

Rapid self-healing, multiple recyclability and mechanically robust plant oil-based epoxy resins enabled by incorporating covalent bondings

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Experimental Materials

1,4-phenylenediboronic acid (BDA) and 4-dimethylaminopyridine (DMAP) were provided by Shanghai Titan Technology Co., Ltd. 1-thioglycerol was bought from Saan Chemical Technology (Shanghai) Co., Ltd. N-heptane was provided by Tianjin Baishi Chemical Industry Co. Ltd. Linseed oil (LO), rubber seed oil (RSO) and epoxidized soybean oil were purchased from Guangzhou Fufei Technology Co., Ltd. Olive oil (OO) was provided by Tianjin Longke Chemical Products Co., Ltd. Formic acid was bought from Tianjin Yongda Chemical Reagent Co. Ltd. H₂O₂ and acetone were provided by Guangzhou Fufei Technology Co., Ltd. MgSO₄ was purchased from Fuchen (Tianjin) Chemical Reagent Co., Ltd. Triethylamine (TEA), anhydrous magnesium sulfate (MgSO₄), NaHCO₃ and ethyl acetate were obtained from Aladdin Reagent (China). N-heptane, diethyl ether and diiodo-methane were bought from Tianjin Damao Chemical Reagent (China). All materials were used as received without further purification.

Preparation of 2, 2'-(1, 4-Phenylene)-bis [4-mercaptan-1, 3, 2-dioxaborolane] (BDB).

The monomer BDB was synthesized by the reaction between 1,4-phenylenediboric acid with 1-thioglycerol at room temperature by the method reported previously (*Macromolecules* 2019, 52 (10), 3805-3812). In detail, 1,4-phenylenediboric acid (3.0 g) and 1-thioglycerol (4.01 g) were dissolved in the mixed solvent of tetrahydrofuran (80 mL) and deionized water (0.1 mL). After the addition of $MgSO_4$ (5.0 g) into the solution, the mixture was allowed to react for 24 h at room temperature. Then, the precipitated white powders were collected by suction filtration, washed with n-heptane for at least five times, and dried in vacuo to give BDB in 99% yield. 1H NMR, ^{13}C NMR and mass spectrometry were applied to characterize the chemical structure of BDB.

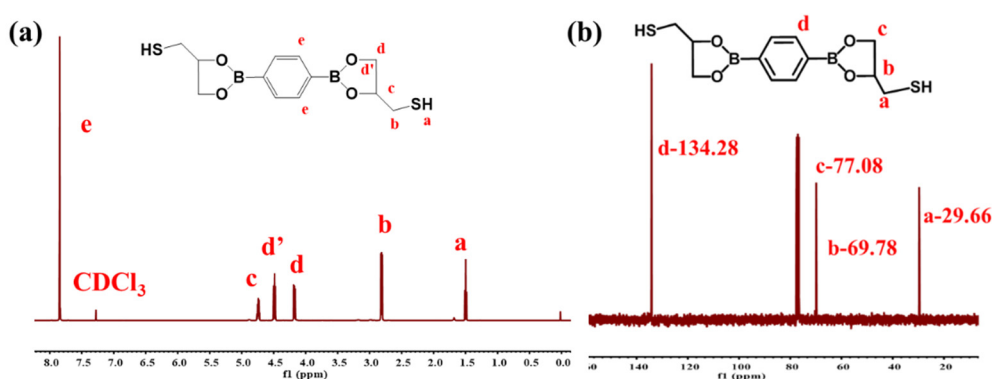


Figure S1. 1H NMR spectra of BDB (a). (1H NMR (CDCl₃, 600 MHz): BDB- δ 7.84 (s, 4H), 4.75 (m, 2H), 4.49 (dd, J=8 Hz, 7Hz, 2H), 4.19 (dd, J=13 Hz, 5.5Hz, 2H), 2.82 (dd, J=7.5 Hz, 5Hz, 4H), 1.49 (t, J=7.5 Hz, 2H)). ^{13}C NMR spectra of BDB (b). (^{13}C NMR (CDCl₃, 600 MHz): BDB- δ 134.28, 77.08, 69.78, 29.66 ppm. The carbon atoms adjacent to the boron were not detected).

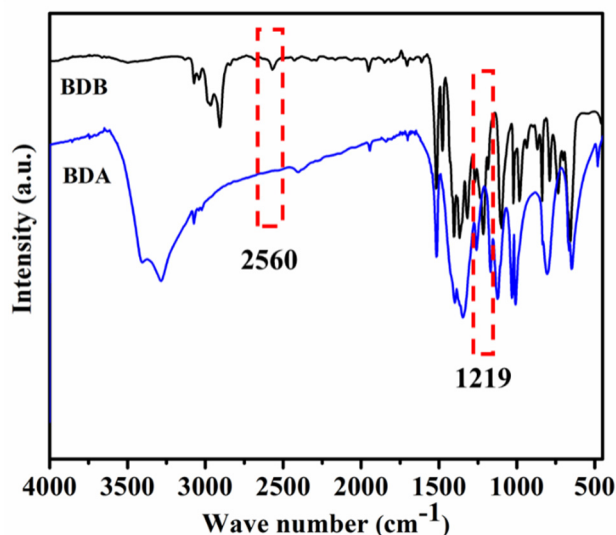


Figure S2. FT-IR spectra of BDB.

