Supporting information

Fully biobased, catalyst-free vitrimers from tannic acid: facile combination of mechanical robustness, recyclability and sustainability

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Table S1 Formulations

	EVO ([epoxy]=0.075 mol	tannic acid	Maleic anhydride
S3	ESO=20.00 g	8.51 g	7.36 g, 0.075 mol
S4	ESO=20.00 g	6.38 g	7.36 g, 0.075 mol
S5	ESO=20.00 g	5.06 g	7.36 g, 0.075 mol
L3	ELO=12.68 g	8.51 g	7.36 g, 0.075 mol
L4	ELO=12.68 g	6.38 g	7.36 g, 0.075 mol
L5	ELO=12.68 g	5.06 g	7.36 g, 0.075 mol

Table S2 Summary of thermomechanical properties of pristine vitrimers

	Tensile strength/MPa	Elongation at break/%	Young's Modulus/MPa*	Rubbery Platform at T_g +80°C/MPa	Crosslink density /mol·cm^{-3}	T_g/°C	T_{d5}/°C
S3	35.2±3.0	18.1±0.4	365.8	4.49	436.6	76.2	292
S4	27.7±0.9	15.6±0.6	325.7	4.54	432.1	68.5	307
S5	21.9±1.1	26.6±6.7	224.7	5.41	505.3	59.5	322
L3	52.4±4.1	8.0±1.4	520.3	6.68	578.3	109.7	282
L4	47.2±1.3	7.8±0.6	737.9	14.80	1259.7	117.9	256
L5	51.6±2.4	11.0±1.1	519.9	15.85	1296.7	136.9	291

*calculated using 2% stress on the representative tensile curves

Table S3 Summary of thermomechanical properties of 3rd recycled vitrimers

	Tensile strength/MPa	Elongation at break/%	Young's Modulus/MPa*	Storage modulus at T_g +80℃/MPa	Crosslink density /mol·cm^{-3}**	T_g/℃	T_{d5}/℃
S3-r3	19.0±0.7	17.2±2.4	375.8	0.147	14.41	56.1	261
S4-r3	18.0±1.8	30.9±13.4	328.0	0.374	37.59	45.5	265
S5-r3	14.6±0.3	59.7±5.1	206.0	2.005	200.79	47.2	296
L3-r3	17.0±0.2	4.0±0.1	401.0	1.972	175.83	96.5	266
L4-r3	13.9±1.0	4.4±0.1	323.7	1.734	156.10	92.2	271
L5-r3	25.8±2.6	7.7±0.1	314.7	1.583	146.42	80.3	274

*calculated using 2% stress on the representative tensile curves

Calculation of activation energies for viscous flow of S3 and L3 vitrimers

Characteristic relaxation time (τ^*, s) indicating the time it takes for *G* to reduce to 1/e of the initial modulus at different temperatures were obtained from the stress relaxation experiments：

Table S4 Characteristic relaxation times (s) of S3 and L3 vitrimers

	160℃	170℃	180℃	190℃	200℃
S3	5870	3590	2399	1520	--
L3	--	5570	1963	1216	524

The natural logarithm of τ^* was plotted versus 1000/T, where T indicates the absolute temperature (K). Linear fittings $y = ax + b$ were obtained:

Table S5 Arrhenius fitting parameters for viscous flow of S3 and L3 vitrimers

sample	a	b
S3	8.94098±0.1998	-11.9701±0.44624
L3	15.88668±1.44212	-27.30334±3.15052

Because the viscous flow of vitrimers can be described using Arrhenius Equation:

$$\ln(\tau^*) = \frac{E_a}{RT} + ln(\tau_0)$$

where E_a (kJ/mol) represents the activation energy for vitirmer viscous flow, *R* =8.314 J/mol·K^{-1} is the universal gas constant, *T* is the absolute temperature (K). E_a is then given by:

$$E_a = a \times R$$

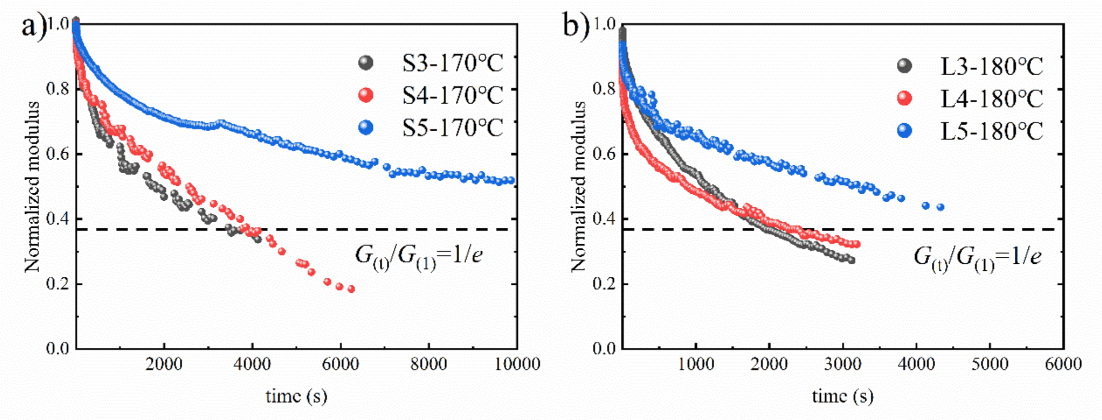

Figure S1 Stress relaxation curves of a)ESO-based vitrimers at 170℃ and b)ELO-based vitrimers at 180℃

