Bio-based vitrimers from divanillic acid and epoxidized soybean oil

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Supplementary information

S1 ^{1}H and ^{13}C NMR spectra of DVA and BuDVA

^{1}H NMR of DVA and BuDVA:

DVA: ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.54 (s, 2H), 9.33 (s, 2H), 7.46 (d, J = 2.0 Hz, 2H), 7.42 (d, J = 2.0 Hz, 2H), 3.89 (s, 6H).

BuDVA: ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.88 (s, 2H), 7.56 (d, J = 2.0 Hz, 2H), 7.42 (d, J = 2.0 Hz, 2H), 3.88 (s, 6H), 3.81 (t, J = 6.3 Hz, 4H), 1.34 (p, 4H), 1.05 (h, 4H), 0.66 (t, J = 7.4 Hz, 6H).

^{13}C NMR spectrum of DVA:

DVA: ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.11 (C1), 148.28 (C2), 147.17 (C3), 125.40 (C4), 124.26 (C5), 120.52 (C6), 111.01 (C7), 55.83 (C8).

(The ^{13}C NMR spectrum of BuDVA was reported in our previous study.[1])

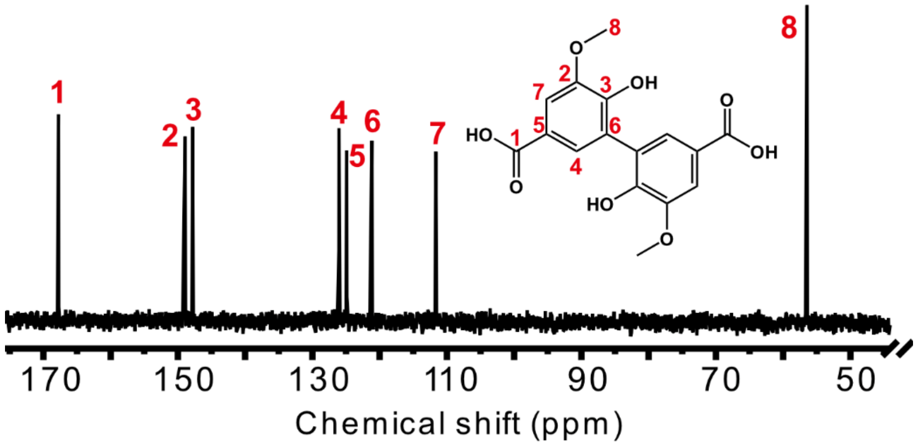

Fig. S1 ^{13}C NMR spectra of DVA in DMSO-d_6.

S2 Swelling experiment

The swell ratios and gel contents of OHESO-*x* and BuESO-*x* were measured to evaluate the crosslinking densities of cured vitrimers. A solvent extraction method according to ASTM D2765-16 with THF as solvent was used. Cured vitrimer films (10 mm × 5 mm × 0.3 mm) were weighted as W_s and enveloped using metal mesh (weighted W_{s+m}). The specimens were then immersed in THF, and the solvent was stirred and refluxed at 90 °C for 24 hours. After cooling to room temperature, the swollen specimens were removed from the solvent, wiped the THF on the surface, and then weighed (W_g). The specimens were dried at 100 °C under vacuum until the weight reached a constant (W_d). The swelling ratio and gel content can be given by:

$$\text{Swell ratio} = (1 + \frac{W_\mathrm{g} - W_\mathrm{d}}{W_\mathrm{d}}) \times 100\%$$

$$\text{Gel content} = (1 - \frac{W_\mathrm{s+m} - W_\mathrm{d}}{W_\mathrm{s}}) \times 100\%$$

Table S1 Swell ratios and gel contents of cured vitrimer films

Code	Swelling ratio (%)	Gel content (%)
OHESO-0.7	159.5 ± 17.9	81.4 ± 3.8
OHESO-1.0	154.9 ± 17.1	84.8 ± 2.3
OHESO-1.5	149.4 ± 17.2	80.4 ± 1.7
BuESO-0.7	165.8 ± 23.6	89.2 ± 1.9
BuESO-1.0	175.5 ± 18.5	94.2 ± 7.0
BuESO-1.5	146.5 ± 10.5	89.6 ± 1.1

