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Supporting Information for

Super-Strong Reusable Hot Melt Adhesives Prepared from Hyperbranched Epoxy Resin

Xu Han[1], Yu Wu[1], Haoran Han[1], Zejun Xu[1,*], Tingcheng Li[1], Yu Jiang[1], Sufang Chen[2], Daohong Zhang[1,*]

[1]Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, Hubei R&D Center of Hyperbranched Polymers Synthesis and Applications, South-Central Minzu University, Wuhan 430074, China.

[2]Key Laboratory for Green Chemical Process of Ministry of Education, Hubei Key Laboratory of Novel Reactor and Green Chemical Technology, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan, Hubei 430205, PR China.

Corresponding Author

* Dr. Zejun Xu, Email: 345366713@qq.com; ORCID：0000-0002-9467-9960.

*Dr. Daohong Zhang, Email: daohong.zhang@scuec.edu.cn, zhangdh27@163.com; ORCID：0000-0002-1640-0805.

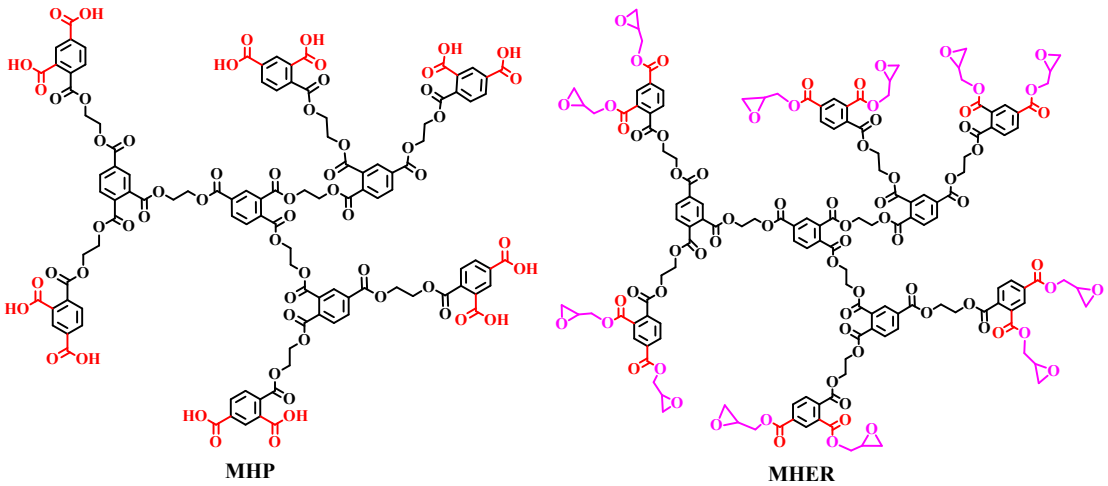
Supporting Methods

Materials. Diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent weight of approximately 196 g/mol was purchased from Yueyang Baling Petrochemical Chemical Co., Ltd. 1,2,4-Benzeneticarboxylic anhydride (TMA), ethylene glycol, tetrabutyl orthotitanate (TBT), dimethyl benzene, 2-amino-4-hydroxy-6-methylpyrimidine (UPy), tetrahydrofuran (THF), 1,1'-carbonyldiimidazole (CDI), acetone, N,N-dimethylformamidedimethy (DMF), dimethylsulfoxide (DMSO), polyether amine (D400), n-hexane, dichloromethane (DCM), ethanol, glycidol, and 4-dimethylamino-pyridine (DMAP) were bought from Meryer (Shanghai) Biochemical Technology Co., Ltd.

Synthesis of MHER and D400-UPy-CDI. TMA (38.43 g, 0.20 mol), ethylene glycol (11.17 g, 0.18 mol), DMF (20 mL), benzene (35 mL), and TBT (0.57 mL) were added into a four-neck flask equipped with a mechanical stirrer, reflux condenser, water-trap (Dean-Stark) and nitrogen inlet. The flask was put in a microwave reactor set at 160 °C, 900W and stirred for 50 min. A yellowish solution was produced and put into a plate for cooling at room temperature to obtain a yellowish solid (MHP) with a yield of 99.2%. The molecular weight and polydispersity index (PDI) of MHP were shown in Table S1.

