

Supporting Information for

Degradable and recyclable bio-based thermoset epoxy resin

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S1. EXPERIMENTAL SECTION

S 1.1. Materials

2,5-furandicarboxylic acid (FDCA, 99%) was purchased from Mianyang Dagao New Material Co, Ltd. Tris(2-hydroxyethyl)isocyanurate (THEIC) was obtained from Aldrich. 3-Mercaptopropionic acid (MPA), p-toluenesulfonic acid, N,N-dimethylformamide (DMF), 1,4-dioxane, allylglycidyl ether (AGE), ethylene glycol (MEG) and other materials were purchased from Shanghai Chemical Reagent Co, Ltd. 1-Hydroxycyclohexyl phenylketone (pho-toinitiator 184) was sourced from BASF Chemical Company. Diglycidyl ether of bisphenol-A (DGEBA) with epoxy equivalent weight of about 196 g/mol was supplied by Yueyang Chemical Corp, China. DETA-AN as a curing agent was synthesized by the addition reaction of equal molar acrylonitrile (AN) and diethylene triamine (DETA)¹.

S1.2 Synthesis of bio-based hyperbranched epoxy resin

Synthesis of hyperbranched polyester (HFTH). According to the synthesitic process in Scheme 1, 0.1 mol of THEIC and 0.09 mol of FDCA were placed in a 250 mL three-necked flask equipped with a condenser, mechanical stirrer, and nitrogen inlet. 10 mL of DMF, 40 mL of xylene and 0.2 mL of n-butyl titanate were added and heated to 140 °C under N₂. Under mechanical stirring, the temperature was raised to 170 °C, and the reaction was continued for 12 h. The organic solvent was distilled off under reduced pressure to obtain a brownish-yellow solid (HFTH) with a yield of 98.0%. ¹H NMR spectral data of EFTH-n in DMSO-d₆ (400 MHz, δ in ppm) in Fig.S1b: 7.29 (-C=CH-, a), 4.75 (-OH, f), 4.40 (O-CH₂-CH₂-, b), 4.09(-CH₂-CH₂-N-, c), 3.88 (-

CH₂-CH₂-O-, e), 3.38 (-O-CH₂-CH-, d).

Synthesis of bio-based hyperbranched epoxy resins (EFTH-n). 5.0 mmol of HFTH, 30.0 mmol of MPA, 40 mL of 1,4-dioxane and 50 mL of toluene were stirred in a 250 mL flask at 120 °C for 12 h. After cooling to room temperature, the solution in the bottle was layered, the upper layer solution was poured out, and the lower brownish substance was washed three times with toluene and then dried in vacuum at 50 °C for 3 h to obtain a pale yellow solid (TFTH-6) with a yield of about 88.98%. 0.1 mmol of TFTH-6, 20 mL of 1,4-dioxane, 0.6 mmol of AGE and 0.09 g of photoinitiator (184) were added into a flask under continuing magnetic stirring. Then, the flask was exposed to a power density of 80 W/cm² at room temperature for about 5 min. After dioxane was removed under vacuum at about 50 °C, a dark yellow viscous material (named EFTH-6) containing 6 mol epoxy group was obtained with a yield of 97.08%. EFTH-n (n=3, 9, 12) containing 3 mol, 9 mol, and 12 mol functionalities were prepared by a similar synthesis procedure as EFTH-6 with yields of 96.12%, 95.67%, and 95.07%, respectively. The epoxy equivalent weights of EFTH-3, EFTH-6, EFTH-9, and EFTH-12 were 1678 g/mol, 870 g/mol, 679 g/mol, and 628 g/mol, respectively. ¹H NMR spectral data of EFTH-n in DMSO-d₆ (400 MHz, δ in ppm) in Fig.S2b: 7.29 (-C=CH-, a), 4.75 (-OH), 4.41(O-CH₂-CH₂-, b), 4.11 (-CH₂-CH₂-N-, c), 3.99 (-CH₂-CH₂-O-, e), 3.81 (-O-CH₂-CH₂-, i), 3.52 (-N-CH₂-CH₂-, m), 3.36 (-O-CH₂-CH-, d), 3.05 (-CH₂-CH₂-O-, l), 2.88 (-N-CH₂-CH₂-, h), 2.71 (-CH₂-CH₂-S-, n), 2.63 (-CH₂-CH-CH₂-, g), 2.56(-CH₂-CH₂-S-, f), 2.48 (-CH-CH₂-O-, o), 2.29 (-S-CH₂-CH₂-, j), 1.72 (-CH₂-CH₂-CH₂-, k).