As shown in Figure S2. Compared with BDA, the characteristic peaks of -OH group at 3000-3500 cm^{-1} disappeared in the resulting monomer BDB, and the new characteristic peaks of -SH group appeared at 2560 cm^{-1} . Moreover, the -B-O absorbance peaks appeared in the resulting monomer BDB. The above results demonstrated the successful synthesis of BDB.

Synthesis and characterization of epoxidized vegetable oils

The epoxidized vegetable oils with different epoxy functionalities were synthesized from various vegetable oils by the method reported previously (*ACS Appl. Mater. Inter.* 2015, 7 (2), 1226-1233). Specifically, the vegetable oils and formic acid were mixed (the ratio of vegetable oil to formic acid is 1: 4.5) in a 100 mL flask equipped with mechanical stirring and reflux condensation at 50 °C, then H_2O_2 (30 %) was dropwisely added into the mixture over a period of 2 h with vigorously stirring (the molar ratio of double bonds in vegetable oils to H_2O_2 : 1:1.8). After stirring for 8h at 50 °C, the reaction mixture was neutralized by NaHCO_3 and extracted with diethyl ether. The resulting epoxidized vegetable oils were obtained after drying with MgSO_4 , filtration and removal of ethyl ether in vacuo. ^1H NMR and GPC were applied to characterize the chemical structure of the epoxidized vegetable oils.

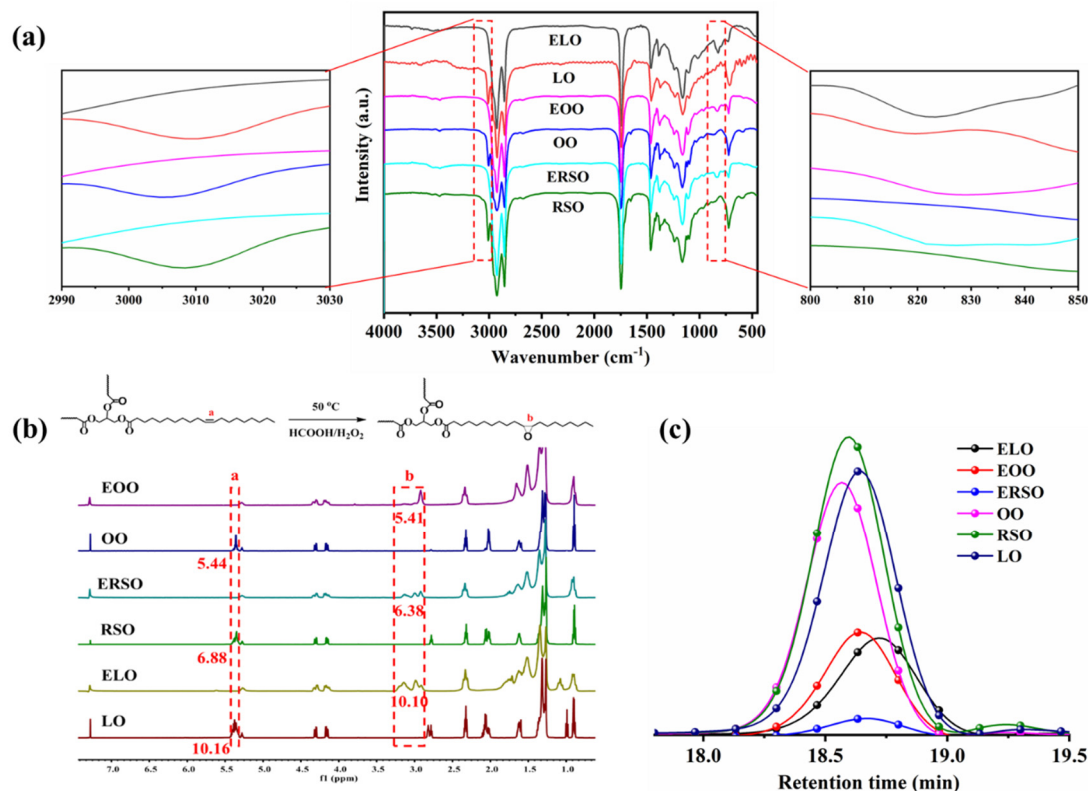


Figure S3. FT-IR spectra (a), ¹H NMR spectra (b), and GPC curves (c) of vegetable oil and epoxidized vegetable oil.

The successful preparation of epoxidized vegetable oils was confirmed by FT-IR, ¹H NMR, and GPC curves. Figure S3 (a) shows FT-IR spectra of the original vegetable oils and resulting epoxidized vegetable oils. Obviously, compared with original vegetable oils, the C=C double bonds (between 3000 and 3010 cm⁻¹) of resulting epoxidized vegetable oils disappeared and the peaks of epoxy groups at 824 and 842 cm⁻¹ were formed.

As shown in Figure S3 (b), the carbon-carbon double bonds in original vegetable oil (between 5.3 and 5.6 ppm) disappeared after epoxidation, and the epoxy groups (between 2.8 and 3.2 ppm) were formed in epoxidized vegetable oil. The H numbers of C=C double bonds and epoxy groups (the peaks area at 4.1-4.2 ppm is set to a constant of 2 to normalize the H numbers of original vegetable oil and epoxidized vegetable oil) were shown in Table S1, and the conversion ratios of C=C double bonds to epoxy groups are all more than 95% of different vegetable oils, which

illustrated the successful preparation of epoxidized vegetable oils.