MHP (4.3 mmol, 10.0 g), glycidol (0.08mol, 6 g), DMAP (2.1 mmol, 0.26 g) and THF were added into a three-neck flask equipped with a mechanical stirrer, reflux condenser and water-trap (Dean-Stark) in microwave reactor. Then the solution was stirred at 65 °C for 70 min under a microwave power of 350 W. A yellowish liquid

(MHER) with a yield of 88.3 % was obtained after THF was removed by rotary evaporation. The viscosity was determined to be 1.54 Pa·s at room temperature, and the epoxy equivalent weight was approximate 476 g/mol. The molecular weight and polydispersity index (PDI) of MHER were shown in Table S1.



Scheme S1. Chemical structures of MHP and MHER.

2-ureido-4[1H]-pyrimidinone (10.2 g, 80.0 mmol), N, N'-Carbonyldiimidazole (18.0 g, 112.0 mmol), and 400 ml DMSO were added into a 250 mL three-neck flask equipped with a mechanical stirrer, reflux condenser and water-trap (Dean-Stark) and stirred at 80°C for 2h. Then filtered with acetone and washed 2-3 times to obtain a yellowish solid (UPy-CDI) with a yield of about 75 %. Upy-CDI (13.0 g, 59.3 mmol) was dissolved by polyether amine D400 (95 g, 594 mmol) at 40 °C for 15 min in a 500 mL three-neck flask equipped with a condenser and stirred, reacting at 40 °C for 12 h to afford D400-UPy-CDI with a yield of about 51 %.

Preparation of hot melt adhesives. A typical HEA-8 was prepared by the following process. MHER (0.32 g, 0.10 mmol), D400-UPy-CDI (0.60 g, 1.00 mmol) and

DGEBA (3.68 g, 10.27 mmol) were mixed at 25 °C. The mixture was transferred into a polytetrafluoroethylene (PTFE) mold and reacted at 100 °C for 1 hour to get the HEA-8. HEA-0, HEA-4, HEA-12 and HEA-16 were also prepared through the similar procedure according to the formulation in Table S2.

Instruments and characterization. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 spectrometer operating at 4 cm^{-1} resolution between 600 and 4000 cm^{-1} range. All spectra were averaged over 16 Scans. The spectra at high temperatures were obtained using an FT-IR spectrophotometer. ^{1}H NMR measurements were conducted on a Bruker Avance III-400 NMR spectrometer at 25 °C，d-$CHCl_3$ was used as solvent. The ^{1}H NMR spectra were recorded at 400 MHz. Gel permeation chromatograph (GPC) was measured on a Waters 1525 using DMF as the fluent at 35 °C, and the flow rate was 0.3 mL min^{-1}. The acid value was determined by color-indicator titration according to ASTM D974.

The adhesion properties of the HEA were evaluated at room temperature using an INSTRON 5966 by applying a parallel force to the adhesive with a displacement rate of 10 mm min^{-1}. Two paper clips held substrates together, and the stainless wires with a thickness of 0.2 mm were used to control the thickness and the contact area (25 mm × 12.5 mm) of the hot melt adhesives while heating. Afterward, they were placed into the oven for 10 minutes at 100 °C and placed at ambient temperature for 12 h to reach the ultimate adhesion strength prior to testing. The gripping length on both sides of the test specimens was 25 mm. Tests were performed on 5 samples for each formulation to determine the average lap-shear strength, and the error bars in the

figure represent the standard deviation. Tensile properties were evaluated using a universal tester (INSTRON 5966, Instron, USA) according to ASTM D638 with a 20 KN load and a crosshead speed of 2 mm min^{-1}.

Dynamic mechanical analysis (DMA) was carried out on a TA Instruments DMA Q800 at a frequency of 1 Hz and a heating rate of 5 °C min^{-1}. The tests were conducted using the single cantilever mode, and the specimen dimensions were 20.0 × 15.0 × 1.0 mm^3.

Temperature and frequency sweep rheological experiments were performed in a stress-controlled TA company Discovery rheometer. Temperature sweep measurements were carried out from 25 to 130 °C at a frequency of 1 Hz and a strain in the linear viscoelastic range of the materials. Frequency sweep experiments were carried out in the linear viscoelastic regime of the materials, from 0.01 Hz to 100 Hz. The experiments were carried out using the 15 mm disposable parallel plate geometry.[1, 2] where G′ is the storage modulus, G″ is the loss modulus.

