Supporting information for

Self-healable, reprocessable and anti-flammable eugenol-derived covalent adaptable thermosets based on dynamic covalent boronic esters and thiol-ene click chemistry

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Characterization

The proton, boron and carbon nuclear magnetic resonance (NMR) spectra were performed using an AVANCE III 400 NMR spectrometer (Bruker, Germany). The samples were dissolved in deuterated dimethyl sulfoxide prior to measurements.

Fourier transform infrared (FTIR) spectra were obtained on the Thermo Fisher Nicolet 6700 FTIR spectrophotometer by the KBr disc method, while the wavenumber was ranged from 4000 cm^{-1} to 400 cm^{-1} with a scanning time of 32.

The flight mass spectrometer is determined by a matrix-assisted laser desorption time-of-flight mass spectrometer (Bruck Company) and the test mode is ESI mode.

Differential scanning calorimeter (DSC) was conducted using a TA instrument (Q2000, USA) at a heating rate of 5°C min^{-1} (from -50 to 100°C).

Dynamic mechanical analysis (DMA) was conducted using a TA instrument (DMA Q800, America) at a heating rate of 5°C min^{-1} (from -50 to 100°C). The dimension of the cured samples for measurement was 30 mm× 10 mm× 3 mm.

The tensile property was measured by an electromechanical universal testing machine (MTS criterion 43, USA) at a crosshead speed of 2 mm/min. The average value from at least 5 repetitive measurements was reported.

Transmittance of samples (thickness of 3 mm) is measured by a Solidspec-3700 UV/vis spectrometer (Japan).

Thermal decomposition behavior of the samples was evaluated using a Q5000 Thermogravimetric analyzer (TGA) (TA Instruments, USA) in N_2 and air. The sample (approximately 5.0 mg) was heated from 50 to 800 °C with a ramp rate of 20 °C/min.

Limiting oxygen index (LOI) measurement was carried out on an HC-2 LOI apparatus (Jiangning, China) following ASTM D2863-97, and the dimension of the samples was 100 mm × 6.5 mm × 3 mm.

The heat release rate of the samples was assessed by a microscale combustion calorimeter (MCC, FTT, UK).

The microstructure of the residual char was studied by using an LabRAM-HR Confocal Raman Microprobe with a 532 nm argon-ion laser.

The elemental composition of the residual char was obtained by an ESCALAB 250Xi X-ray photoelectron spectrometer (XPS) (Thermo Fisher Scientific, USA).

Stress relaxation tests were conducted by DMA Q800 instrument with a strain value of 20 % in a "stress relaxation" mode.

Scratch-repairing tests were carried out by an optical microscope. First, use the tip of a needle to make a crack in the surface of the sample. The initial shape of the crack was recorded by optical microscope. Then, the sample was placed at 80 °C for 15 min. The shape of the self-healing crack was recorded by optical microscope.

The progress of the shape memory experiment was as follows: First, the sample was placed at 80 °C for 10 min. Under external force, the sample was bent to a certain angle, which was defined as the maximum deformation angle (θ_{max}). The deformed samples were then placed in ice water for 5 min to fix the shape. Then, the angle of sample bending was defined as the fixed deformation angle (θ_{fixed}). Finally, the fixed samples were placed at 80°C again. It could be observed that the sample slowly returned to its initial shape. The angle when it was fully returned was defined as the final deformation angle (θ_{final}).

Table S1. The formulations of the eugenol-based covalent adaptable thermosets

Sample	EUEP (g)	BSH (g)	DiPETMP (g)	DMPA (g)
EDH	11.00	0.00	13.10	0.20
EBD-10%	11.00	13.95	1.30	0.20
EBD-20%	11.00	12.40	2.60	0.20
EBD-30%	11.00	10.85	3.90	0.20

Table S2. DSC and DMA data of EDH and eugenol-based covalent adaptable thermosets

Sample	T_g (°C)		E' (T_g+30 °C)	υ_e (mol/m^3)
	DSC	DMA	(MPa)	
EDH	20.8	32.7	15.1	1.8×10^3
EBD-10%	46.8	55.5	2.1	0.2×10^3
EBD-20%	46.6	54.6	7.6	0.8×10^3
EBD-30%	43.8	47.5	7.0	0.8×10^3