As shown in Figure S3 (c), both original vegetable oils and resulting epoxidized vegetable oils were single peaks, which illustrated the uniformity of the samples. Moreover, compared with original vegetable oils, the epoxidized vegetable oils have a higher molecular weight, which is attributed to the formation of epoxy groups. The specific values are shown Table S1.

Table S1. Properties of the OO, RSO, LO and their epoxidized vegetable oils.

Sample	C=C double bonds per triglyceride	Epoxy groups per triglyceride	Molecular weight	PDI
OO	2.72	0	1344/1354	1.01
RSO	3.44	0	1305/1321	1.01
LO	5.08	0	1375/1402	1.02
EOO	0	2.71	1525/1552	1.02
ERSO	0	3.19	1480/1499	1.02
ESO	0	4.12	1420/1458	1.02
ELO	0	5.05	1426/1458	1.02

Epoxidized linseed oil (ELO), epoxidized soybean oil (ESO), epoxidized rubber seed oil (ERSO), epoxidized olive oil (EOO).

The successfully preparation of BDB and epoxidized vegetable oil were confirmed by ^1H NMR, ^{13}C NMR, FTIR, and GPC. The conversion ratios of C=C double bonds to epoxy groups are all higher than 95 %. The yield of the epoxidized vegetable oils from linseed oil, rubber seed oil and olive oil all reached 98 %. Epoxidized soybean oil was bought and used as received without any further purification.

Preparation of vegetable oil-based epoxy resins

BDB, epoxidized vegetable oils were mixed uniformly in a siliconized glass tube with predetermined proportions with DMAP (The amount of DMAP: 2.5 wt. % of BDB and vegetable oil monomer) as the catalyst. The mixture was poured into a siliconized glass mold and cured at 160 °C-180 °C for 30 min to obtain the resulting epoxy resins. the films were heated at 80 °C for 48 h before test. The recipe and curing process for the epoxy resins are shown in Table S2.

Table S2. The molar ratio of raw materials and curing temperature

Sample	Molar ratios of SH:C=C	Curing temperature (°C)
BESO-0.8:1	0.8:1	160
BESO-0.9:1	0.9:1	160
BESO-1.0:1	1.0:1	160
BESO-1.2:1	1.2:1	160
BESO-1.4:1	1.4:1	160
BESO-1.6:1	1.6:1	160
BESO-1.8:1	1.8:1	160
BESO-2.0:1	2.0:1	160
BESO'-0.9:1	0.9:1	180
BESO'-1.0:1	1.0:1	180
BESO'-1.2:1	1.2:1	180
BESO'-1.4:1	1.4:1	180
BEOO	1.2:1	160
BERSO	1.2:1	160
BELO	1.2:1	160

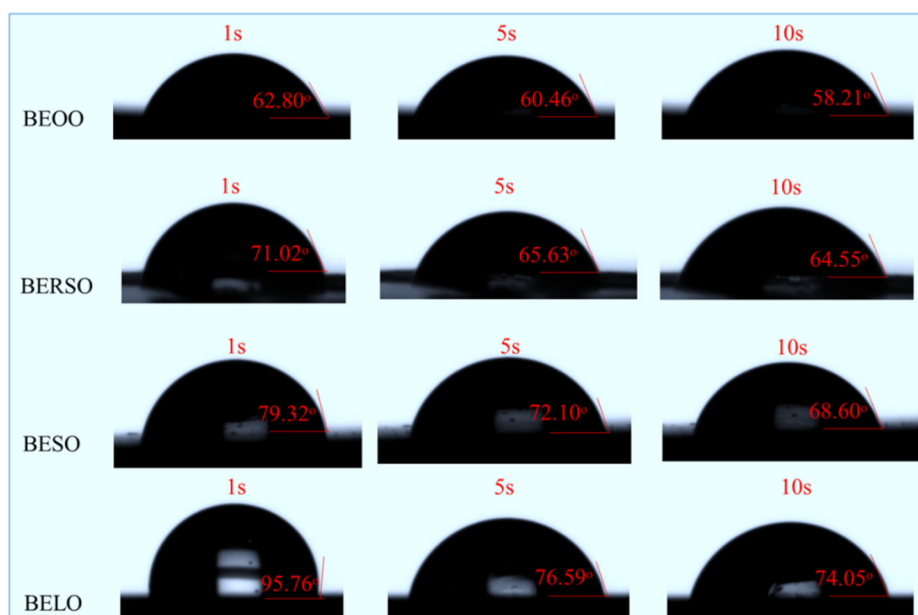


Figure S4. Water contact angle of epoxy resins based on different epoxidized vegetable oils (prepared with optimal curing condition: curing temperature 160 °C; the molar ratio of BDB and epoxidized vegetable oils 1.2:1 and the curing time 20 min).

Characterization

^1H NMR and ^{13}C NMR spectra of the monomers were recorded on Bruker AV 600 (600 MHz) instrument at 25 °C in CDCl_3 . The mass spectra of the monomers were measured by LC-MS: AB Sciex API 3200.