Solvent resistance experiments were performed by soaking HEA-8 bonded stainless specimens in different solvents, including acetone, toluene, water, or ethanol, at room temperature for 72 hours. Lap shear tests were conducted immediately without any treatment.

A differential scanning calorimeter DSC-Q2000 was used to analyze the thermal behavior of the samples. 5-10 mg of the samples were scanned from -50 to 100 °C at a heating rate of 10 °C min^{-1} under a 50 ml min^{-1} nitrogen flow. The glass transition temperatures (*Tg*) were taken from the inflection point in the curve.

Thermal gravimetric analysis (TGA) was performed on a TGA 209 F3 from NETZSCH Instruments. The samples were measured at a heating rate of 10 °C min^{-1} over the temperature range of 30-600 °C under a nitrogen atmosphere.

The Izod impact strength was measured using an INSTRON CEAST 9050 impact tester (Torino, Italy) with a 25 J pendulum according to ASTM D256. A minimum of ten specimens were tested for each composition. After the impact tests, the morphology of the samples was studied with a Hitachi SU8010 SEM at a voltage of 3.0 kV. The fractured surfaces of all samples were tested after sputter coating with palladium.

Supporting Figures

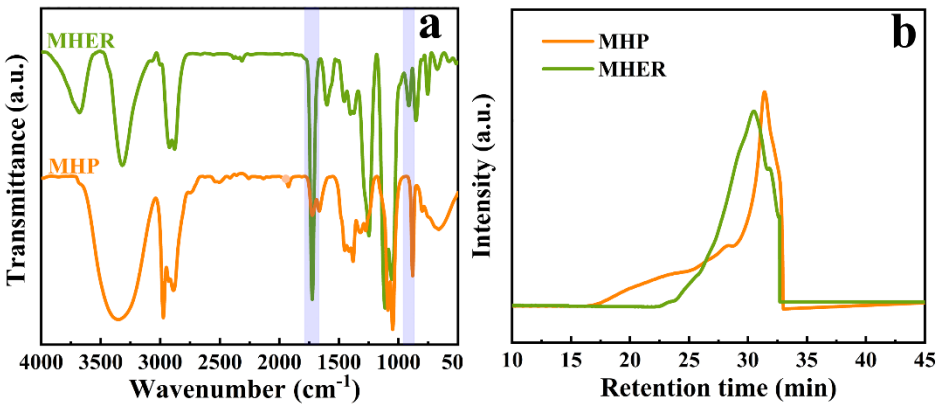


Figure S1. The FT-IR and GPC spectra of MHP and MHER (a. FT-IR, and b. GPC).

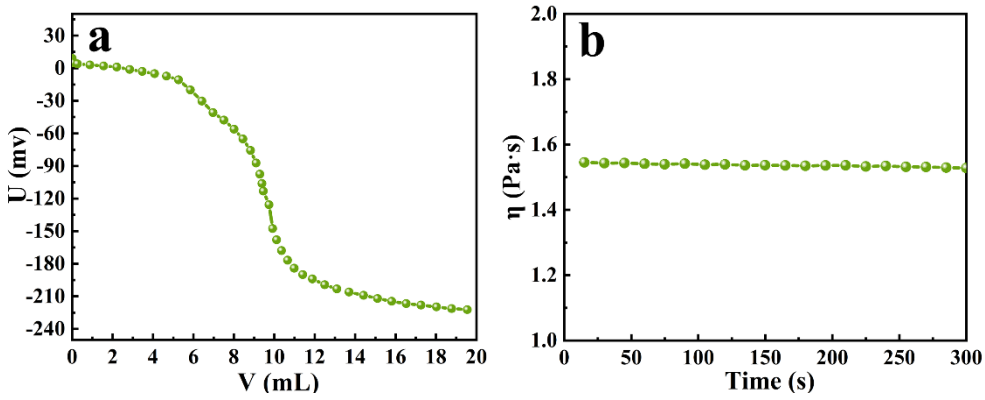


Figure S2. Properties of MHER (a. organochlorine value, and b. viscosity).

