Electronic supplementary information for:

"Sustainable Alternative for Bisphenol A Epoxy Resin: High-Performance and Recyclable Epoxy Vitrimers Derived from Protocatechuic Acid"

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Experimental section

Materials. Protocatechuic acid was purchased from *J&K Scientific*. Allyl bromide, dimethyl formamide (DMF), dichloromethane (CH_2Cl_2), ethyl acetate (EA), petroleum ether (PE), sodium hydroxyl (NaOH) and were obtained from *Adamas Reagent*. Potassium carbonate, triethyl benzyl ammonium chloride (TEBAC), *m*-chloroperbenzoic acid (*m*-CPBA) and zinc acetylacetonate ($Zn(acac)_2$) were provided by *Aladdin*. Maleic anhydride was bought from *TCI (Shanghai) Chemical Industry Development Co., Ltd.* All the reagents above mentioned were used directly without further purification.

Characterization. Nuclear magnetic resonance spectrum (^1H NMR and ^{13}C NMR) were characterized by JEOL ECZ400 NMR spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. Fourier transform infrared spectra (FT-IR) were recorded on a Thermo Scientific Nicolet iS210 instrument using a Smart Orbit Diamond from 400 to 4000 cm^{-1}. Elemental analysis were carried out by an Elementar instrument with a VARIO EL III. High resolution mass spectra (HRMS) were tested on a Bruker 5973N instrument. The thermal curing process were characterized by differential scanning calorimetry (DSC, TA, Q200) at a heating rate of 10 min/^oC in N_2 from 40 ^oC to 350 ^oC. Dynamic thermal analysis (DMA) were operated on a DMA Q800 V21.1 Build 51 instrument with a heating rate of 3 °C/min

in air. The stress relaxation experiments were carried out using the DMA method at different temperatures, the starting strain was set as 2%, and the changes of storage modulus were recorded with the increasing of time. Thermogravimetric analyses (TGA) were carried out on a NETZSCH TG 209 apparatus under N_2 atmosphere at a heating rate of 10 °C/min from room temperature to 1000 °C. The mechanical properties of the cured resins were tested on a universal testing machine (INSTRON 5583) at room temperature, the properties were calculated as the average value of three measurements.

Synthesis of allyl ether PA-TE from protoatechuic acid. To a mixture of protocatechuic acid (10.00 g, 63 mmol), triethyl benzyl ammonium chloride (TEBAC, 2.95 g, 13 mmol) and K_2CO_3 (53.80 g, 389 mmol), 200 mL of DMF and allyl bromide (47.17 g, 389 mmol, 34 mL) were added. The reaction was kept at 50 ^oC for 24 hours, then it was cooled down to room temperature. 200 mL of water was added and extracted by ethyl acetate, the organic phase was collected and washed with saturated brine (100 mL ×3). After dried with anhydrous Na_2SO_4 and concentrated by removing the solvent, the residue was purified by flash column chromatography with a mixture of ethyl acetate and petroleum (1:10, v/v) as the eluent. **PA-TE** was obtained in a quantitative yield as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 6.84 – 6.77 (m, 1H), 6.08 – 5.88 (m, 3H), 5.41 – 5.28 (m, 3H), 5.22 (dt, *J* = 20.3, 5.7 Hz, 3H), 4.72 (dd, *J* = 4.0, 2.8 Hz, 2H), 4.58 (dd, *J* = 5.9, 3.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 152.6, 147.9, 133.0, 132.7, 132.5, 123.8, 122.8, 118.2, 118.1, 114.6, 112.4, 69.9, 69.7, 65.5. HRMS-ESI (m/z): Calcd. for $C_{16}H_{19}O_4$ $[M+H]^+$ 275.1277. Found 275.1278. Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61; Found: C, 69.91; H, 6.51.

Synthesis of epoxy monomer PA-EP. To a mixture of *m*-chloroperbenzoic acid (*m*-CPBA, 50.39 g, 292 mmol) and 300 mL of CH_2Cl_2, **PA-TE** (17.80 g, 65 mmol) was added, the reaction system was then stirred at room temperature for 48 hours. The precipitate were removed by filtration and the filtrate was washed with 0.1 M $Na_2S_2O_3$ (200 mL ×3) aqueous solution and saturated brine (100 mL×3),the organic

layer was collected and dried over with anhydrous Na_2SO_4. After filtration and concentration, the residue was purified through flash column chromatography with an eluent (EA/PE = 1/1). The target epoxy monomer **PA-EP** was obtained in a yield of 81% as an orange viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 6.84 – 6.77 (m, 1H), 6.08 – 5.88 (m, 3H), 5.41 – 5.28 (m, 3H), 5.22 (dt, *J* = 20.3, 5.7 Hz, 3H), 4.72 (dd, *J* = 4.0, 2.8 Hz, 2H), 4.58 (dd, *J* = 5.9, 3.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8, 152.8, 148.0, 124.6, 122.9, 115.2, 112.9, 70.2, 70.12, 69.8, 69.8, 65.5, 50.1, 50.1, 49.6, 44.8, 44.7. HRMS-ESI (m/z): Calcd. for $C_{16}H_{22}NO_7$ $[M+NH_4]^+$ 340.1391. Found 340.1393.Anal. Calcd. for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63; Found: C, 59.23; H, 5.59.