S1.3 Degradation of cured EFTH-n/DGEBA

The cured EFTH-n/DGEBA specimen was ground into fine powder. The powder of 0.4 g was put into a 20 mL bottle which contains 10.0 g of 2.0 mol/L H₃PO₄ formulated with equal amounts MEG and H₂O₂ (5 g MEG and 5 g H₂O₂). The bottle was heated to 90 °C and maintained for 4 h before being cooled to room temperature. The residual solid in the bottle was filtered and washed three times using distilled water, and dried under vacuum at 80 °C for 2 h. The degree of degradation (D_d) of the powder was calculated using Eq. 1:

$$D_d = \frac{W_0 - W}{W_0} \times 100\% \quad (1)$$

where W_0 is the mass of powder before degradation and W is the mass of residual solid after degradation. The degradation solution was neutralized with 2.0 mol/L NaOH before being extracted with CH₂Cl₂. The resultant organic layer was analyzed for composition using a gas chromatography-mass spectrometry (GC-MS).

S1.4 Characterization

The EFTH-n/DGEBA blends containing various EFTH-n contents were prepared by directly mixing EFTH-n, DGEBA and a stoichiometric amount of curing agent DETA-AN. The mixed samples were poured into a silicone rubber mold and cured at 25 °C for 12 h and then at 80 °C for 5 h. The cured specimens were cooled gradually to room temperature and preserved for about 12 h. The mechanical performance of the cured EFTH-n/DGEBA was measured according to standard methods. The impact strength of the cured materials (specimen dimensions 80 mm × 10 mm × 4 mm) was measured on a CEAST 9050 impact tester according to ISO 179. The tensile (specimen

dimensions 80 mm × 5 mm × 4 mm) and flexural strength (specimen dimensions 80 mm × 10 mm × 4 mm) of the cured materials were tested on a universal testing machine (Instron 5966, Instron, Norwood, MA) according to ASTM D638-14 using a loading rate of 5 mm/min and ASTM D790M-92 using a loading rate of 10 mm/min, respectively. Dynamic mechanical thermal analysis (DMA) of the cured materials (20 mm × 10 mm × 4 mm) was performed on a DMA Q800 instrument (TA Instruments, USA) over a temperature range from -120 to 200 °C at the rate of 10 °C/min and the frequency of 1 Hz.

FT-IR analyses were recorded on a Vertex 70 spectrometer (Bruker Corporation, Germany) with a potassium bromide crystal. The spectra were recorded within a range between 4000 cm⁻¹ and 400 cm⁻¹ with a 4.0 cm⁻¹ resolution using 16 scans. ¹H NMR measurements were conducted using an Avance III-400 NMR spectrometer (Bruker Corporation, Germany) with tetramethylsilane as an internal standard and DMSO-d₆ as solvent. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) experiments were performed on a MALDI-TOF system (Bruker Corporation, Germany) using trans-2-[3-(4-tert-Butylphenyl)-2-Methyl-2-propenylidene]Malononitrile as matrix and DMF as solvent.

The size distribution of particles of DGEBA and 12wt% EFTH-6/DGEBA blends with a concentration of 1 mg/mL in tetrahydrofuran were measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano S90 laser particle size analyzer. The measurements were carried out at a 90° angle and at 25 °C.

Scanning electron microscope (SEM) (SU8010, Japan Hitachi) was used to

examine the morphology of fractured surfaces of the cured samples. A thin section of the fractured surface was cut and mounted on an aluminum stub using conductive (silver) paint and then sputter-coated with gold prior to fractographic examination. SEM micrographs were obtained under conventional secondary electron imaging conditions, with an accelerating voltage of 20 kV.