S3 FT-IR spectra of OHESO-x and BuESO-x vitrimers

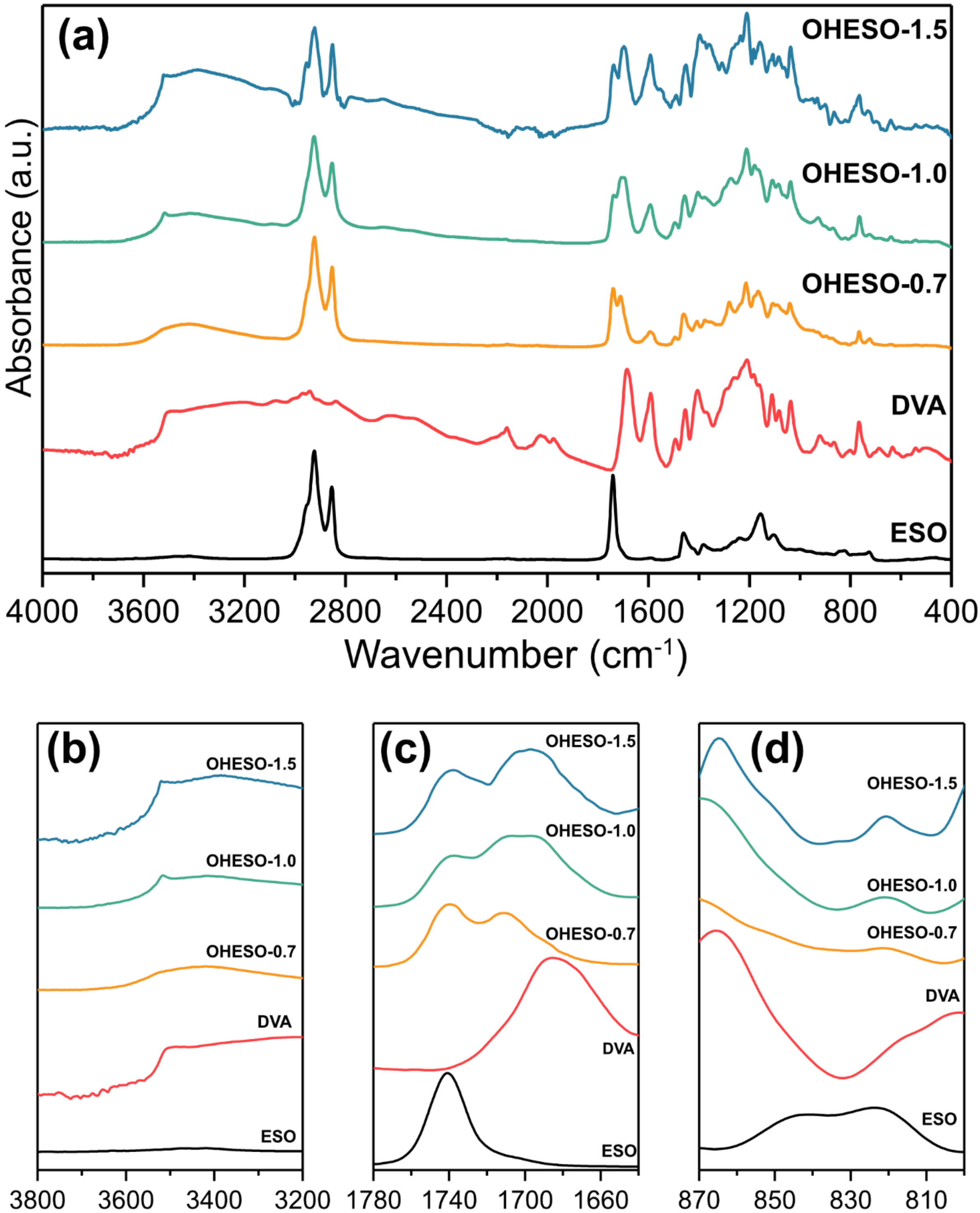

Fig. S2 FT-IR spectra of ESO, DVA and OHESO-*x* vitrimers.