Preparation of epoxy vitrimers. To a quartz mortar were added **PA-EP** (E51) and maleic anhydride (**MA**), the mixture was grinded to a uniform liquid. Then the catalyst $Zn(acac)_2$ was added to this liquid and further grinded to fully mix the monomers and catalyst. The mixture was transferred to polyimide films and covered by two steel sheets. The sheets were put into a vulcanizer and cured with a procedure consisted of 120 ^{o}C for 3 hours and 150 ^{o}C for 1 hour under a pressure of 10 MPa. After cooling to room temperature, the cured epoxy vitrimers were prepared.

Recycling of the epoxy vitrimers. The epoxy vitrimers were cut into small pieces and put inside two polyimide films, the sandwich-like samples were then hot-pressed at 230 ^{o}C for 2 hours under a pressure of 10 MPa. After cooling to room temperature, the reprocessed epoxy vitrimers were thus obtained.

Supplementary figures and tables

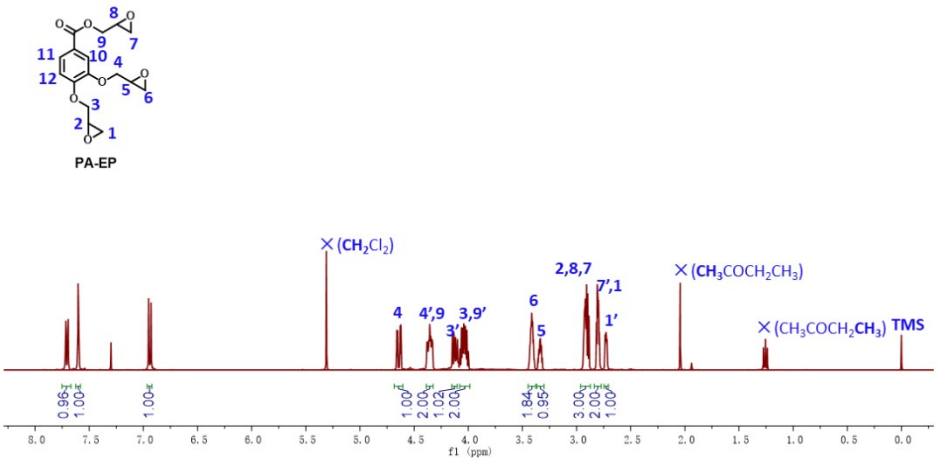

Figure S1. ^{1}H NMR spectrum of **PA-EP** ($CDCl_3$, 400 MPa)

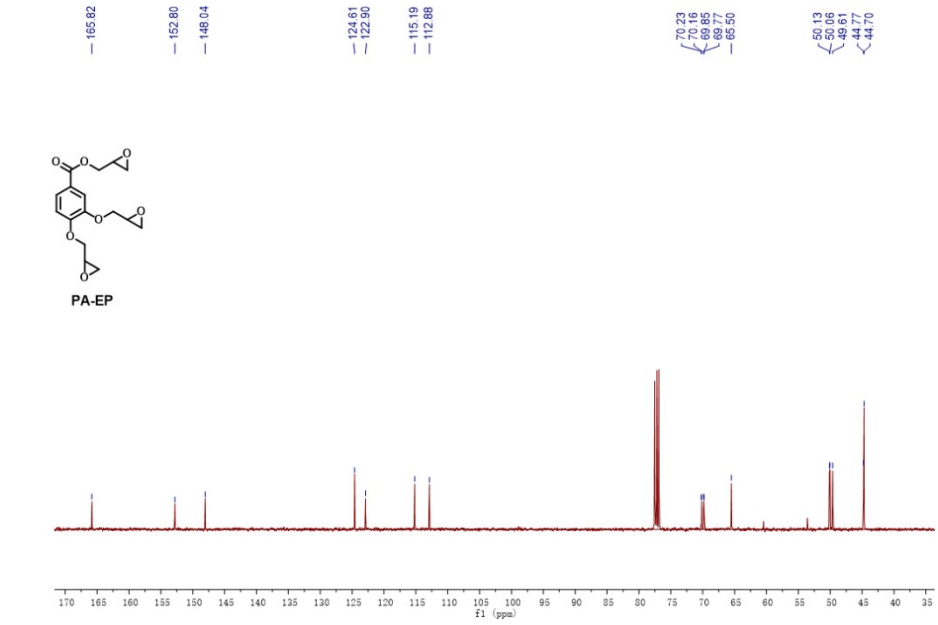

Figure S2. ^{13}C NMR spectrum of **PA-EP**. ($CDCl_3$, 101 MPa)

Table S1. The swelling experiments of **PaE-10%** in various solvents.