GC-MS analysis was performed on an Agilent Model 6890 gas chromatographer coupled to an Agilent Model 5973 quadrupole mass spectrometer. Using CH_2Cl_2 as a solvent, the concentration of the degradation solution was found to be 10^{-6} mg/mL.

A DXR2xi Raman imaging spectrometer (Thermo Fisher Scientific, Inc., USA) was used to obtain the in-situ Raman mapping of the EFTH-n/DGEBA composites using a confocal Raman system with a spatial resolution of approximately $0.5 \mu\text{m}$. A monolithic Olympus BX40 microscope with a 50 x objective lens (8 mm) and a 633 nm laser source (5 mW) were used, and the slits and pinholes were set to $50 \mu\text{m}$ and $50 \mu\text{m}$, respectively.

Phase mode atomic force microscopy was performed using an SPM-9700HT atomic force microscope (Shimadzu Enterprise Management (China) Co., Ltd.). Topographic (height) and phase images were recorded simultaneously at ambient conditions. Samples were scanned using a high speed scanner on size of $10 \mu\text{m} \times 10 \mu\text{m} \times 1 \mu\text{m}$.

According to the classical rubber elasticity theory², the crosslink density of the cured EFTH-n/DGEBA composites can be calculated from Eq. 2.

$$E_r = 3V_eRT \quad (2)$$

where E_r is the rubbery storage modulus taken at $T_g + 50$ °C, and V_e is the crosslink density (mol/cm³), and R is the gas constant (8.314 J/K/mol), and T is the temperature at which the storage modulus is measured (K).

The positron annihilation lifetime spectra (PALS) was used to analyze the free volume properties of hyperbranched polymers³. The relationship between the average radius and free-volume holes in quantum mechanics proposed by Tao-Eldrup and τ_3 can be expressed as:

$$(\tau_3)^{-1} = 2 \left[\frac{1 - R}{R + 0.165} + \frac{1}{2} S \left(\frac{2 \pi R}{R + 0.165} \right) \right] \quad (3)$$

$$V = \frac{4}{3} \pi R^3 \quad (4)$$

$$f_v = c V_3 \quad (5)$$

where τ_3 is the orthopositronium (o-Ps) lifetime (ns), R is the vacancy radius (nm), V is the average volume of each small hole (nm³), I_3 is the positron strength (%), c is a constant (0.018 nm⁻³), and f_v (the sum of all hole volumes) is the free volume fraction (%).

