Supporting Information

Ultrastrong and high elongation degradable bio-based hyperbranched epoxy resins and carbon fiber composites

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Supplementary Methods

Materials

β-Naphthylamine (98%), maleic anhydride (MA, AR), furan-2, 5-dimethylamine (BAMF, ≥97%), 1-octadecyl mercaptan (99%), 4-amino-1-butanol (98%), 3-mercaptopropionic acid (MPA，98%), Formaldehyde aqueous solution (37%), 4-dimethylaminopyridine, 1-hydroxy cyclohexyl phenylketone, 4,4-Diaminodiphenyl methane (DDM), allyl glycidyl ether (AGE), 2,2-Dimethoxy-2-phenylacetophenone (DMPA), 1-hydroxycyclohexyl phenyl ketone, N, N-dimethylformamide (DMF), tetrahydrofuran (THF), acetone, toluene and other organic solvents were purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd, China. Diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent weight of approximately 196 g/moL was supplied by Yueyang Chemical Corp, China. Carbon fiber fabric (T800) was supplied by Anqing Kawei Technology Co., Ltd. The average diameter and density of the carbon fibers were 5 μm and 2.60 g/cm^3, respectively.

Instruments and characterization

The epoxy value was determined by testing in strict accordance with GB/T 1677-2008. The FT-IR measurements were conducted and analyzed on the Bruker VERTEX 70 FT-IR spectrometer. The ^1H NMR measurements were performed using the Bruker AVANCE III-400 nuclear magnetic resonance spectrometer, with DMSO serving as the solvent. Molecular weight and polydispersity index (PDI) of hyperbranched polymers were measured by sol-gel permeation chromatography (GPC) system (Waters 1515) using a Waters 2414 as a detector and DMF as the eluent at 35 ^oC.

Tensile property testing was carried out in accordance with ASTM D638-14. The dimensions of the composite materials were 80.0 mm × 10.0 mm × 4.0 mm, and the tensile rate was 5.0 mm/min. Flexural property testing was conducted according to ASTM D790M-92. The dimensions of the composite materials were 80.0 mm × 10.0 mm × 4.0 mm, with a fixture span of 60.0 mm, and the tensile rate was 5.0 mm/min. Impact property testing was performed following ASTM D256-97.

The dimensions of the composite materials were 80.0 mm × 10.0 mm × 4.0 mm, with a fixture span of 60.0 mm and a pendulum energy of 25 J.

The interlaminar shear strength (ILSS) of composites was tested according to ASTM D2344/D2344M-13 standards. The span-thickness ratio was approximately 4, and the loading speed is 1 mm/min. The tensile strength of fiber monofilament was tested using an INSTRON 5943 universal testing machine according to ASTM C1557-14 standard, and the load rate was 1 mm/min. The fiber bundles and monofilament samples used in the test were randomly selected from the carbon fiber twill fabric. At least 10 monofilaments were selected for testing in each group. At room temperature (25°C), Kruss k100 automatic surface tensiometer was used to test the forward contact angle and backward contact angle of the carbon fiber using water as test solvent. The surface of different carbon fibers and the fracture morphology of composites were observed via scanning electron microscope (SEM, SU8010, Japan Hitachi) at 3.0 kV accelerating voltage. The specimens were sputter-coated with gold in advance for electrical conductivity.

Thermomechanical property tests were conducted employing the DMA Q800 apparatus fabricated by TA Instruments. The dimensions of the composite material samples were measured as 40.0 mm (length) × 10.0 mm (width) × 2.0 mm (thickness). The testing frequency was set at 1 Hz, and the heating rate was maintained at 3 °C per minute throughout the temperature interval spanning from -120 °C to 200 °C. According to classical rubber elasticity theory, the crosslinking density of the cured BAFI/DGEBA copolymer can be calculated from the following equation (1)

$$E = 3V_{\mathrm{e}}R\mathrm{T} \quad (1)$$

where E is the rubbery storage modulus taken at T_g + 30 °C, V_e is the crosslink density (mol/cm^3), and R is the gas constant (8.314 J/K/moL), and T is the temperature at which the storage modulus is measured (K).