Solvent	H_2O	EtOH	$CHCl_3$	Acetone	Ethyl Acetate	Toluene	THF	DMSO[a]	DMF[a]	CH_3CN
Swelled								✓	✓	✓
Not Affected	✓	✓	✓	✓	✓	✓	✓			

[a]the solvents become yellow after swelling tests.

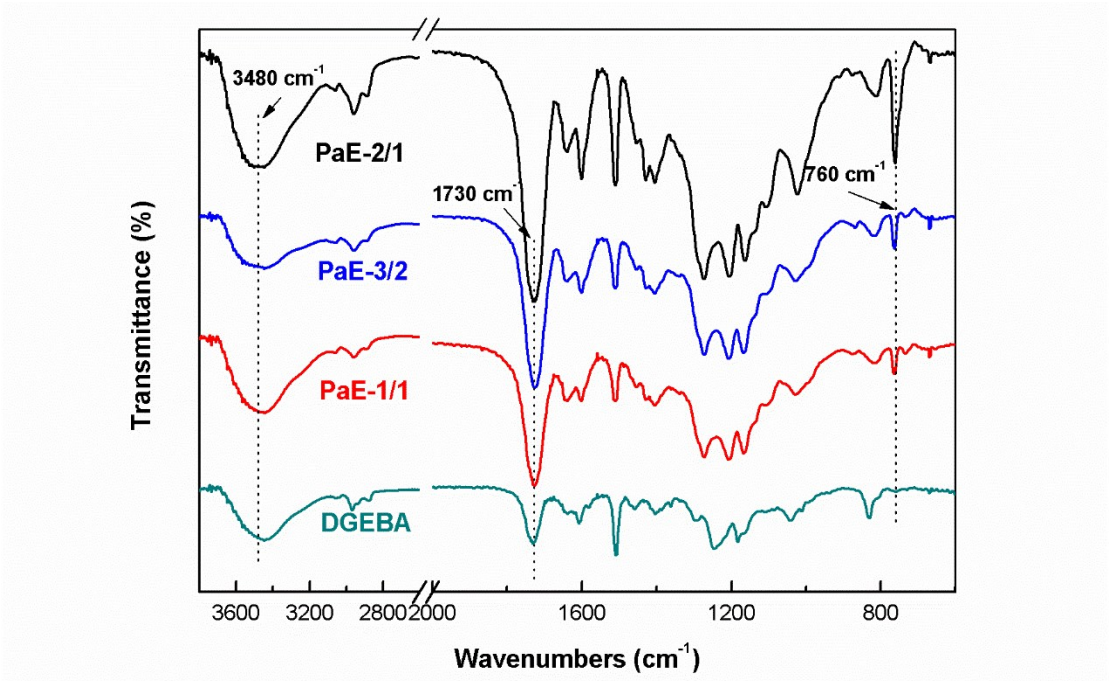

Figure S3. FT-IR spectra of different epoxy vitrimers.

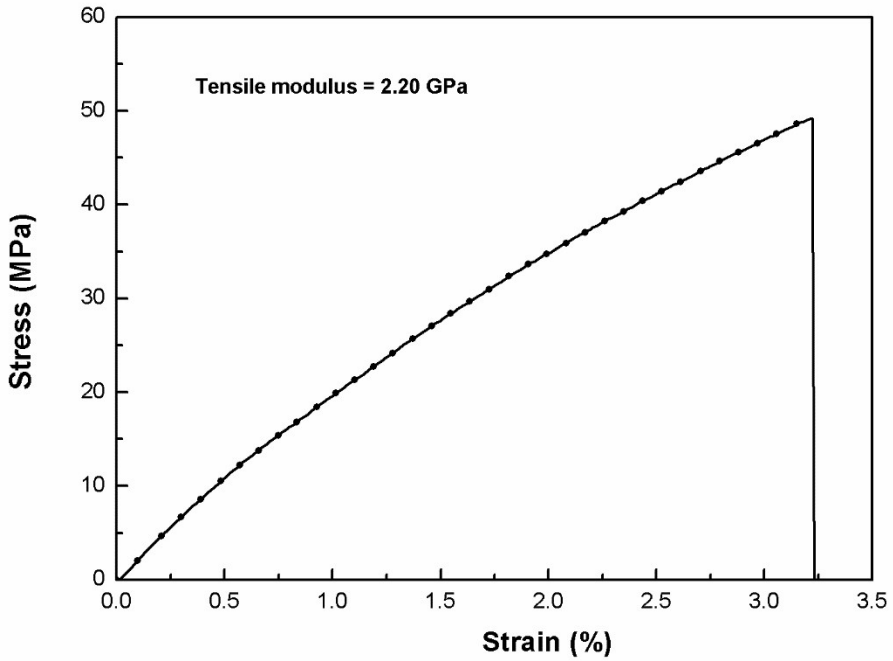

Figure S4. Tensile test of reprocessed epoxy vitrimer **PaE-2/1.**