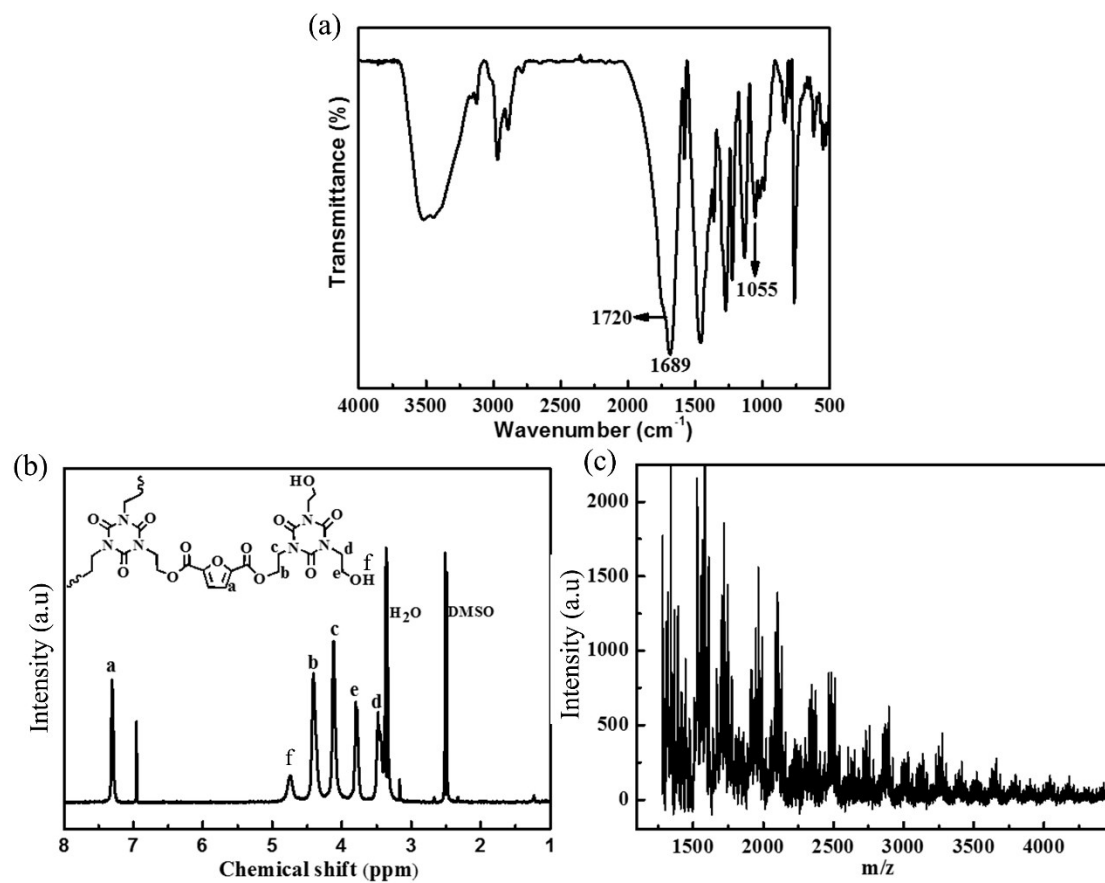


Fig. S1. (a) FT-IR, (b) ^1H NMR and (c) MALDI-TOF mass spectra of HFTH.

