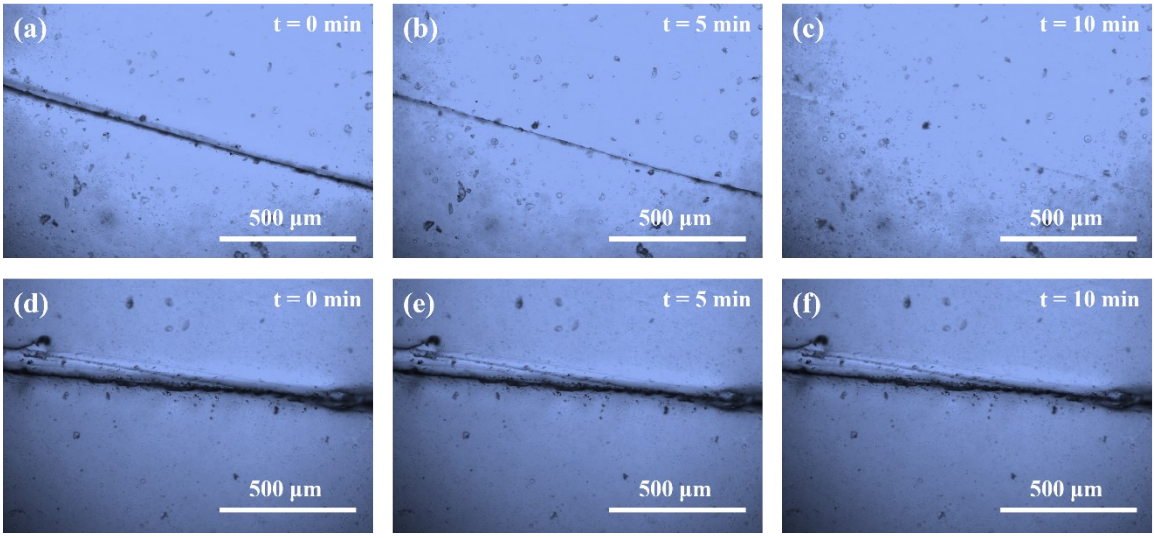

Figure S7. Polarized optical micrographs of (a-c) $DRPU_{0.52}$ and (d-f) PU without DA bonds.

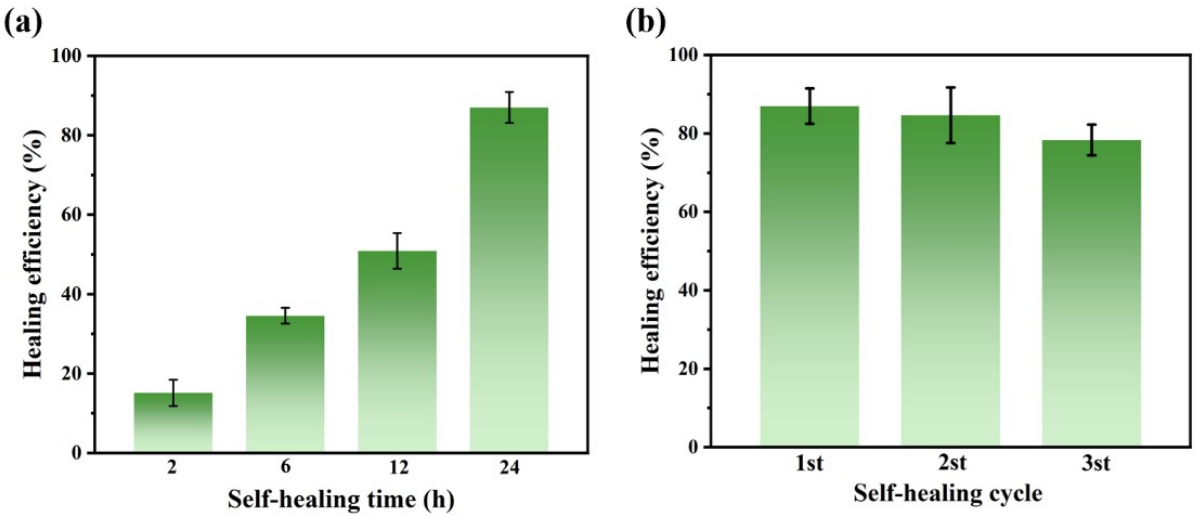

Figure S8. Healing efficiency of $DRPU_{0.52}$ at (a) different healing times and (b) different healing cycles.