Dynamic mechanical thermal analysis (DMA) was performed on the BAFI-n/DGEBA composites (40.0 mm (length) × 10.0 mm (width) × 2.0 mm) using a DMA Q800 instrument (TA Instruments, USA) over a temperature range of 35-200 ℃ at the rate of 0.5 ℃/min and the frequency of 0.5, 1, 5, 10, 20, 30, 40, 50 Hz. Through the Williams-Langeland-Ferry formula (2)：

$$\frac{1}{log\frac{f}{f_r}} = \frac{c_2}{c_1}\left(\frac{1}{T_g - T_{gr}}\right) + \frac{1}{c_1} \quad (2)$$

In the equation, fr denotes the reference frequency of 1 Hz, f represents the frequency employed in the DMA multi-frequency mode, Tg signifies the glass transition temperature at each frequency, while c_1 and c_2 are constants (dimensionless and in units of K), determined experimentally.

The linear expansion coefficient (△α) of BAFI-n/DGEBA tested on TMA Q400. We calculate the linear expansion coefficient at a temperature of 40 ℃ ~200 ℃at a rate of 10 ℃/min by studying the difference in slope. According to the free volume theory, the formula (4) and (5) are as follows:

$$c_1 = \frac{B}{2.303f_g} \qquad c_2 = \frac{f_g}{\triangle\alpha} \quad (3)$$

$$f_g = \left(\frac{\Delta\alpha * B * \frac{c_2}{c_1}}{2.303}\right)^{\frac{1}{2}} \quad (4)$$

where B is a constant (about 1), and fg is the free volume fraction and α is the thermal expansion coefficient (CTE). △α is the difference between the expansion coefficient between rubber state and glass state, which is α_r-α_g.

Synthesis of bio-based sulfhydryl compound containing a hexahydro-s-triazine structure (ABM) and bio-based maleimide monomers (BOMIA)

Firstly, within an N_2 atmosphere, 4-amino-1-butanol (56 mmoL, 5 g), and formaldehyde solution (67 mmoL, 5.46 g) were introduced into a 250 mL three-necked flask. Subsequently, 50mL of anhydrous ethanol was employed as the solvent for dissolution. The resulting mixture was then stirred at 80 ℃ for duration of 8 h. Upon completion of the reaction, the anhydrous ethanol was removed via rotary evaporation, thereby yielding a yellow transparent oily liquid as 4,4',4''-(1,3,5-triazinane-1,3,5-triyl)tris- (butan-1-ol) (ABH) with a yield of approximately 78%. ABH (16 mmoL, 5 g) and MPA (59 mmoL, 6.29 g) were then added into a 250 mL three-necked flask, with THF serving as the solvent and DMAP (0.34 g) acting as the catalyst and anhydrous sodium sulfate for dehydration. The reaction was carried out at room temperature for 24 h. Subsequently, anhydrous sodium sulfate was separated, and THF was removed via rotary evaporation to yield a yellow, transparent, oily liquid 1,3,5-triazinane-1,3,5-triyl)tris(butane-4,1-diyl)tris(3-mercaptopropanoate) (ABM) with a yield of approximately 86%. FT-IR (KBr, cm^{-1}) of ABH and ABM are shown in Fig. S1a: 2536 cm^{-1} (-SH), 1072 cm^{-1} (C-H), 1710 cm^{-1}(-COO-) and 1367 cm^{-1} (C-N).

Add maleic anhydride (35 mmoL, 3.43g) to a 250 mL three-neck flask containing acetone as the solvent. At 10 ℃, add a β-naphthylamine (35 mmoL,5 g) acetone solution dropwise to the flask using a constant-pressure dropping funnel. After completion of the addition, react at 60 ℃ for 2 hours. Then add acetic anhydride (58 mmoL, 5.98g) as a dehydrating agent and triethylamine (6 mmoL, 0.65 g) as a catalyst, reacting for 3.5 hours. Subsequently, obtain a yellow powder through extraction, liquid-liquid separation, and rotary evaporation, designated as N-NMI. Under an N_2 atmosphere, N-phenylmaleimide (13 mmoL, 3 g) and furan-2,5-diyldimethanamine (43 mmoL, 2.54 g) were added into a 250 mL three-necked flask, with 50 mL of toluene utilized as the solvent.