FTIR spectra of the monomers were recorded on the Thermo-Nicolet Nexus 670 FT-IR spectrum from 400 to 4000 cm^{-1} . Gel Permeation Chromatography (GPC) measurement of the monomers was carried out using THF-eluted Waters e2695 with a 2414 RI detector.

A DSC 214 Polymer instruments was used for differential scanning calorimetry (DSC) analysis with temperature ranging from -50 °C to 150 °C, and DSC Q2000 TA instruments was used to determine the thermal curing behavior with temperature ranging from -50 °C to 350 °C.

Thermogravimetric Analysis (TGA) of the samples were recorded on the TRIOS Discovery TGA 550 from 30 -700 °C with a heating temperature of 10 °C/min. The transmittance of the sample films was measured by the Abbe Refractometer.

The tensile properties of the samples were performed using the Shimadzu AGS-X electronic universal testing machine at the 100 mm/min extension rate. The sample films were cut into 25 mm × 10 mm splines for testing, and each sample was averaged 4 times in parallel.

The water and diiodo-methane contact angle measurements were recorded on Kruss Hamburg DSA 100 instrument with the seat-drop method.

The gel content test of the sample films was conducted by immersing samples in acetone at room temperature for 72 h. The solvent was replaced with fresh acetone for 12 h. After immersing for every 24 h, the samples were weighted after drying at 60 °C. The gel content was obtained from average values of at least four replicates of each sample. The gel fraction was defined as the following equation:

$$\text{Gel content (\%)} = m_1 / m_0 \times 100\% \quad (1)$$

Where m_0 and m_1 are the weight of samples before and after immersing in acetone.

For self-healing tests, each sample was cut into rectangle samples (length × width × thickness: 25 mm × 10 mm ×). These samples were cut into two separate pieces, then the two pieces were contacted together by gentle pressing for 1 min to allowing healing. The seal-healing experiments were carried on different humidity, different time and different temperature. In order to monitor the self-healing behavior under temperature for different healing time, the polarized optical microscopy and scanning electron microscope (SEM) were used to observe the healing process. The self-healing value was defined as the following equation:

$$\text{Healing efficiency (\%)} = T_1 / T_0 \times 100\% \quad (2)$$

Where T_0 and T_1 are the tensile strength (or elongation at break or toughness or Young's modulus) of samples before and after self-healing.

For recycling experiments, the samples were cut into small pieces and remolded at 160 ° C with a pressure of 40 MPa for 20 min. The tensile testing was carried to compare the performance of the samples before and after recycling.

Table S3. Mechanical properties of epoxy resins based on ESO with different molar ratios and curing temperature.

Samples	Curing Temperature (°C)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Toughness (MPa)
BESO-0.9:1	160	16.32 ±1.10	76.03 ±5.00	111.60 ±0.25	9.41±1.02
BESO-1:1	160	21.79 ±0.22	51.79 ±24.49	257.75 ±0.54	9.39 ±5.01
BESO-1.2:1	160	29.40 ±0.53	32.42 ±8.74	319.95 ±0.36	6.89 ±2.48
BESO-1.4:1	160	39.76 ±2.30	18.74 ±2.89	471.95 ±0.71	5.05 ±0.86
BESO-0.9:1	180	25.08 ±2.00	38.50 ±3.00	230.16 ±0.29	6.90 ±2.14
BESO-1:1	180	27.31 ±1.30	23.67 ±9.13	278.79 ±0.17	3.74 ±0.96
BESO-1.2:1	180	31.00 ±1.14	21.59 ±7.08	355.20 ±0.73	4.08 ±2.17
BESO-1.4:1	180	41.89 ±0.32	24.53 ±1.61	557.75 ±0.93	7.37 ±0.62

Table S4. Thermal and mechanical properties of epoxy resins from different epoxidized vegetable oils

Sample	Epoxy groups per triglyceride	TGA		DSC (T_g / °C)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Toughness (MPa)	Water contact angle (θ)
		T_5	T_{50}						
BEOO	2.71	290.92	333.81	24.48	5.87±0.60	59.54±10.44	17.15±0.23	2.04±0.41	60.08±0.19
BERSO	3.19	281.32	325.09	39.97	13.82±1.03	78.41±25.84	100.13±0.26	7.77±2.53	66.57±2.29
BESO	4.12	268.93	321.57	61.12	30.72±2.24	26.43±8.67	332.25±0.45	5.26±2.38	71.70±0.44
BELO	5.05	242.38	315.81	86.90	43.19±3.69	24.94±0.62	374.59±0.64	5.73±0.82	75.85±0.25