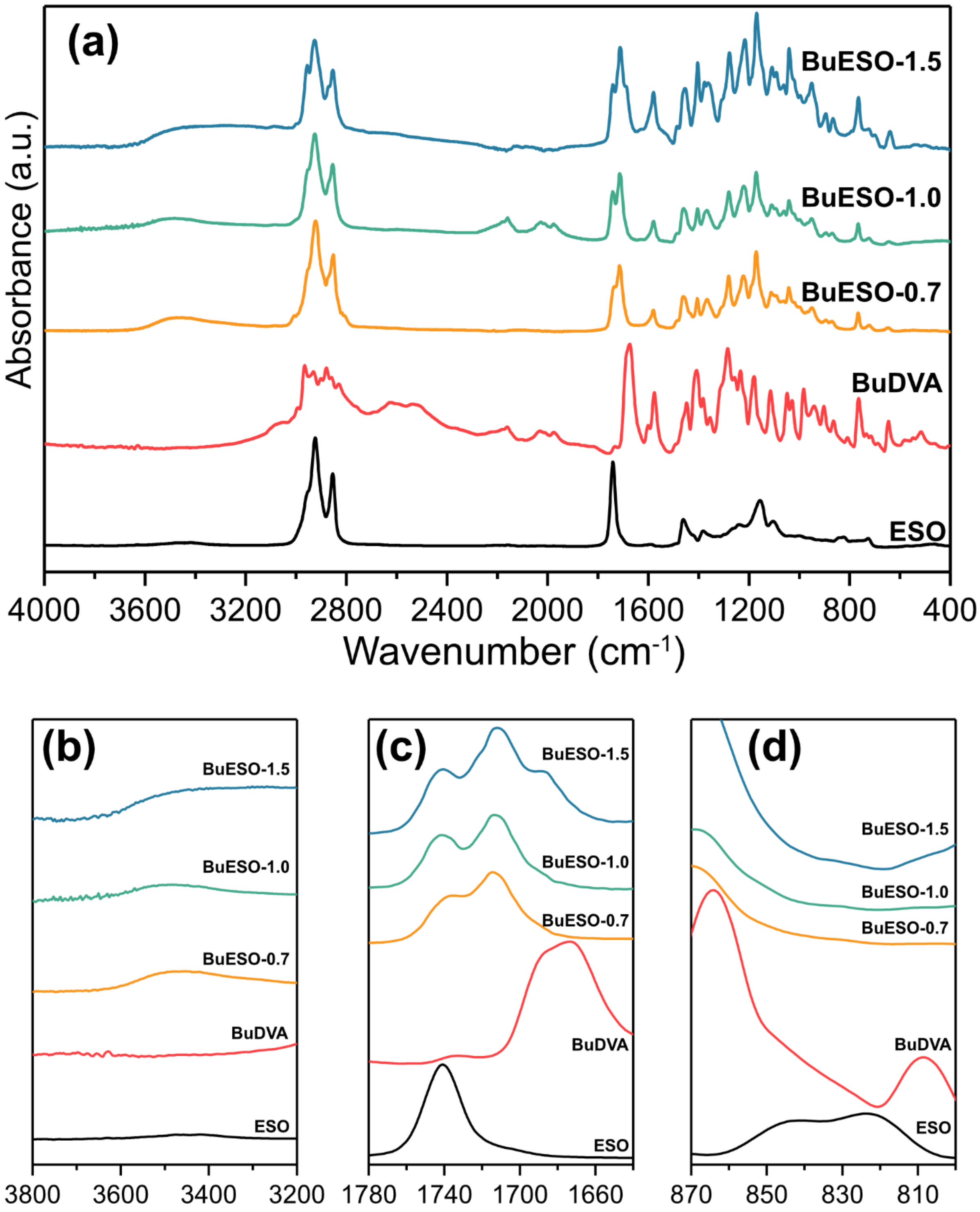

Fig. S3 FT-IR spectra of ESO, BuDVA and BuESO-*x* vitrimers.