After dissolution, the reaction was conducted at 90 ℃ for 12 h. Toluene was removed by rotary evaporation, and the residue was dried at 85 ℃ for 12 h to obtain an brownish-yellow powder named BAMF-NNMI. Thereafter, BAMF-NNMI (12 mmoL, 4.5 g) and 1-octadecyl mercaptan (12 mmoL, 3.69 g) were added into a 250 mL three-necked flask, with DMF as the solvent. The mixture was heated at 45 ℃ for 4 h. DMF was then removed by rotary evaporation to obtain an brown powder, BOMF-NNMI. BOMF-NNMI (9 mmoL, 6 g) and maleic anhydride (20 mmoL, 2.04 g) were added into a 250 mL three-necked flask, with DMF as the solvent. The reaction was carried out at 70 ℃ for 3 h and subsequently at 160 ℃ for 12 h. The solution was concentrated and then precipitated in ice water. The resulting brown solid powder was dried at 110 ℃ for 4 hours, yielding a brown solid powder named BOMIA (B_2). FT-IR (KBr, cm^{-1}) of N-NMI and BAMF-NNMI are shown in Fig. S1c: 1398 cm^{-1} (C-N), 1706 cm^{-1} (C=O), 3419cm^{-1} (N-H). BOMIA in Fig. S1e: 2920cm^{-1} and 2848 cm^{-1}($-(CH_2)_{17}CH_3$), 1469 cm^{-1} (C-S-C), 1014 $cm^{-1}$and 750 cm^{-1} (imide ring).

Synthesis of BAFH-n and BAFI-n

The preparation process of BAFI-12 is described as an example. ABM (9.4 mmoL, 5.35 g), BOMIA (8.5 mmoL, 6.74 g), and 1-hydroxy cyclohexyl phenyl (0.36 g) were added to a beaker with DMF (50 mL) as the solvent. The mixture was stirred by magnetic force under ultraviolet light for 80 minutes, and then AGE (9.6 mmoL, 1.09 g) was added and the mixture was stirred magnetically under UV light for 70 min, then the solvent was removed by vacuum distillation to obtain a dark brown liquid in 95.60 % yield. FT-IR (KBr, cm^{-1}) of BAFH-n is shown in Fig. S2a: 2665 cm^{-1} (-SH); FT-IR (KBr, cm^{-1}) of BAFI-n is shown in Fig. S2d: 905 cm^{-1}(epoxy group). The average-molecular weights (Mn) of BAFH-6, BAFH-12, and BAFH-24 are 3600 g/mol, 7660 g/mol, and 22180 g/mol, respectively, being close to their theoretical molecular weights in Table S1. Mn of BAFI-6, BAFI-12, and BAFI-24 are 4125 g/mol, 10100 g/mol, and 30270 g/mol in Fig. S2f, respectively.

Preparation of BAFI-n/DGEBA copolymer

The composite resins BAFI-n/DGEBA curing mechanism are shown in Scheme 1. As an example, the process of preparing 12 wt% BAFI-12/DGEBA copolymer is described here. BAFI-12 (0.35 mmoL, 5 g) was mixed with DGEBA (36.67 g) at room temperature, the stoichiometric cross-linking agent (DDM, 57.4 mmoL, 11.38 g) was added by continuous stirring and stirred, and the mixture was homogenized by stirring it at high temperature and mixed with DGBEA at room temperature, and the homogenized mixture was mixed at a high temperature to expel air bubbles quickly, and when there were no air bubbles, the mixture was quickly poured into silica gel molds. The molds were then cured at 60°C for 1h, 80 ^{o}C for 3 h, 120 ^{o}C for 2 h, and finally at 160 ^{o}C for 1h.

Preparation of PCF and TCF.

Carbon fiber fabric (T800, 3.0 g) was placed in a Soxhlet extractor containing 50 mL acetone and refluxed at 80 °C for 48 h to remove the surface sizing agent, and the resulting carbon fiber fabric was named PCF. Subsequently, 3.00 g of PCF was submerged in a solution comprising 3.00 g of BAFI-12, 100 mL of DMF, and 0.18 g of DMPA. This mixture was then irradiated in a 500 W UV reactor for 70 minutes to induce a thiol-ene click reaction. The resulting carbon fiber fabric was rinsed with DMF to remove any unreacted mercaptans, followed by drying at 80 °C for 36 h to yield functionalized carbon fiber fabric (TCF).