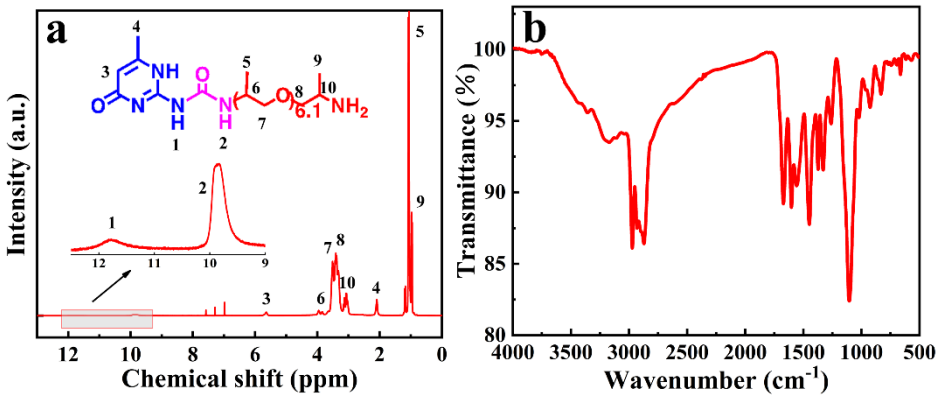


Figure S3. The ^{1}H NMR and FT-IR spectra of D400-UPy-CDI (a. ^{1}H NMR, and b. FT-IR).

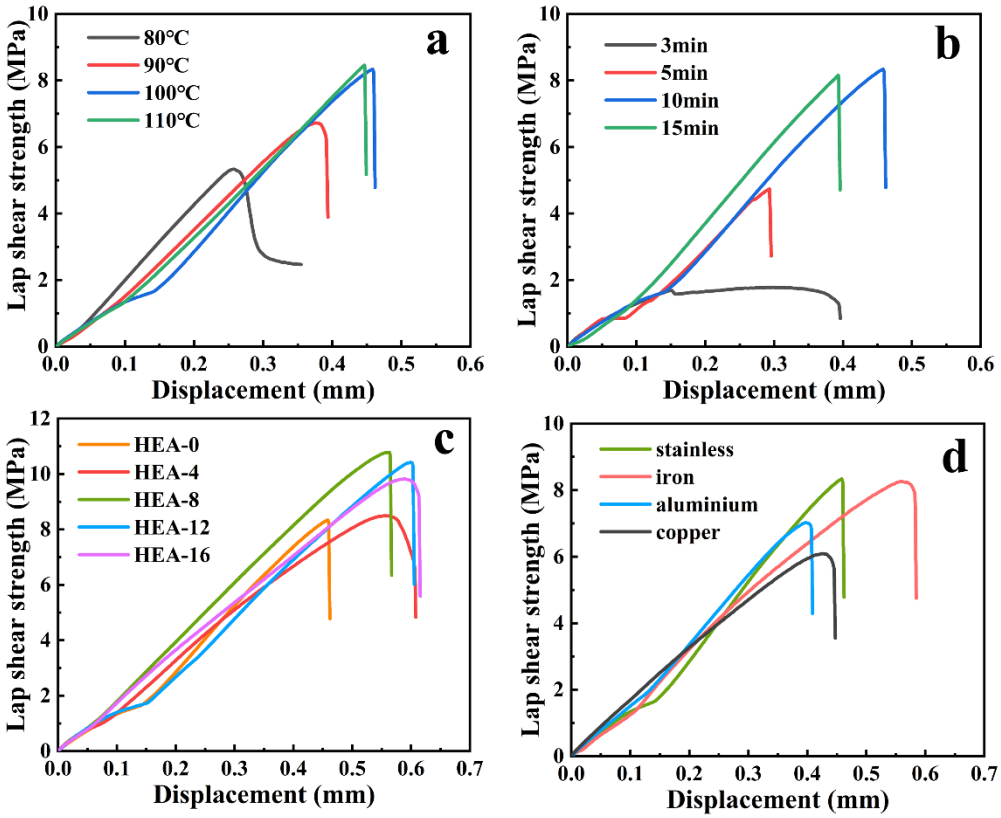


Figure S4. Lap shear strength-displacement curves of adhesive (a. HEA-0 on stainless steel with different bonding temperatures, b. HEA-0 on stainless steel with different bonding times, c. HEA-*x* on stainless steel, d. HEA-0 on different substrates).