S4 As-measured DMA curves

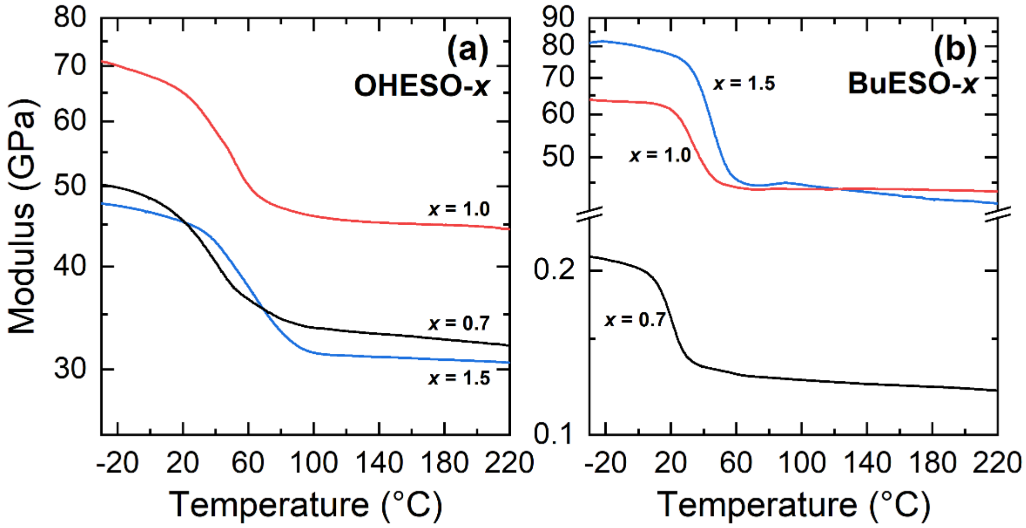

Fig. S4 DMA curves of as-measured storage moduli versus temperatures at a heating rate of 3 °C/min.

S5 Fitting function of vitrimer films and evaluation of activation energy

According to several previous works[2-4], the stress relaxation curves of OHESO-*x* and BuESO-*x* at each temperature (except for OHESO-1.0 at T = 190 °C) were fitted by a stretched exponential function expressed as below,

$$G_t/G_0 = e^{\left(-\frac{t}{\tau_{\text{fit}}}\right)^{\beta}} + c$$

Table S2 Values of τ_{fit} and parameters of relaxation function

Codes	T (°C)	τ_{fit} (10^3 s)	Parameters	
			β	c
OHESO-1.0	170	36.3	0.81	-0.09
	180	25.3	0.91	-0.11
	190	Not well fitted[a]		
	200	5.6	0.80	-0.32
OHESO-0.7	200	21.9	0.26	0.18
OHESO-1.5	200	40.1	0.53	-0.14
BuESO-1.0	170	221.9	0.75	-0.04
	180	180.4	0.76	-0.04
	190	76.4	0.73	-0.04
	200	30.2	0.62	-0.04
BuESO-0.7	200	6.4	0.56	0.08
BuESO-1.5	200	82.0	0.63	-0.06

[a] The relaxation curve cannot be well fitted by the relaxation function.

The fitting curves are shown as follow.