Preparation of PCF/DGEBA and TCF-BAFI-12/DGEBA Composites

Seven pieces of PCF with a size of 10 cm × 10 cm were immersed in a transparent mixture of DGEBA (11.59 g) and DDM (15.2 mmol, 3.01 g) respectively, and then stacked layer by layer in the metal mold and cured under the hot press at 80 ℃ for 1 h, 120 ℃ for 3 h, and 160 ℃ for 1 h to produce DGEBA/PCF composites. Seven pieces of each fabric were immersed in a mixture containing DGEBA (11.15 g), BAFI-12 (0.11 mmol, 1.52 g) and DDM (17.5 mmol, 3.47 g). The assembly and curing process identical to that described above was employed to produce TCF-BAFI-12/DGEBA composites.

Degradation and recycling of cured TCF-12wt% BAFI-12/DGEBA copolymer

The composites with dimensions of 10 cm (length) × 1 cm (width) × 1 mm (thickness) was immersed in a 1 mol/L phosphoric acid in (THF:H_2O_2=1:1) solution to decompose for 12 hours at 80 ℃. After the degradation reaction was completed, the solution was cooled to room temperature. The degradation solution was directly neutralized with 1mol/L NaOH/H_2O solution and then extracted. The recovered carbon fiber fabric was washed with acetone and distilled water and placed at 80 ℃ for 12 h to obtain recycled carbon fiber fabric (RCF). The degradation solution was separated by filtration to give the degradation product RBAFI with a recovery of about 96%.

Supporting Figures and Discussion

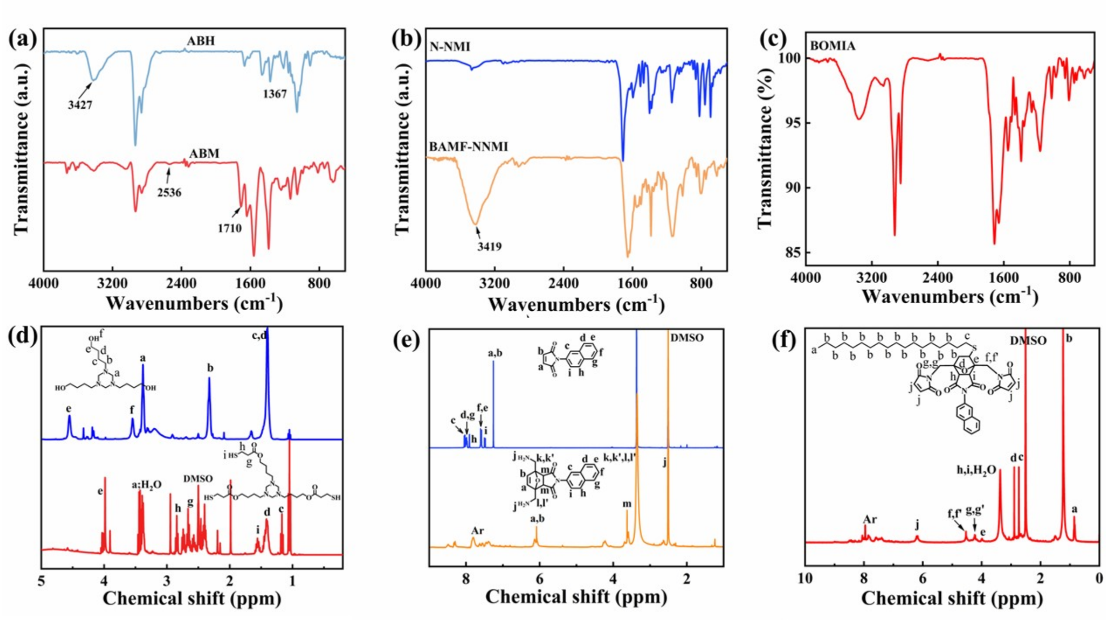

Fig. S1. Spectra of ABH, ABM, N-NMI, BAMF-NNMI and BOMIA. (a-c) FT-IR and (d-f) ^{1}H NMR.