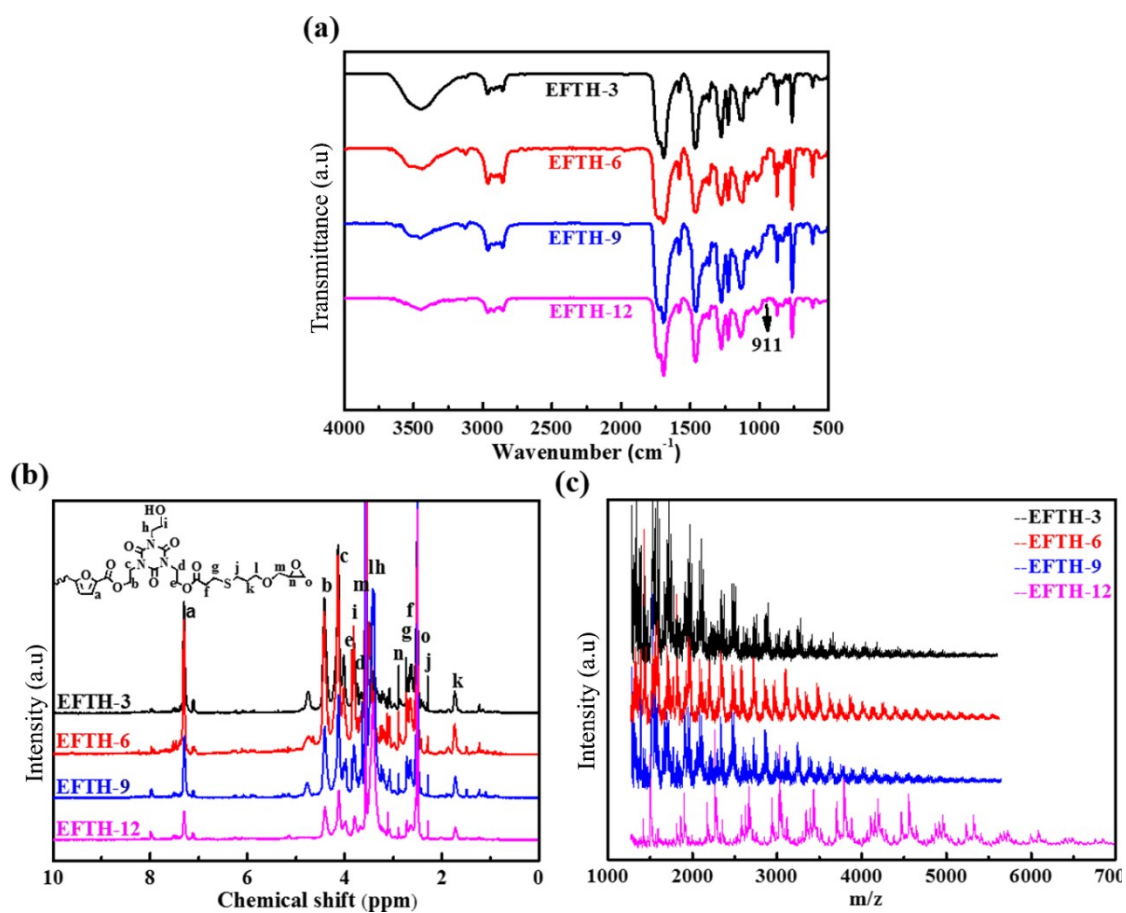


Fig. S2. (a) FT-IR, (b) ¹H NMR and (c) MALDI-TOF mass spectra of EFTH-n.

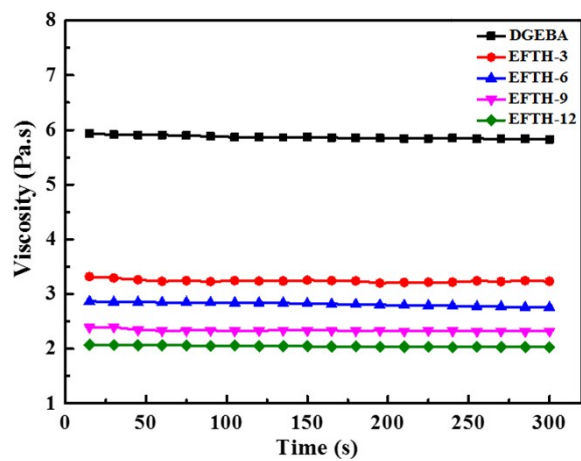


Fig. S3. Dependence of viscosity of pure DGEBA and EFTH-n on time.