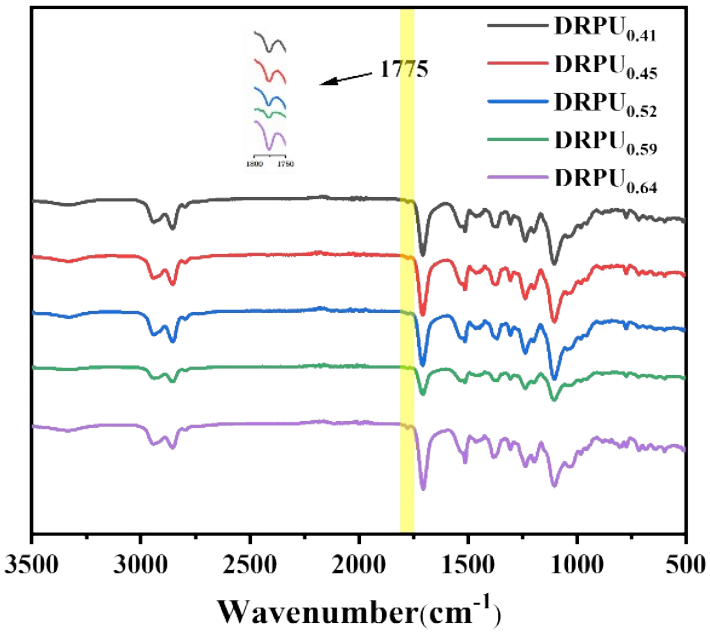

Figure S9. FT-IR spectra of DRPUs after hot press and healing.

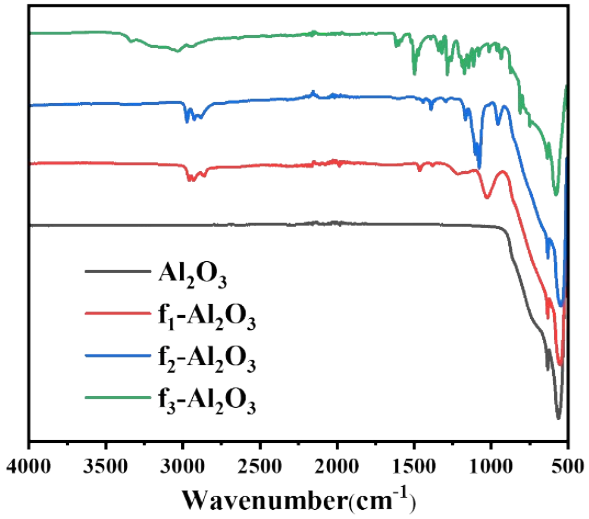

Figure S10. FT-IR spectra of f-Al_2O_3 with three modification methods.

Supporting References:

R1. Thuy Thu Truong, Son Hong Thai, Ha Tran Nguyen, Dung Thuy Thi Phung, Loc Tan Nguyen, Hung Quang Pham, Le-Thu T. Nguyen. tailoring the hard–soft interface with dynamic diels–alder linkages in polyurethanes: toward superior mechanical properties and healability at mild temperature. Chem. Mater. 2019, 31(7), 2347–2357.

R2. Hao Ouyang, Xue Li, Xili Lu, Hesheng Xia. Selective laser sintering 4d printing of dynamic cross-linked polyurethane containing diels–alder bonds. ACS Appl. Polym. Mater. 2022, 4(5), 4035–4046.

R3. Prasanta Kumar Behera, Sagar Kumar Raut, Prantik Mondal, Shrabana Sarkar, Nikhil K. Singha. Self-Healable polyurethane elastomer based on dual dynamic covalent chemistry using diels–alder "click" and disulfide metathesis reactions. ACS Appl. Polym. Mater. 2021, 3(2), 847–856.

R4. Heru Santoso, Sabrina Aufar Salma, Frita Yuliati, Shayrilla Chairunnisa Nur Afifa, Sumarno Sumarno. Polyurethanes synthesized from diisocyanate trimers and polyethylene glycol undergo crosslinking via thermally reversible Diels–Alder reactions. Macromol. Res. 2025, 33, 1015–1028.

R5. Changhong Lin, Dekun Sheng, Xiangdong Liu, Shaobin Xu, ance Ji, Li Dong, Yan Zhou, Yuming Yang. NIR induced self-healing electrical conductivity polyurethane/graphene nanocomposites based on Diels−Alder reaction. Polymer 2018, 140, 150-157.

R6. Li Yang, Xili Lu, Zhanhua Wang, Hesheng Xia. Diels–Alder dynamic crosslinked polyurethane/polydopamine composites with NIR triggered self-healing function. Polym. Chem., 2018,9, 2166-2172.

R7. Xingyu Mou, Yiqin Guo, Xuejun Lai, Jianping Ding, Hongqiang Li, Xingrong Zeng. Self-Healing and Reprocessable Polyurethane Elastomer with Triple Dynamic Crosslinked Networks. Macromol. Rapid Commun. 2025, e00509.