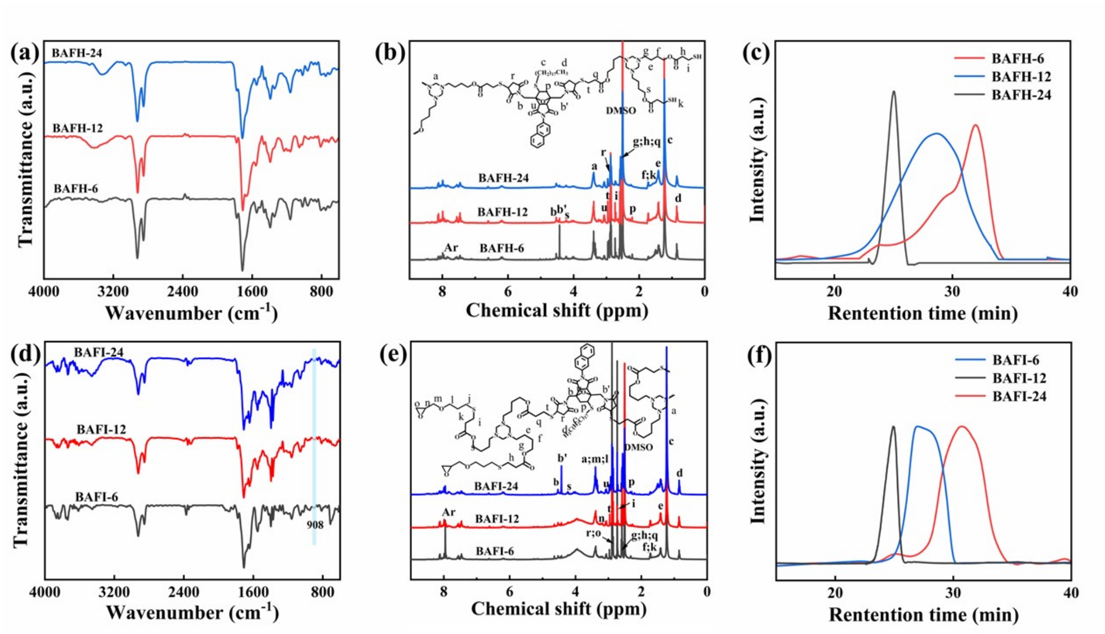

Fig. S2. Spectra of hyperbranched polymers. (a-c) FT-IR, ^{1}H NMR and GPC of BAFH-n, and (e-f) BAFI-n.