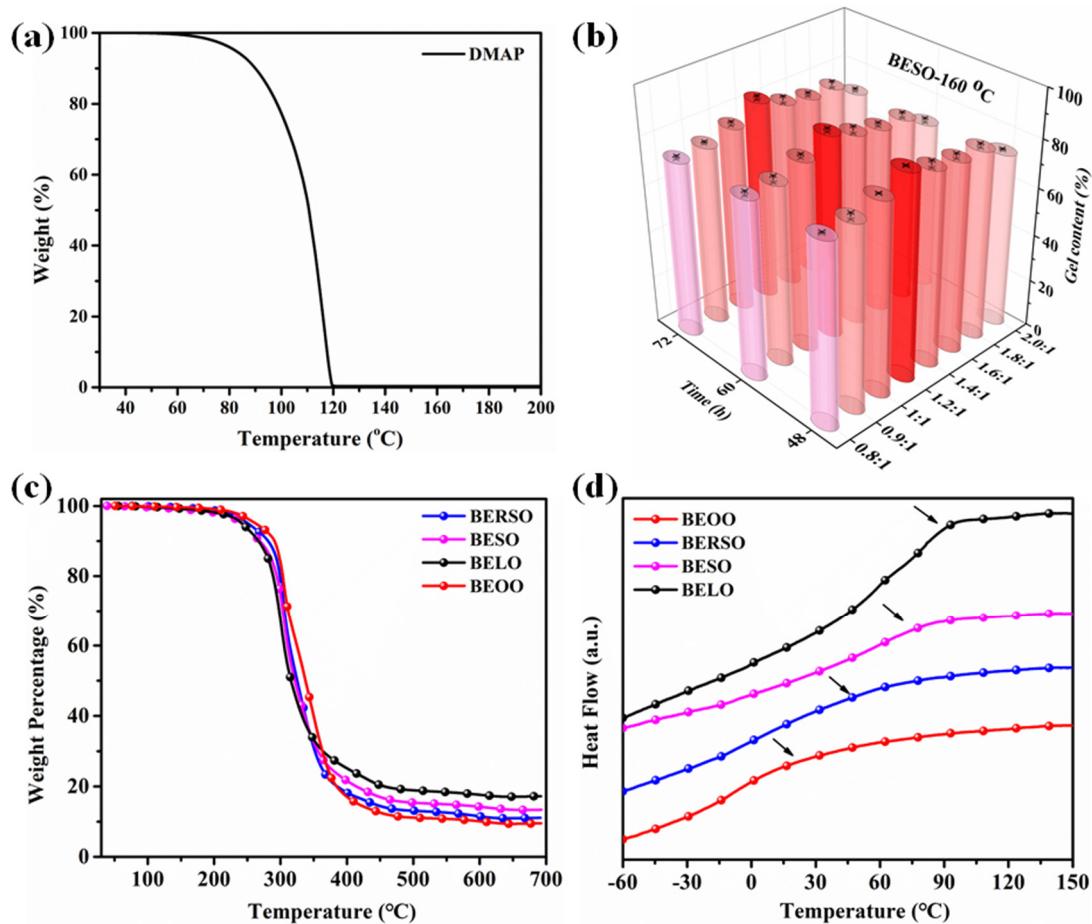


Figure S5. (a) TGA curve for DMAP catalyst. (b) The gel content of ESO-based epoxy resins with different molar ratios and different curing time at 160 °C. TGA curves (c), and DSC curves (d) for epoxy resins prepared from different epoxidized vegetable oils.

The high-resolution XPS spectra of S 2p in epoxy resins prepared from different epoxidized plant oils and different ratios of thiol and epoxy groups at 160 °C are shown in Figure. S6 and Table S5. The S 2p spectra of all samples were deconvoluted into two peaks at 163.3 and 164.4 eV, which were assigned to the S 2p_{3/2} and S 2p_{1/2} peaks for the C-S and S-S covalent bonds (*J. Mater. Chem. A*, **2020**, 8, 14993-15001). This information supported that BDB monomer could fully initiate ring-opening reaction of the epoxidized plant oils and the S-S bond was formed due to self-polymerization of the -SH.

As shown in Table 1, the ratio of the peak areas between S 2p_{3/2} and S 2p_{1/2} (corresponding to the C-S and S-S covalent bonds) was recorded as S(2p_{3/2})/S(2p_{1/2}). With increasing the ratios of thiol and epoxy groups from 1.0 to 1.2, the S(2p_{3/2})/S(2p_{1/2}) decreases from 2.41 to 2.03, indicating more S-S covalent bonds were formed during the thermal curing process. As the epoxy groups of epoxidized plant oils increased from 2.80, 3.4, 4.3, 5.1 for EOO, ERSO, ESO and ELO, the S(2p_{3/2})/S(2p_{1/2}) also decreased although the ratios of thiol to group to epoxy group kept at 1.2:1. It means that more -SH contents promote the formation of more S-S bonds.

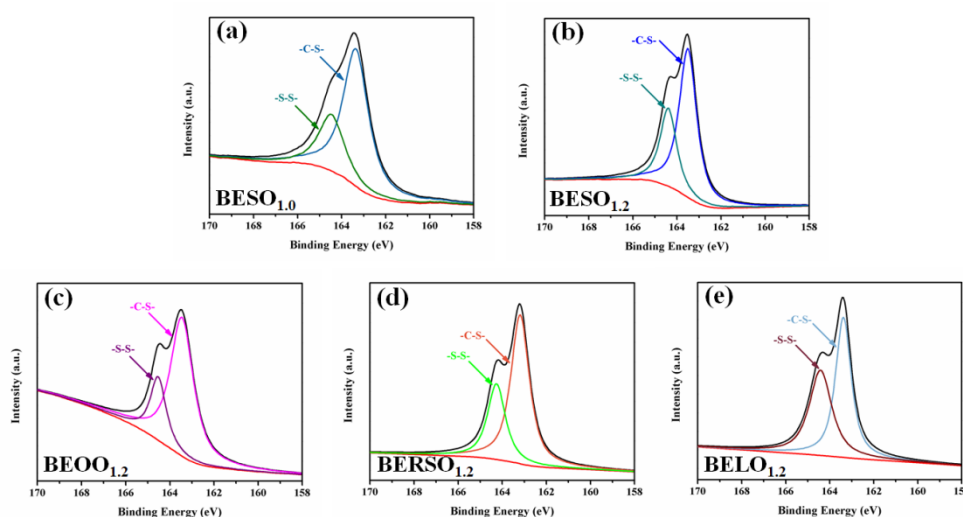


Figure S6. S 2p XPS spectra of epoxy resins prepared from different epoxy vegetable oils and different ratios of thiol and epoxy groups (a) BESO, 1.0, (b) BESO, 1.2, (c) BEOO, 1.2, (d) BERSO, 1.2, (e) BELO, 1.2.