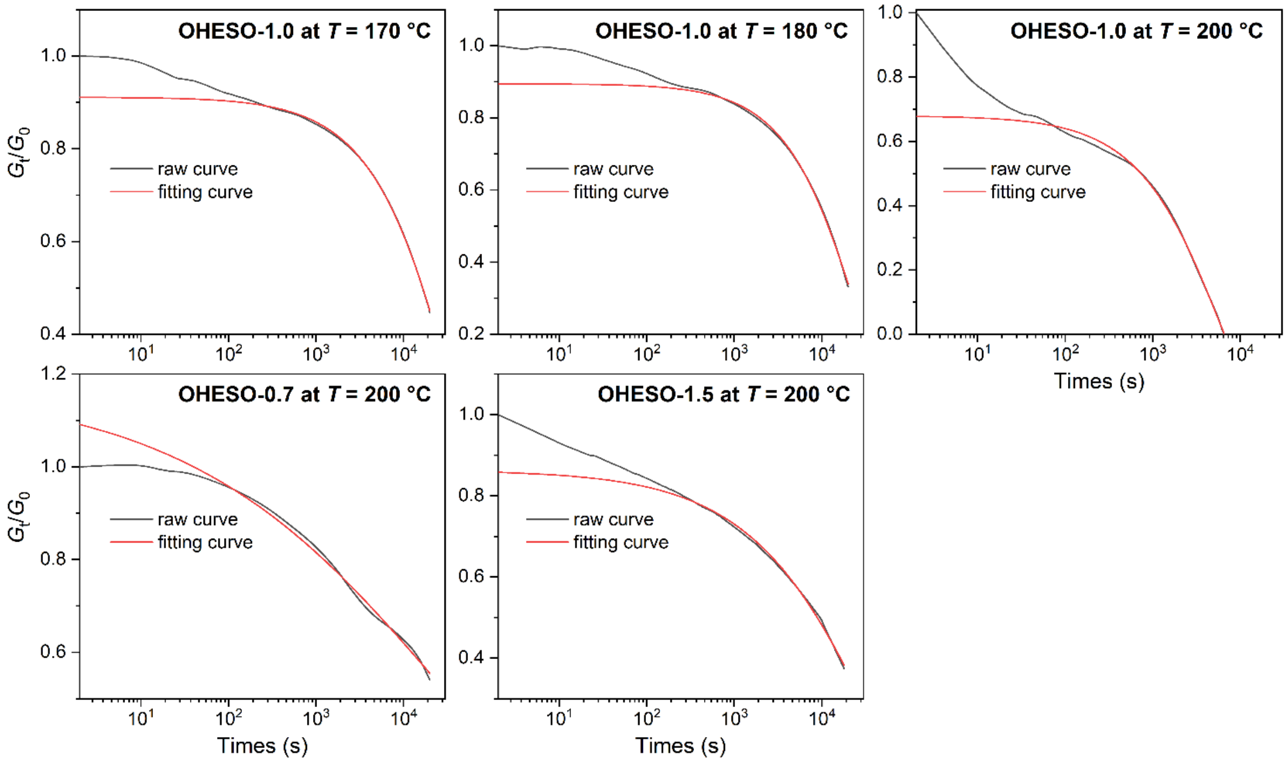

Fig. S5 Normalized stress relaxation curves of OHESO-*x* and their fitting curves.