Table S3. Tensile data of EDH and eugenol-based covalent adaptable thermosets

Sample	Tensile strength (MPa)	Elongation at break (%)
EDH	4.2	66.5
EBD-10%	25.9	3.7
EBD-20%	23.9	5.3
EBD-30%	27.0	7.7

Table S4. TGA data of EDH and eugenol-based covalent adaptable thermosets in N_2

Sample	$T_{5\%}$ (°C)	T_{max} (°C)	V (%/°C)	Residual char yield (%) at 800°C
EDH	340.3	361.2	-22.4	10.5
EBD-10%	314.1	362.2	-48.2	28.1
EBD-20%	309.9	359.4	-45.4	28.4
EBD-30%	322.9	366.0	-43.9	27.6

Table S5. TGA data of EDH and eugenol-based covalent adaptable thermosets in air

Sample	$T_{5\%}$ (°C)	T_{max} (°C)	V (%/°C)	Char residue (%) at 800°C
EDH	329.5	358.0	-21.2	0.2
EBD-10%	315.5	354.6	-51.6	28.2
EBD-20%	316.0	357.6	-43.9	25.4
EBD-30%	320.3	360.6	-43.4	27.1

Table S6. The elemental contents of the residual char of EBD-30%

Sample	C (%)	O (%)	B (%)	S (%)
EBD-30%	27.3	0.3	29.7	2.7

Table S7. DSC and DMA data of original EBD-30% and reprocessed EBD-30%

Sample	T_g (°C)		E' (T_g+30 °C)	υ_e
	DSC	DMA	(MPa)	(mol/m^3)
Original EBD-30%	43.8	47.5	7.0	0.8×10^3
Reprocessed EBD-30%	32.8	43.9	2.6	0.3×10^3

Table S8. The elemental contents of residual char of EBD-30%

Sample	θ_{max} (°)	θ_{fixed} (°)	θ_{final} (°)	t (s)	R_f (%)	R_r (%)	V_r (°/s)
EBD-30%	112	111	3	436	99.1	98.2	0.25

Shape fixation rate (R_f): $R_f = \theta_{fixed}/\theta_{max}*100\%$

Shape recovery efficiency (R_r): $R_r = (\theta_{fixed}-\theta_{final})/\theta_{fixed}*100\%$