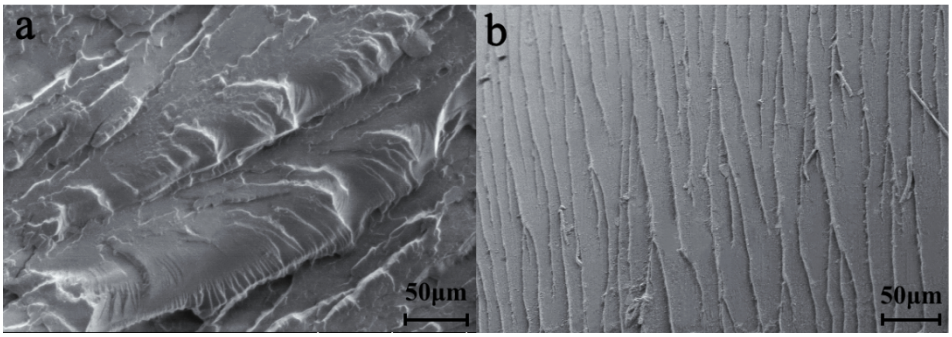


Figure S5. SEM images of the fracture surfaces (a. HEA-0, and b. HEA-8).

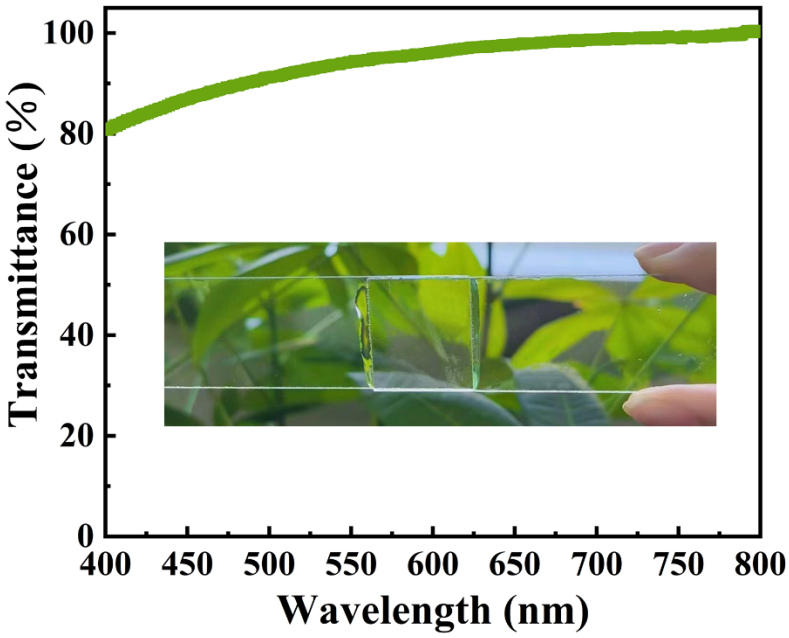


Figure S6. Transparency of HEA-8.

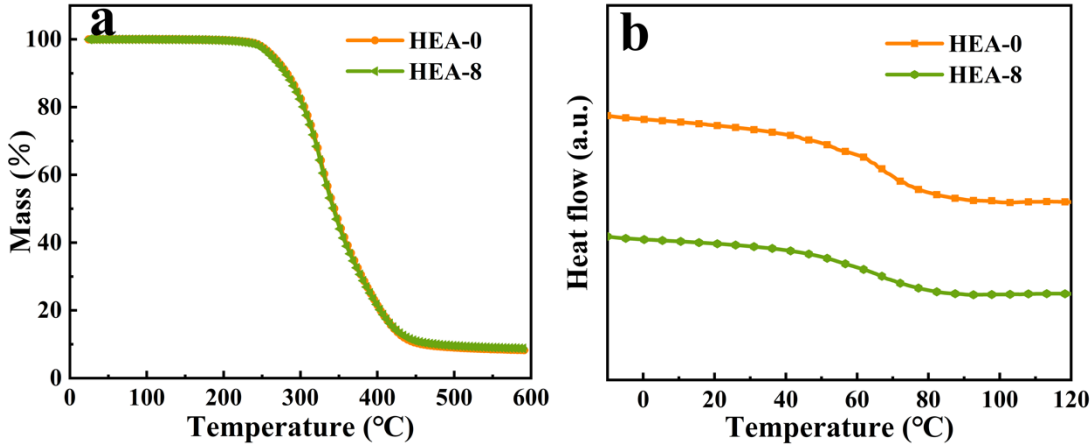


Figure S7. Thermal properties of cured HEA-0 and HEA-8 films (a. TGA curves, b. DSC curves).