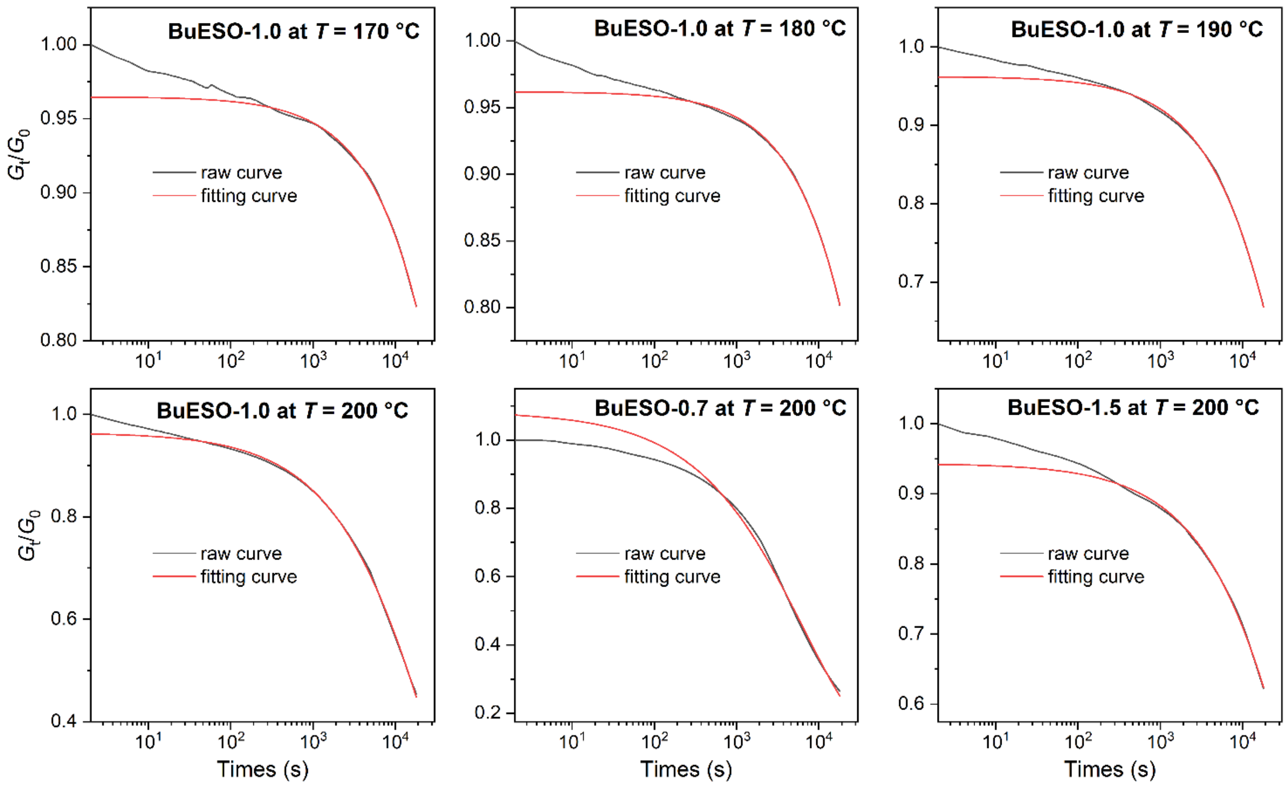

Fig. S6 Normalized stress relaxation curves of BuESO-*x* and their fitting curves.

For OHESO-1.0 and BuESO-1.0, the values of τ_{fit} at T = 170–200 °C are substituted into the following Arrhenius equation (The R represents the ideal gas constant) to obtain the E_a value from the slope of the fitting line.

$$\ln(\tau_{\mathrm{fit}}) = A + \frac{E_{\mathrm{a}}}{RT}$$

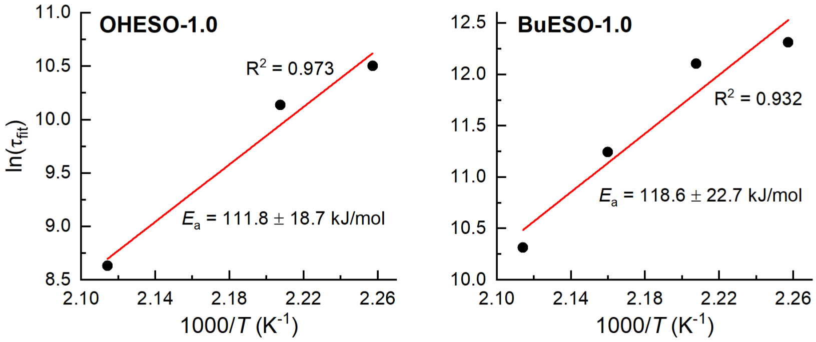

Fig. S7 Arrhenius plot of the relaxation time for OHESO-1.0 and BuESO-1.0.

S6 Reprocessed vitrimer films

Table S3 Mechanical properties of reprocessed vitrimer films

Sample	Times of reprocessing	σ_{max} (MPa)	ε_{max} (%)	E (MPa)
OHESO-1.0	0 (pristine)	13.6 ± 1.1	13.6 ± 2.0	286 ± 49
	1	10.1 ± 1.4	6.8 ± 3.1	228 ± 30
	2	7.7 ± 2.3	12.7 ± 10.7	168 ± 28
	3	8.8 ± 0.9	30.0 ± 17.1	199 ± 24
	4	6.9 ± 1.0	19.2 ± 7.9	163 ± 18
	5	8.6 ± 0.5	31.5 ± 19.5	174 ± 23
BuESO-1.0	0 (pristine)	4.8 ± 0.6	69 ± 12	57 ± 11
	1	2.0 ± 0.2	63 ± 10	22 ± 8
	2	2.5 ± 0.2	71 ± 17	29 ± 14
	3	2.1 ± 0.7	54 ± 16	38 ± 11
	4	2.6 ± 0.6	77 ± 19	30 ± 8
	5	2.7 ± 0.5	50 ± 17	32 ± 11