Table S5. XPS S 2p spectra of epoxy resin samples.

Sample	Position (eV)	Area	Assignment	S(2p3/2)/S(2p1/2)
BESO _{1.0}	163.3	1003.5008	S(2p3/2)	2.41
	164.4	416.2974	S(2p1/2)	
BESO _{1.2}	163.3	766.2443	S(2p3/2)	2.03
	164.4	377.4957	S(2p1/2)	
BEOO _{1.2}	163.3	1008.3022	S(2p3/2)	4.97
	164.4	202.6358	S(2p1/2)	
BERSO _{1.2}	163.3	2137.6930	S(2p3/2)	2.03
	164.4	1051.9300	S(2p1/2)	
BELO _{1.2}	163.3	458.7282	S(2p3/2)	1.16
	164.4	394.1278	S(2p1/2)	

Table S6. Mechanical properties of epoxy resins based on resulting epoxidized vegetable oils with different humidity

Sample (60 °C)	BEOO			BERSO			BESO			BELO		
	50%	70%	90%	50%	70%	90%	50%	70%	90%	50%	70%	90%
T	9.63±0.42	5.87±0.60	2.12±0.12	17.78±0.27	13.82±1.03	3.64±0.13	32.03±0.10	30.72±2.24	18.60±2.34	48.04±2.30	43.19±3.68	36.49±2.04
E	34.59±13.3	59.54±10.4	110.07±20	25.33±4.84	78.41±25.84	99.68±19.0	12.32±2.94	26.43±8.67	33.16±4.13	8.89±2.87	24.94±0.62	16.13±12.76
Y	67.00±0.67	17.15±0.28	4.00±0.08	244.50±3.2	100.13±0.28	17.50±0.20	585.00±9.14	332.25±0.58	148±0.14	819.33±3.93	374.59±0.64	528.73±2.14
T'	2.25±1.19	2.04±0.41	1.57±0.30	3.42±0.74	7.77±2.53	3.62±0.73	2.94±0.93	5.26±2.38	5.53±0.98	2.54±0.90	5.73±0.82	3.05±2.36

T: Tensile strength (MPa), E: Elongation at break (%), Y: Young's modulus (MPa), T': Toughness (MPa).

Table S7. Mechanical properties of epoxy resins based on BEOO and BERSO with different heat treatment temperature.

Sample (H=70%)	BEOO				BERSO			
	30 °C	60 °C	90 °C	120 °C	30 °C	60 °C	90 °C	120 °C
T	1.93±0.05	5.87±0.60	10.88±0.61	10.80±0.39	4.55±0.53	13.82±1.03	16.30±2.33	15.92±0.95
E	167.23±22.8	59.54±10.44	51.86±17.03	40.92±0.03	123.03±11.31	78.41±25.84	33.89±3.25	21.08±7.15
Y	5.25±0.10	17.15±0.28	64.64±0.22	61.66±0.15	19.41±0.07	100.13±0.28	165.65±0.45	162.53±0.23
T'	2.46±0.44	2.04±0.41	3.89±1.46	2.87±0.05	6.26±1.07	7.77±2.53	4.09±0.74	2.21±1.04

T: Tensile strength (MPa), E: Elongation at break (%), Y: Young's modulus (MPa), T': Toughness (MPa).

Table S8. Mechanical properties of epoxy resins based on BESO and BELO with different heat treatment temperature.

Sample (H=70%)	BESO				BELO			
	30 °C	60 °C	90 °C	120 °C	30 °C	60 °C	90 °C	120 °C
T	22.26±2.31	30.72±2.24	40.12±3.01	40.80±1.34	35.97±3.00	43.19±3.68	52.39±2.16	46.37±5.37
E	75.34±25.20	26.43±8.67	19.02±3.42	22.42±4.02	14.57±4.01	24.94±0.62	17.85±3.99	11.70±3.51
Y	272.50±0.43	332.25±0.58	596.46±1.88	500.90±1.51	575.51±1.82	374.59±0.64	746.13±2.54	713.24±2.00
T'	15.53±6.44	5.26±2.38	5.62±1.96	6.02±0.97	2.62±1.45	5.73±0.82	5.70±1.46	2.60±0.76

T: Tensile strength (MPa), E: Elongation at break (%), Y: Young's modulus (MPa), T': Toughness (MPa).