Shape recovery rate (V_r): $V_r = (\theta_{final}-\theta_{final})/t$

Table S9. Tensile data of EBD-30% and reprocessed EBD-30%

Sample	Tensile strength (MPa)	Recovery ratio (%)	Elongation at break (%)
EBD-30%	27.0	/	7.7
Re1-EBD-30%	25.9	95.9	3.3
Re2-EBD-30%	24.5	90.7	1.8
Re3-EBD-30%	23.3	86.3	1.8
Re4-EBD-30%	22.5	83.3	1.6
Re5-EBD-30%	20.4	75.6	1.2
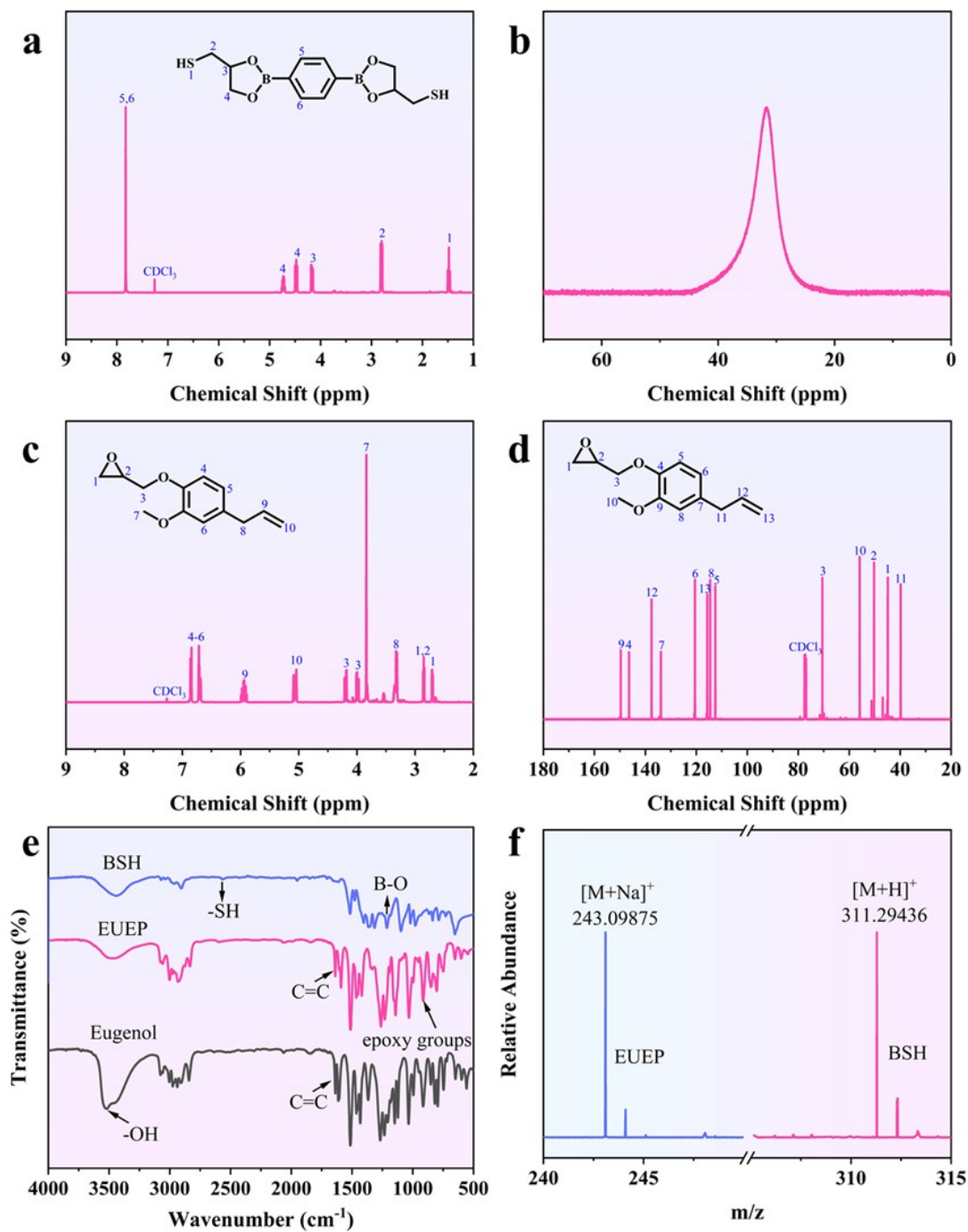
Fig. S1. (a) 1H NMR and (b) 11B NMR spectra of BSH; (c) 1H NMR and (d) 13C

NMR spectra of EUEP; (e) FTIR spectra and of BSH, EUEP and eugenol; and (f)
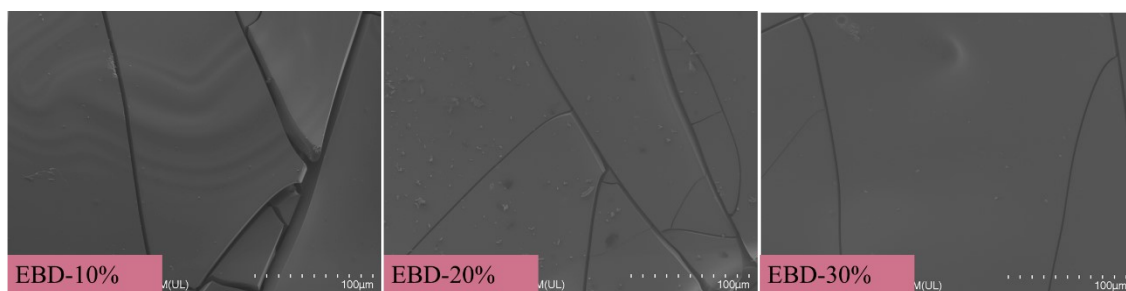
mass spectrum of BSH and EUEP