IR spectra of reprocessed vitrimer films

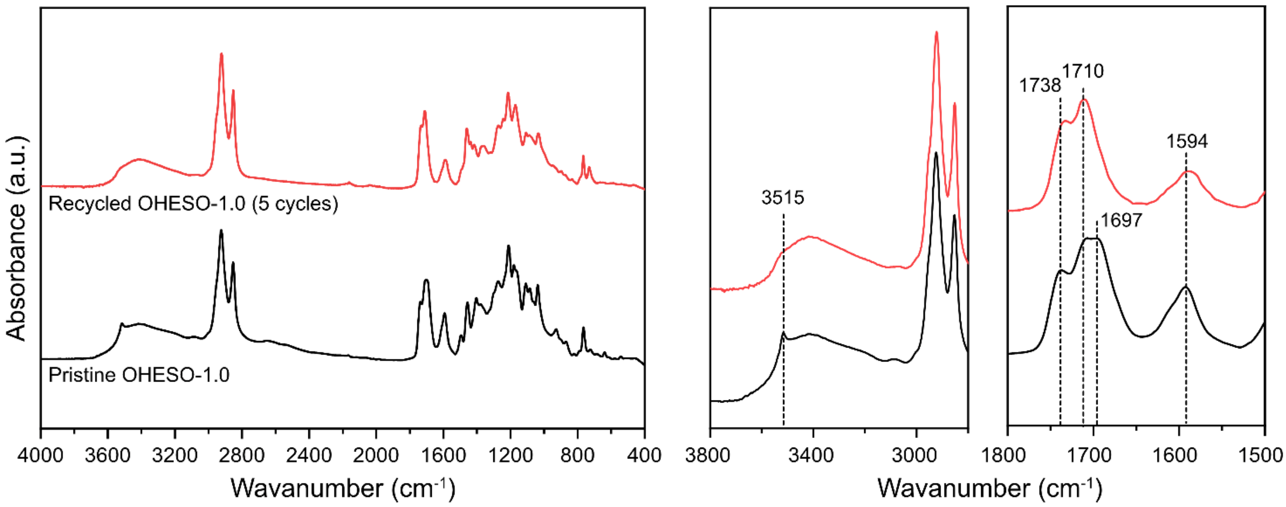

Fig. S8 FT-IR spectra of pristine and recycled (5 cycles) OHESO-1.0.

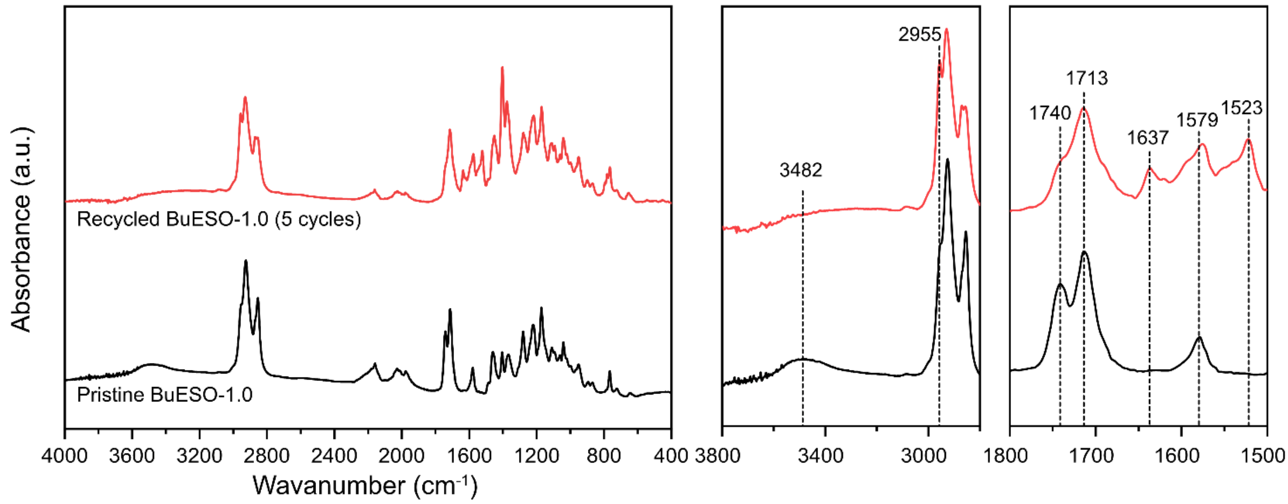

Fig. S9 FT-IR spectra of pristine and recycled (5 cycles) BuESO-1.0.