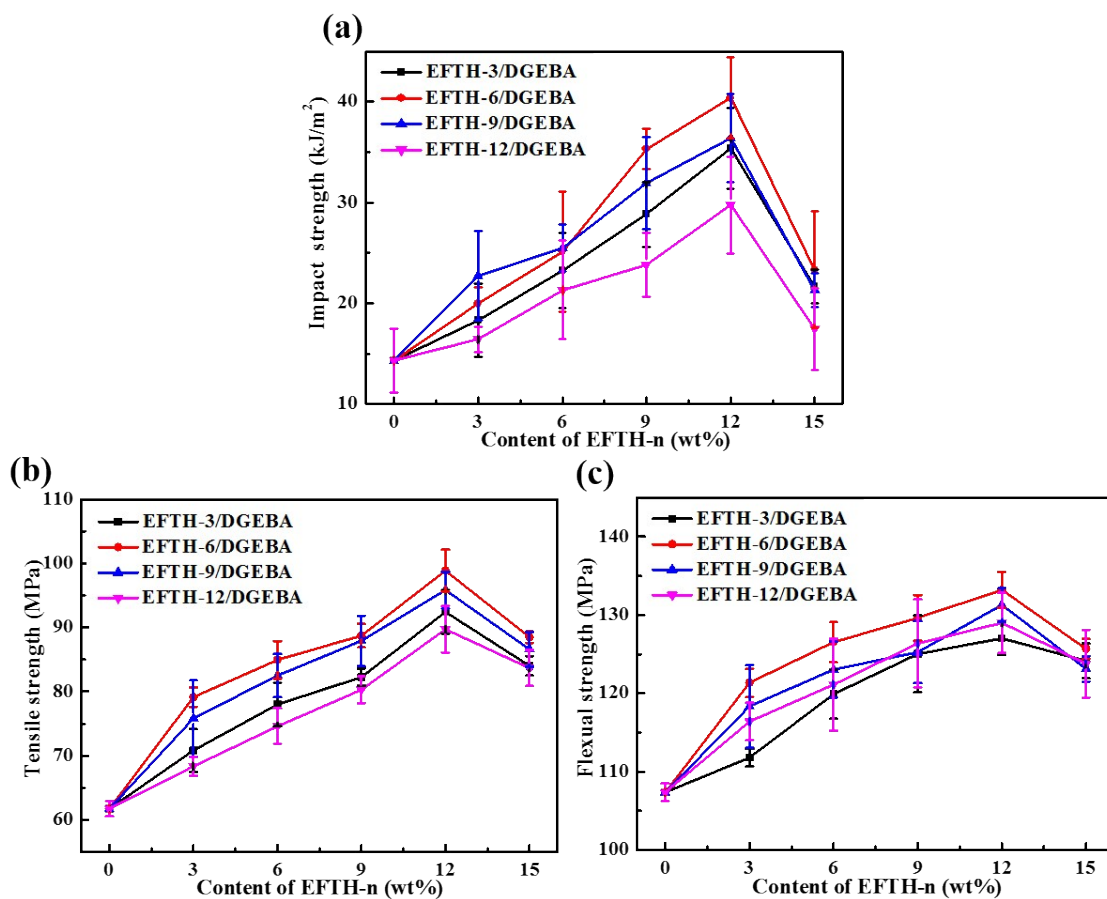


Fig. S4. The mechanical performance of cured EFTH-n/DGEBA composites (a. impact strength, b. tensile strength, and c. flexural strength).

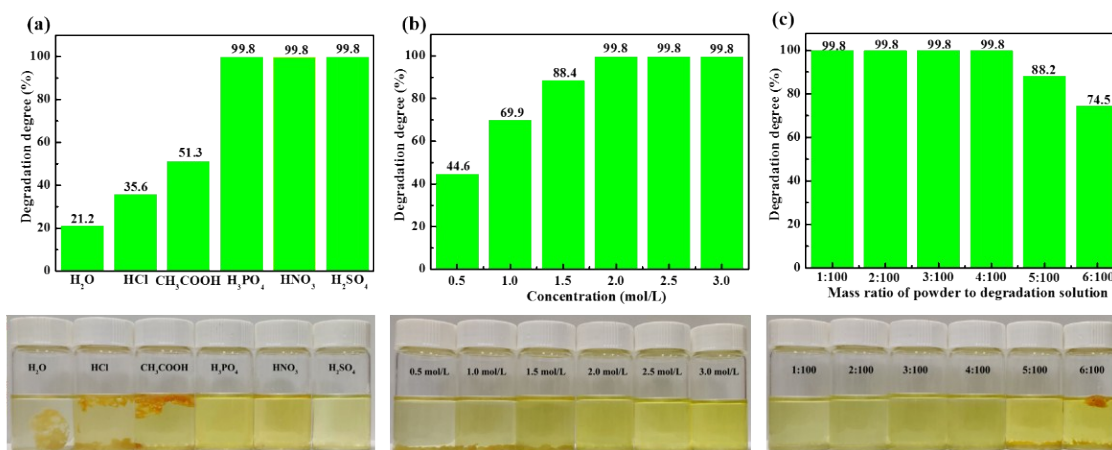


Fig. S5. Degradation degree and optical images of cured EFTH-6/DGEBA under different conditions (a. acids, b. concentration of phosphoric acid solution, c. mass ratio of powder to degradation solution).