Fig. S2. SEM micrographs of residual chars of eugenol-based covalent adaptable
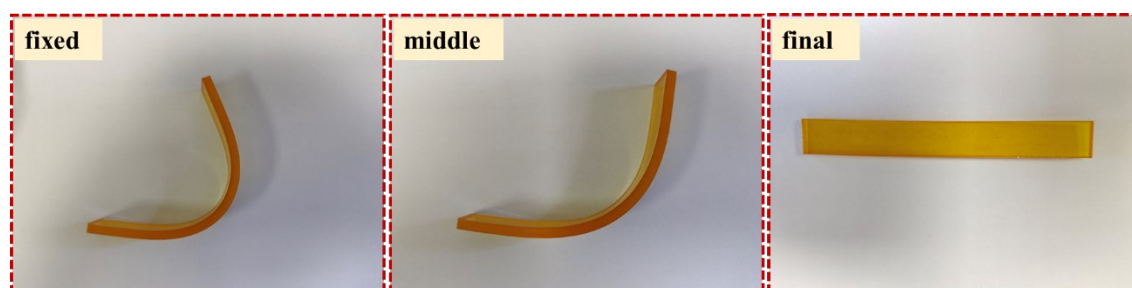
thermosets

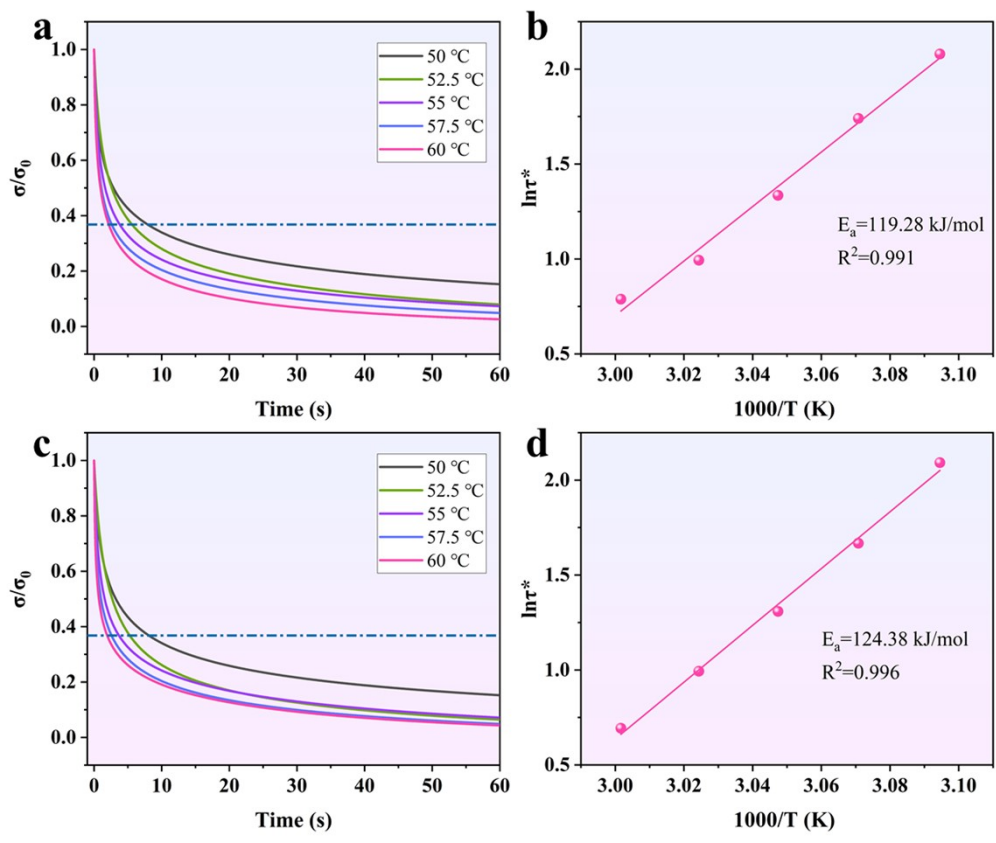**Fig. S3.** The digital photographs of EBD-30% during the shape memory process

Fig. S4. Stress relaxation curves of (a) EBD-10% and (c) EBD-20% and Arrhenius

equation fitting curve of (b) EBD-10% and (d) EBD-20%