S7 Shape memory property of OHESO-1.0

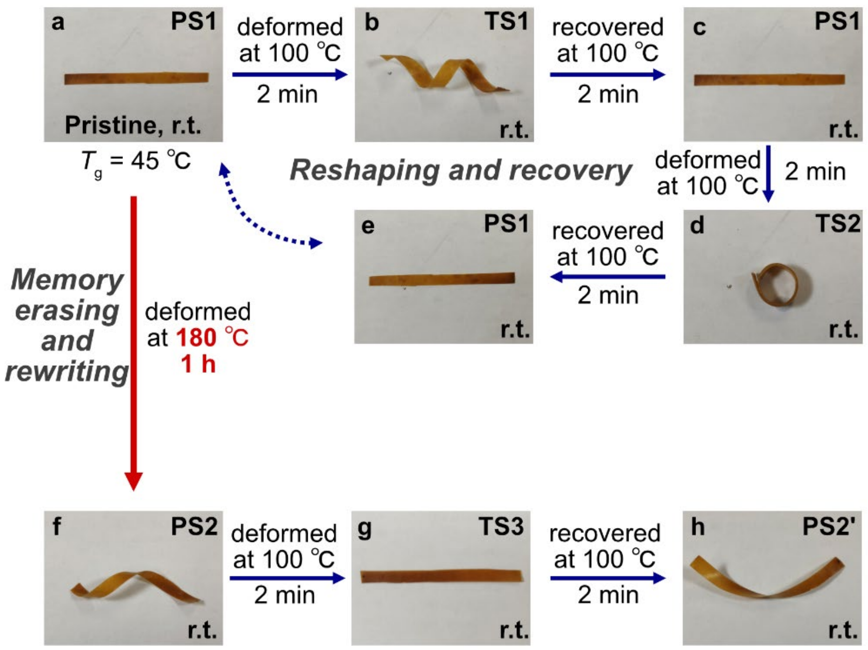

Fig. S10 Shape memory photographs of OHESO-1.0. PS represents the permanent shapes (i.e., shapes in a stable state), and TS represents the temporary shapes (i.e., shapes in a metastable state). All images were taken at room temperature.

The shape memory behavior of OHESO-1.0 was studied as an example in a series of heating-and-reheating processes shown in Fig. S10. A strip of OHESO-1.0 [PS1, Fig. S10 (a)] was firstly cut from a vitrimer film. At this initial state, the molecular chains were in the conformation with high entropy (i.e., thermally stable).[5] Then, the specimen was heated at T = 100 °C (higher than its T_g), and a force was applied to fix it in a helix shape for 2 min. After cooling the reshaped specimens to room temperature and removing the force, a helical specimen was obtained (PS1, Fig. S10 (b)). At this state, the vitrimer was in a metastable stage because the molecular chains were frozen at $T < T_g$ with relatively low entropy. After reheating the helical specimen to T = 100 °C, the specimen recovered almost to its original shape (PS1) in 2 min. During the reheating (TS1 to PS1), the frozen molecular chains became movable, and the entropy increased. The following PS1→TS2→PS1 [Fig. S10 (c)–(e)] was a similar reshaping and recovery process to PS1→TS1→PS1. Furthermore, we re-edited the permanent shape of the specimen by heating the specimen at 180 °C for one hour [PS1→PS2, Fig. S10 (a) to (f)]. At T = 180 °C, the transesterification was activated, and the networks of vitrimer were rearranged to form a new thermally stable permanent topology (PS2). As shown in [Fig. S10 (f) to (g)], although a complete shape recovery was not achieved, the specimen with re-edited permanent shape (PS2) also exhibited satisfactory shape memory behavior (PS2→TS3→PS2′).

Reference

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