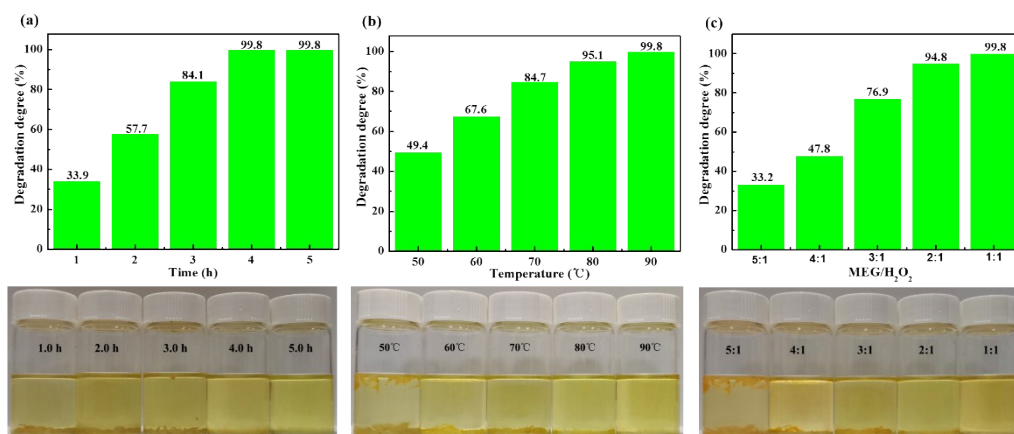


Fig. S6. Degradation degree and optical images of cured EFTH-6/DGEBA under different conditions (a. times, b. temperature, c. mass ratio of MEG/H₂O₂).