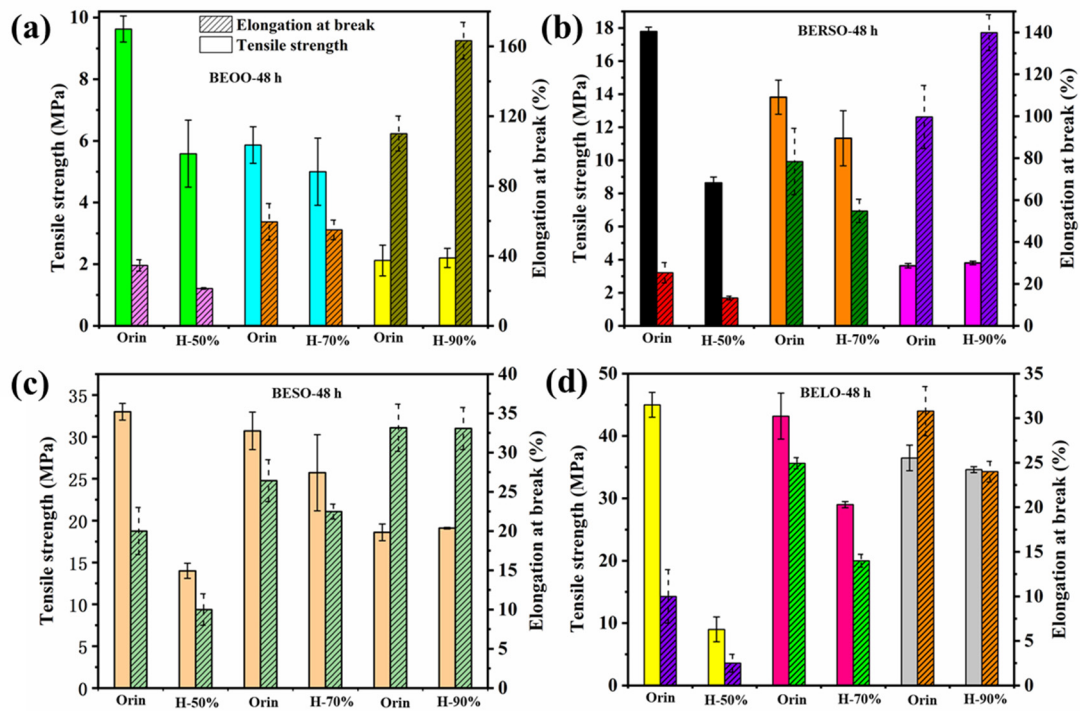


Figure S7. Mechanical properties of epoxy resins healed under different humidity at 60 °C for 48 h.

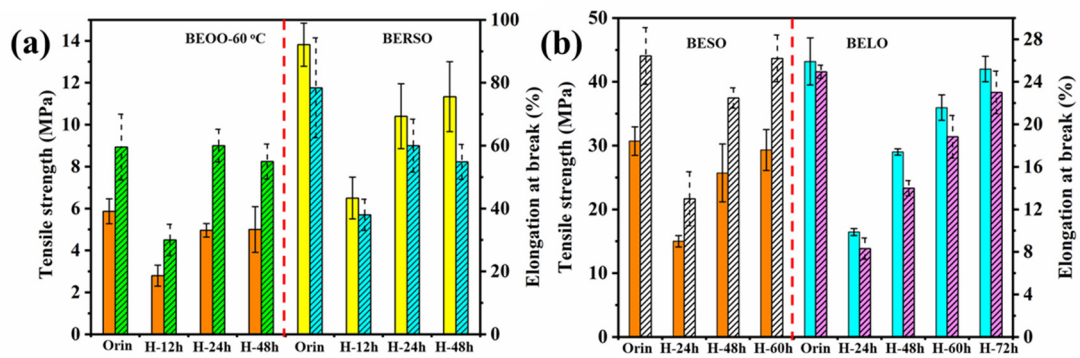


Figure S8. Mechanical properties of epoxy resins healed for different time under 70% humidity at 60 °C.