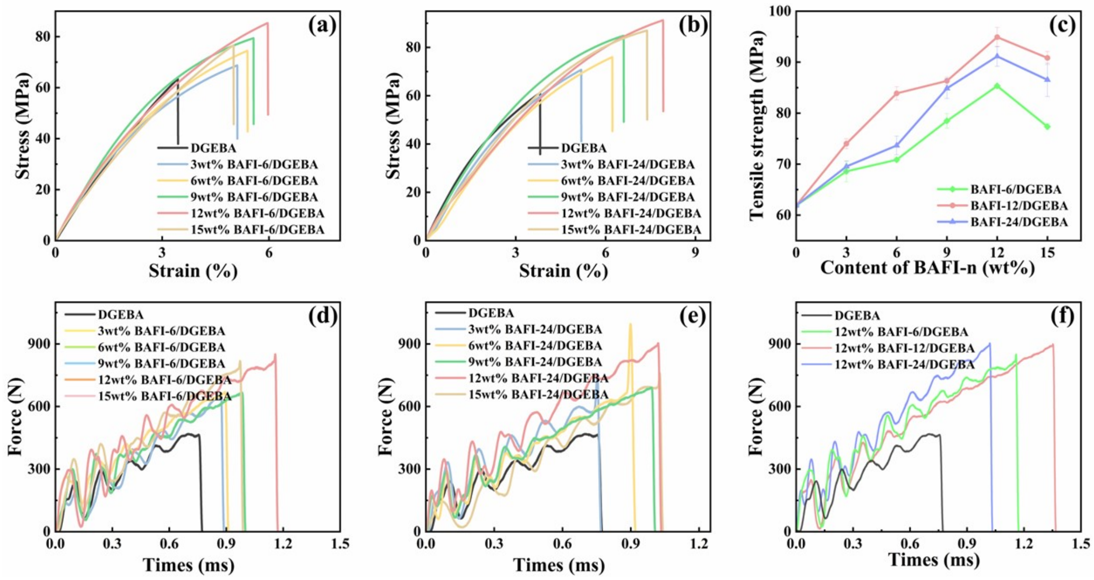

Fig. S3. Tensile and impact properties of BAFI-n. (a) Stress-strain curves of BAFI-6/DGEBA, and (b) Stress-strain curves of BAFI-24. (c) Tensile strength of BAFI-n/DGEBA. (d) Impact force-displacement curve of cured BAFI-6/DGEBA, (e) BAFI-24/DGEBA, and (f) 12wt% BAFI-n/DGEBA.

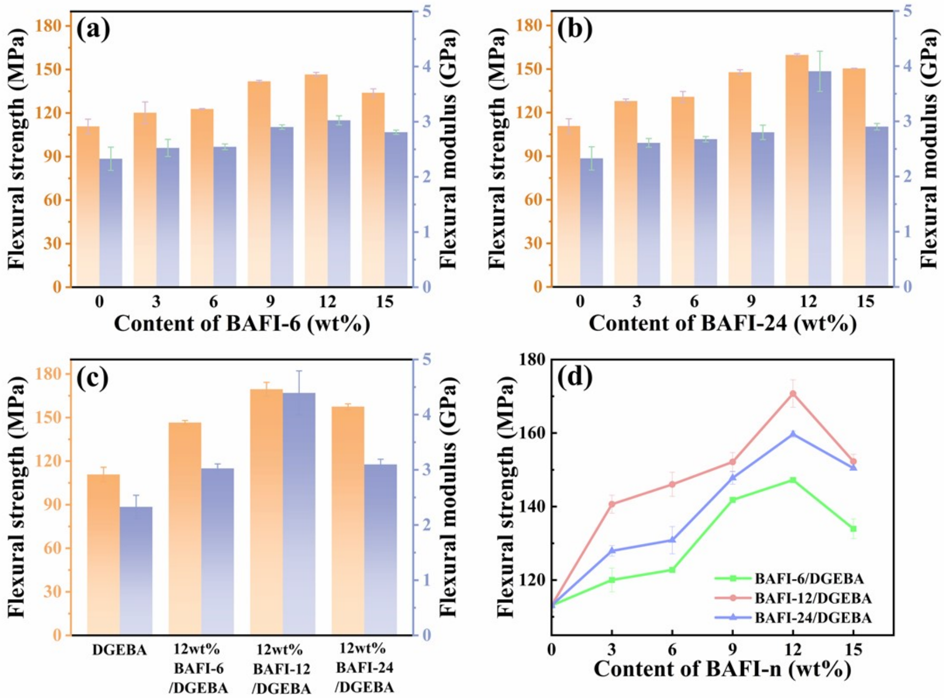

Fig. S4. Flexural properties of BAFI-n. (a)Flexural strength and modulus of BAFI-6/DGEBA, (b) BAFI-24/DGEBA, and (c) 12wt% BAFI-n/DGEBA. (d) Flexural strength of BAFI-n/DGEBA.

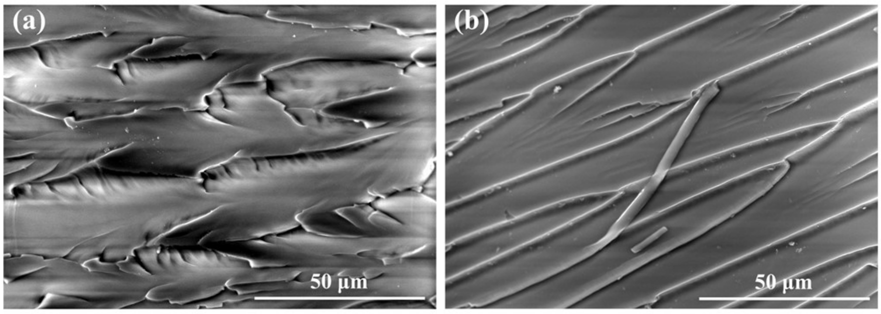

Fig. S5. SEM micrographs of DGEBA and BAFI/DGEBA copolymer. (a) DGEBA. (b) 12wt% BAFI-12/DGEBA.