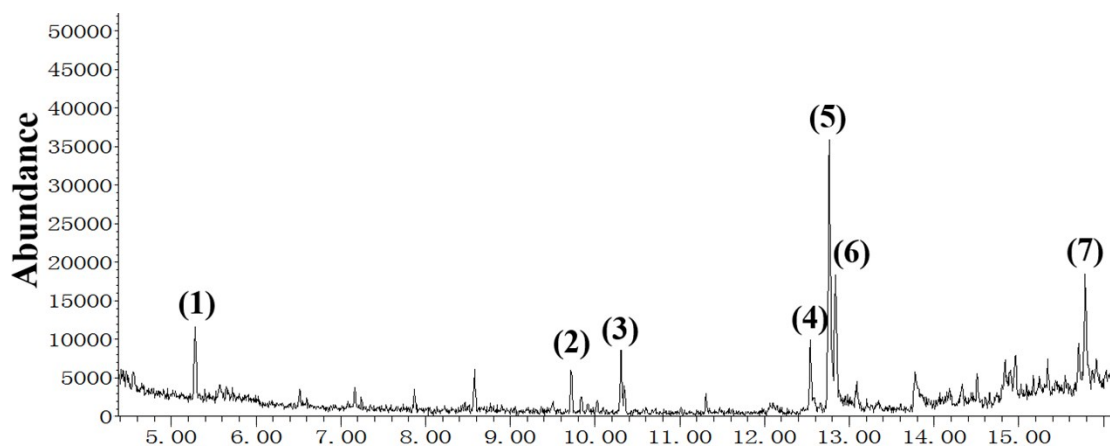

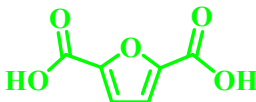
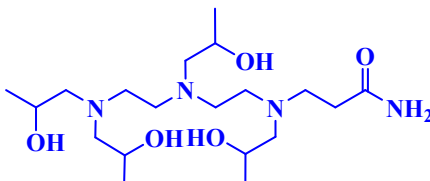
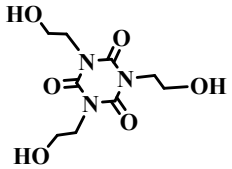
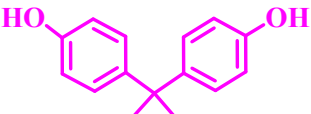
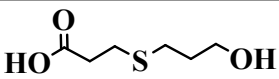
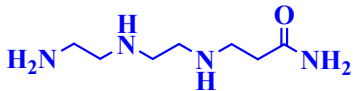
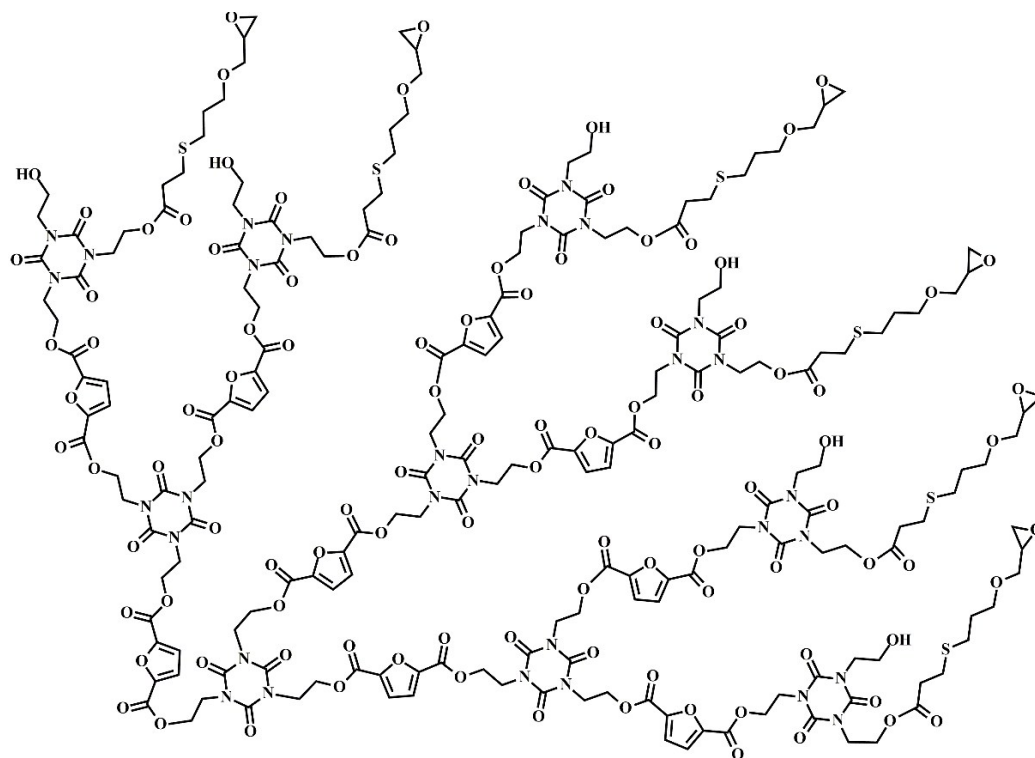


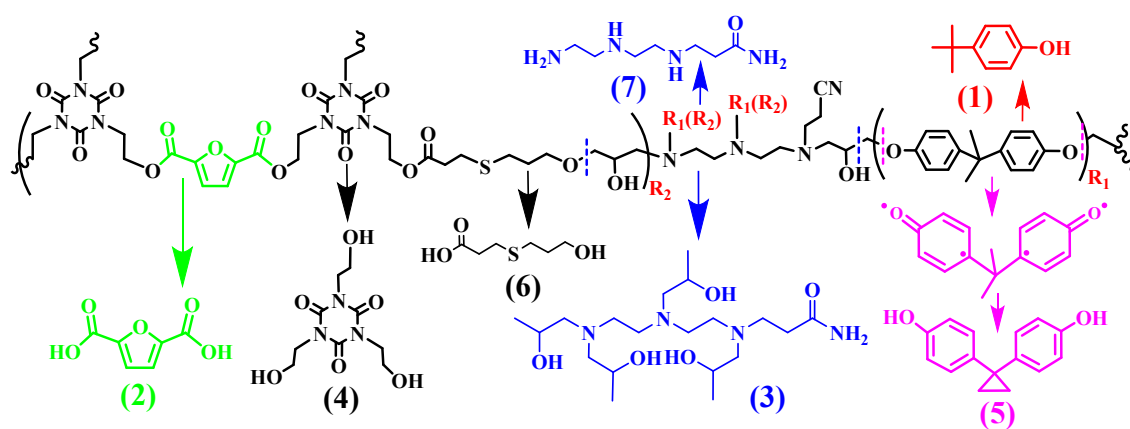
Fig. S7. GC-MS spectrum of the degradation solution of cured 12wt% EFTH-6/DGEBA.

Table S1. Degradation products of cured EFTH-6/DGEBA.

Main degraded products (EFTH-6/DGEBA)	RT (min)	m/z	chemical structure	Area (%)
(1)	5.279	136		3.24
(2)	9.715	156		2.04
(3)	10.303	348		3.87
(4)	12.534	262		2.55
(5)	12.771	226		7.52
(6)	12.834	164		3.91
(7)	15.796	174		4.87



Scheme S1. Chemical structure of EFTH-6.



Scheme S2. Degradation mechanism of the cured EFTH-6/DGEBA.

References

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