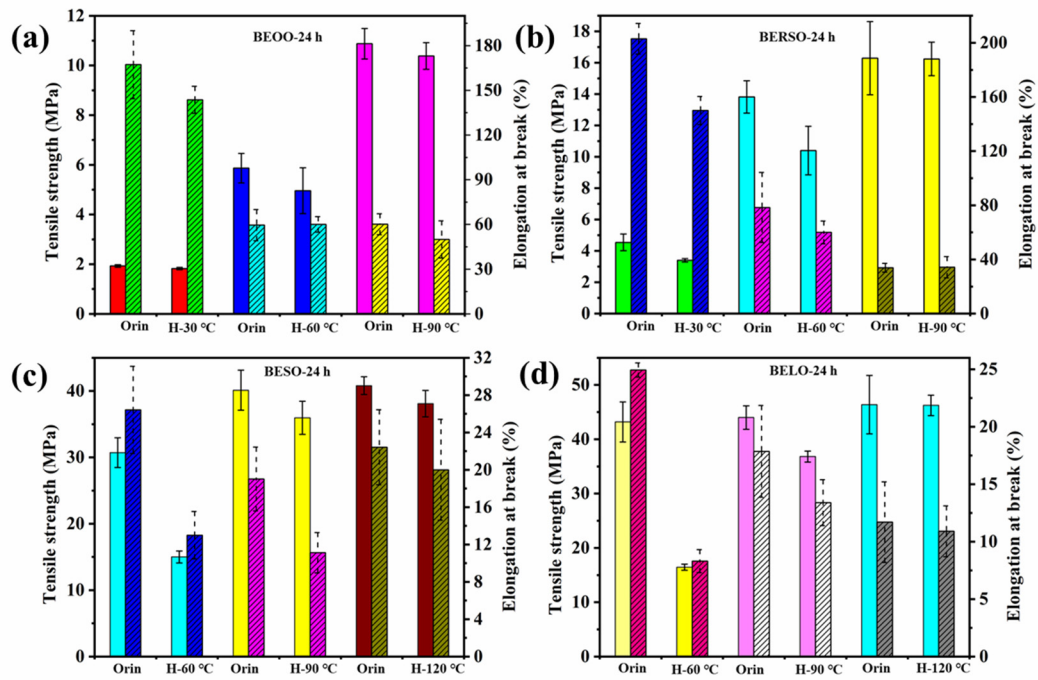


Figure S9. Mechanical properties of epoxy resins healed at different temperature under 70% humidity for 24 h.

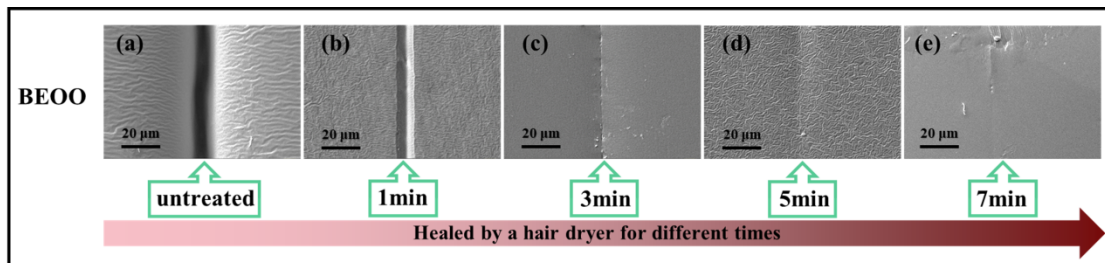


Figure S10. SEM images of self-healing process of the epoxy resins at a distinct temperature

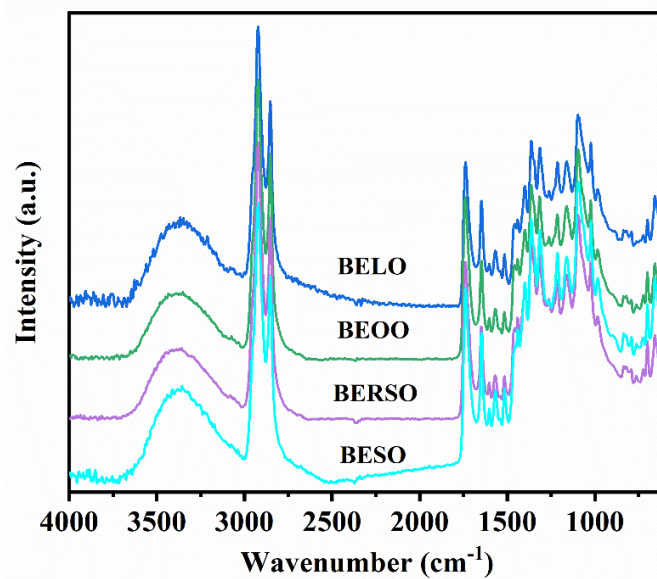


Figure S11. ATR-FTIR curves of the reprocessed epoxy resins

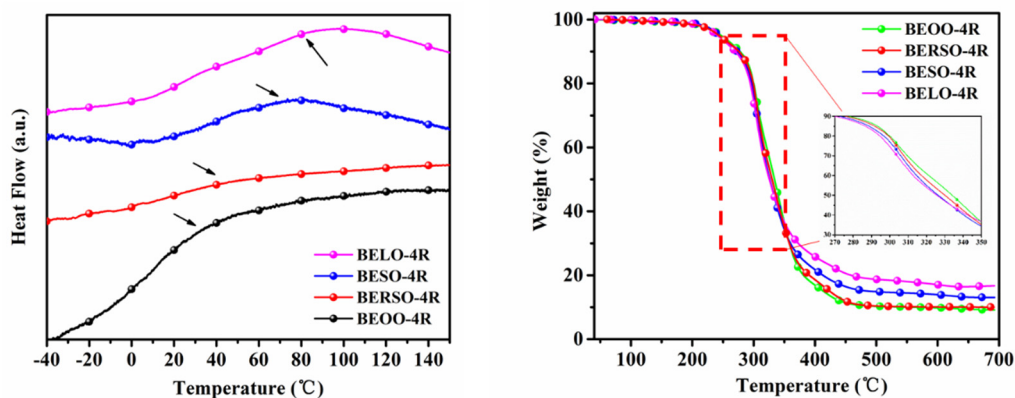


Figure S12. Thermal properties of the reprocessed epoxy resins

Table S9. Thermal properties of the reprocessed epoxy resins

Sample	Original				Recycled	
	T_5 (°C)	T_{50} (°C)	T_g (°C)	T_5 (°C)	T_{50} (°C)	T_g (°C)
BEOO	290.92	333.81	24.48	247.09	334.02	27.95
BERSO	281.32	325.09	39.97	247.46	334.90	40.88
BESO	268.93	321.57	61.12	243.99	326.41	64.96
BELO	242.37	315.81	86.90	241.23	325.64	90.22