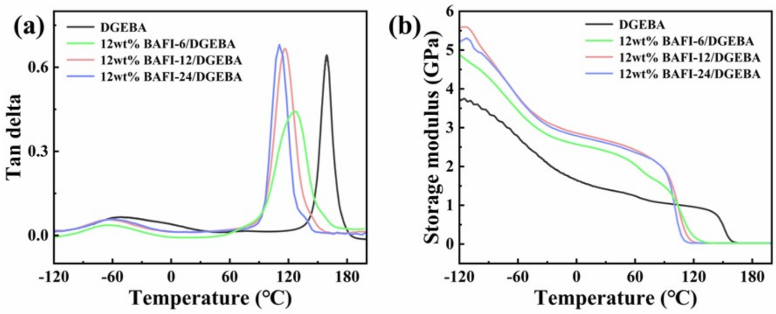

Fig. S6. DMA curves of cured 12wt% BAFI-n/DGEBA. (a) Relaxation curves. (i)DMA curves.

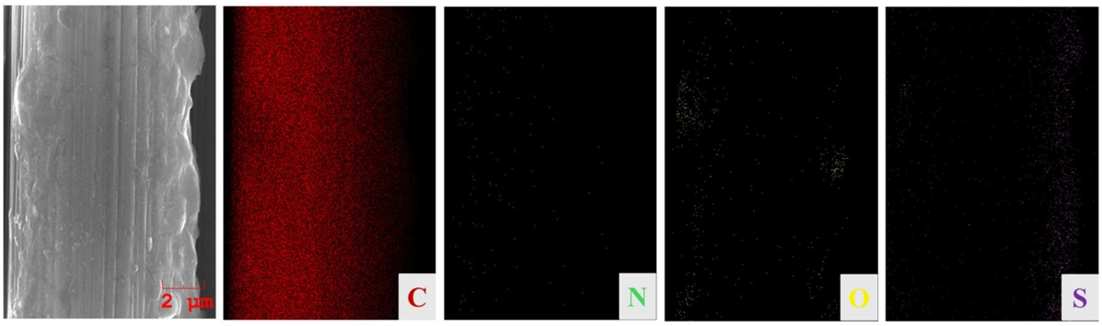

Fig. S7. SEM image of TCF and the corresponding elemental mapping images of C, N, O, and S.

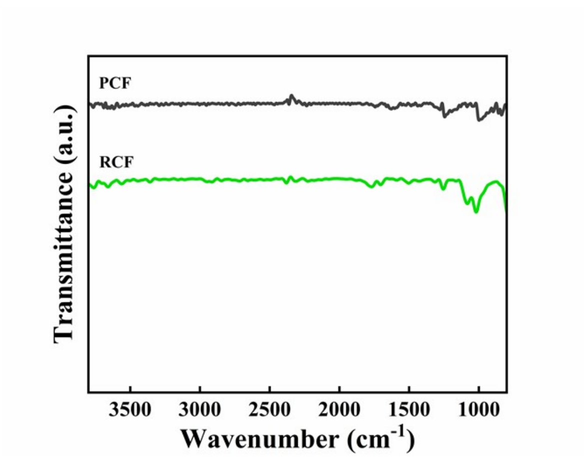

Fig. S8. FT-IR of RCF and PCF.

Supporting Tables

Table S1. Molecular weights and PDI of BAFH-n.

BAFH-n	BAFH-6	BAFH-12	BAFH-24
Theoretical Mn, g/mol	4771	12836	29195
M_n from GPC, g/mol	3600	7660	22180
PDI	1.02	1.38	1.04

Table S2. Molecular weights and PDI of BAFI-n.

BAFI-n	BAFI-6	BAFI-12	BAFI-24
Theoretical Mn, g/mol	5342	14206	31934
M_n from GPC, g/mol	4125	10100	30270
PDI	1.06	1.02	1.05

Table S3. Comparison of tensile strength and strain of the cured BAFI-12/DGEBA copolymer with other cured copolymers.