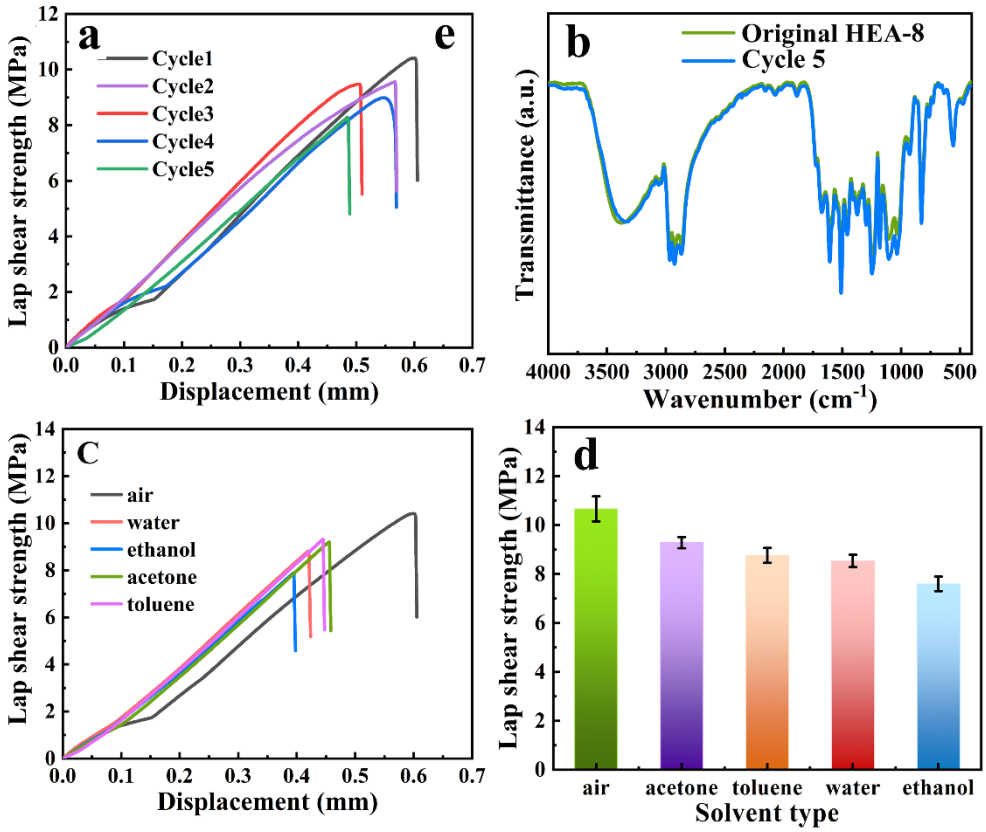


Figure S8. Multi-reused properties of HEA-8 (a. lap shear strength after various cycles, b. FT-IR spectra of original HEA-8 and 5th cycled HEA-8, and c-d. lap shear strength after soaking in various solvents for 72 h at room temperature).

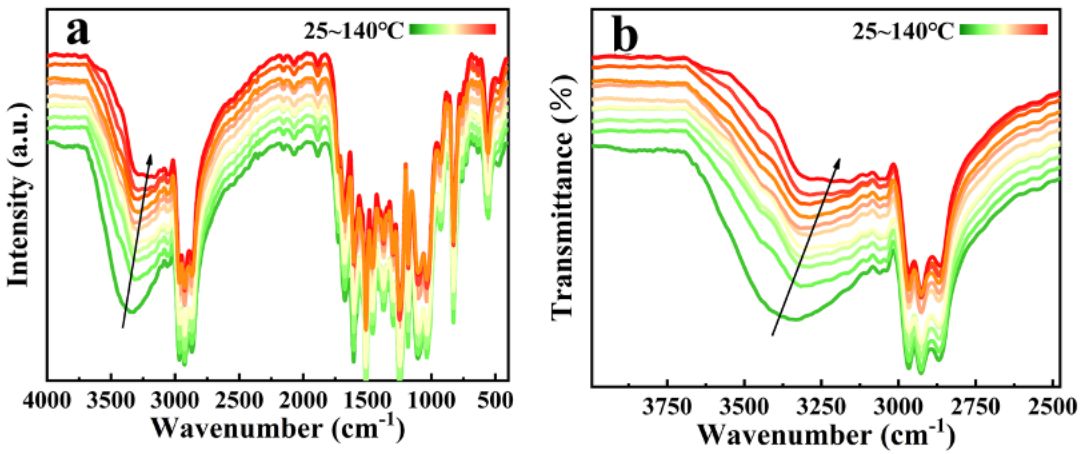


Figure S9. a. FT-IR spectra of HEA-8 during heating from 25 °C to 140 °C, b. Zoomed in the FT-IR between 3390 cm^{-1} to 3300 cm^{-1}.

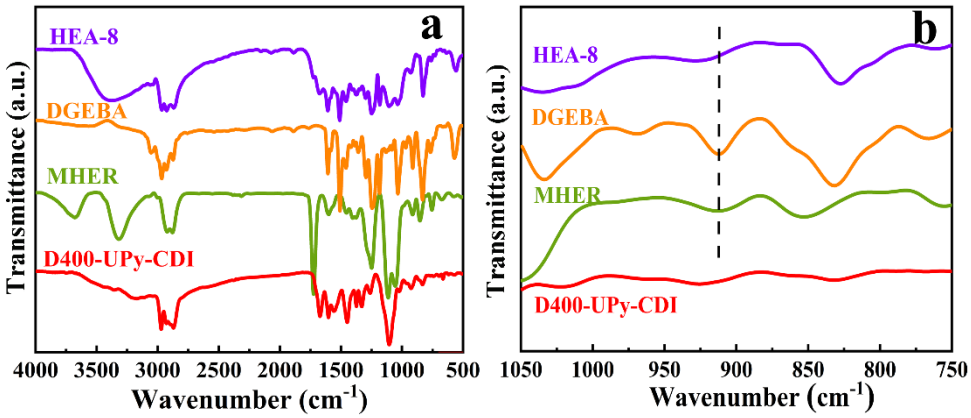


Figure S10. FT-IR spectra (a. HEA-8, DGEBA, MHER and D400-UPy-CDI, and b. the zoomed-in region of 1050-750 cm^{-1}).

Supporting Tables

Table S1. Molecular weights and PDI of MHP and MHER.

Samples	Theoretical Mn, g /mol	Mn from GPC, g/mol	Mw from GPC, g /mol	PDI
MHP	2300	2275	2527	1.25
MHER	3000	2860	3195	1.40

Table S2. Formulation of HEA-*x*.

Samples	DGEBA (g)	MHER (g)	D400-UPy-CDI (g)
HEA-0	4.00	0	1.60
HEA-4	3.84	0.16	1.47
HEA-8	3.68	0.32	1.34
HEA-12	3.52	0.48	1.22
HEA-16	3.36	0.64	1.09

Table S3. The mechanical properties of HEA-*x*.

Samples	Tensile strength (MPa)	Breaking elongation (%)	Toughness (MJ/m^3)	Young's Modulus (MPa)
HEA-0	44.7	3.2	0.8	1406.8
HEA-4	66.2	4.8	2.1	1312.1
HEA-8	79.6	8.6	4.6	909.4
HEA-12	65.5	7.0	3.1	880.5
HEA-16	35.7	4.9	1.0	759.0

Table S4. Thermal properties of HEA-0 and HEA-8.

Samples	HEA-0	HEA-8
E_c (MPa)	1481.3	2235.4
E_d (MPa)	4.3	6.4
T_g from DMA (°C)	88.3	86.7
T_g from DSC (°C)	73.2	71.2
$T_{d5\%}$ (°C)	262.4	261.9
T_p (°C)	324.8	324.2
Char yields at 600 °C (%)	16.2	17.7

E_c refers to the modulus at 35 °C, and E_d refers to the modulus in the rubbery region at T_g + 40 °C. $T_{d5\%}$ refers to the temperature at the weight loss of 5 %, and T_p refers to the temperature at the maximum degradation rate.

References

1. Santinath Singh, S.; Aswal, V. K.; Bohidar, H. B., Internal structures of agar-gelatin co-hydrogels by light scattering, small-angle neutron scattering and rheology. *Eur Phys J E Soft Matter* **2011,** *34* (6), 62.
2. Pan, Y.; Schubert, D. W.; Ryu, J. E.; Wujick, E.; Liu, C.; Shen, C.; Liu, X., Dynamic oscillatory rheological properties of polystyrene/poly(methyl methacrylate) blends and their composites in the presence of carbon black. *Engineered Science* **2018**, 180402.