	Tensile strength (MPa)	Strain (%)
12wt% EFTH-6/DGEBA[1]	98.00	3
DMT 0.1[2]	93.70	5.8
ImON-10[3]	66.10	9.45
E51/HP-HMEP (20 wt%)[4]	98.50	3.6
PEM-1.0[5]	33.63	9.14
12 wt% DSEHP-5/DGEBA[6]	104.50	4.68
10%EHTPB-E51/POSS/DDM[7]	77.89	6.82
ECFGE/DDM-3[8]	48.20	5.19
DGEA/DDM[9]	59.50	2.8
IM-AA1.00[10]	76.5	8.10
VA-FA-EP/DDM[11]	81.31	4.49
12wt% BAFI-12/DGEBA	96.96	10.16

Table S4. DMA data of DGEBA and BAFI-n/DGEBA copolymer.

	T_g (°C)	β (°C)	E_b (MPa)	E_c (MPa)	$V_e \times 10^{-3}$ (mol/cm^3)
DGEBA	158.97	-48.40	1471.34	21.64	1.88
3wt% BAFI-12/DGEBA	141.75	-51.92	2198.71	22.52	2.03
6wt% BAFI-12/DGEBA	136.58	-58.00	2206.59	22.99	2.10
9wt% BAFI-12/DGEBA	126.00	-61.83	2556.35	23.36	2.18
12wt% BAFI-12/DGEBA	116.66	-65.00	2732.00	27.89	2.66
15wt% BAFI-12/DGEBA	111.67	-60.83	2555.00	23.12	2.23
12wt% BAFI-6/DGEBA	127.83	-63.91	2460.18	22.35	2.08
12wt% BAFI-24/DGEBA	110.67	-61.00	2660.00	24.54	2.38

*T_g refers to glass transition temperature. E_b refers to a modulus at room temperature (20 °C). E_c refers to a modulus at temperature of T_g + 30 °C. β refers to β-relaxation peak temperature. V_e refers to crosslinking density.

Table S5. Tg at different frequencies.

	0.5 HZ (°C)	1 HZ (°C)	5 HZ (°C)	10 HZ (°C)	20 HZ (°C)	c_2/c_1
DGEBA	170.48	172.18	176.52	178.69	178.73	5.7318
3 wt% BAFI-12/DGEBA	148.73	150.36	154.95	156.52	158.13	5.2695
6 wt% BAFI-12/DGEBA	129.05	130.69	133.83	135.41	138.50	5.2363
9 wt% BAFI-12/DGEBA	126.97	128.61	132.81	134.86	134.90	5.2170
12 wt% BAFI-12/DGEBA	121.20	122.82	125.96	127.54	130.63	5.1492
15 wt% BAFI-12/DGEBA	117.84	119.48	124.18	125.75	127.32	5.6726
12 wt% BAFI-6/DGEBA	128.76	130.40	135.02	136.57	138.15	5.6513
12 wt% BAFI-24/DGEBA	121.01	122.65	125.79	127.36	130.45	5.2359

Table S6. CTE and fg of DGEBA and BAFI-n/DGEBA.

	$\alpha_{v,g}$ μm/(m·°C)	$\alpha_{v,r}$ μm/(m·°C)	$\triangle\alpha$	f_g (%)
DGEBA	205.9	86.30	119.60	1.725
3 wt% BAFI-12/DGEBA	194.9	83.74	111.16	1.594
6 wt% BAFI-12/DGEBA	188.8	81.76	107.04	1.560

9 wt% BAFI-12/DGEBA	185.7	79.55	106.15	1.551
12 wt% BAFI-12/DGEBA	176.2	73.42	102.78	1.515
15 wt% BAFI-12/DGEBA	192.8	76.14	116.66	1.627
12 wt% BAFI-6/DGEBA	186.1	78.34	107.76	1.626
12 wt% BAFI-24/DGEBA	192.8	76.14	106.15	1.553

Table S7. Surface element analysis of PCF and TCF.

Samples	Atomic element content (%)			
	C	O	N	S
PCF	79.66	17.00	3.34	-
TCF	76.60	16.30	3.45	3.65

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