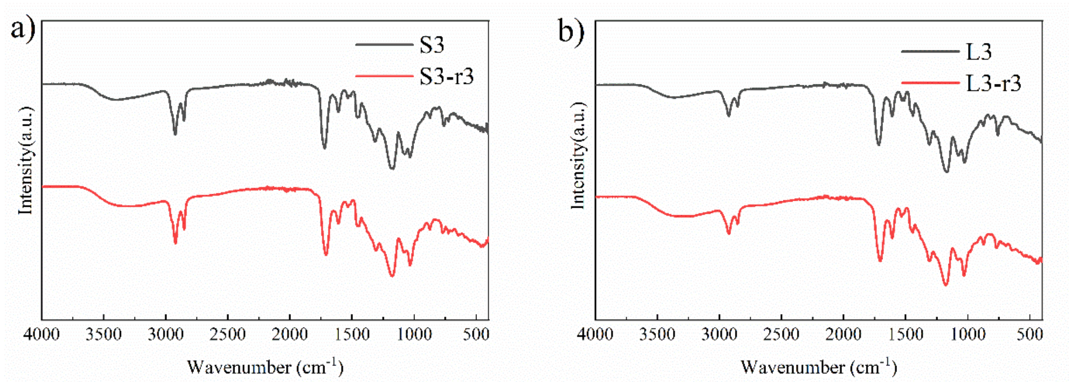

Figure S2 FT-IR spectra od pristine and 3rd recycled a)S3 and b)L3 vitrimers

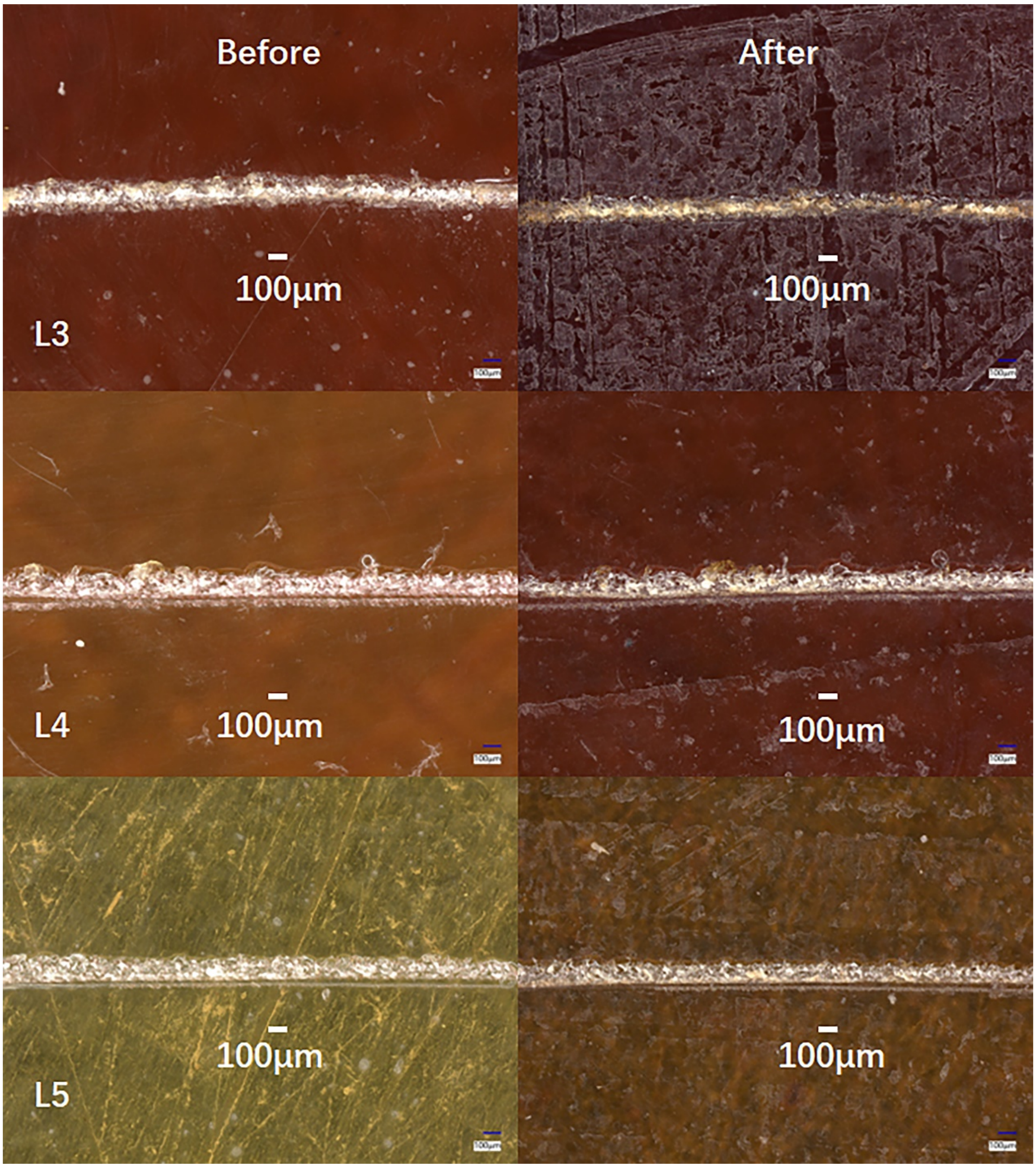

Figure S3 Microscopic photos of cracks on ELO-based vitrimers before and after undergoing a scratch-healing procedure

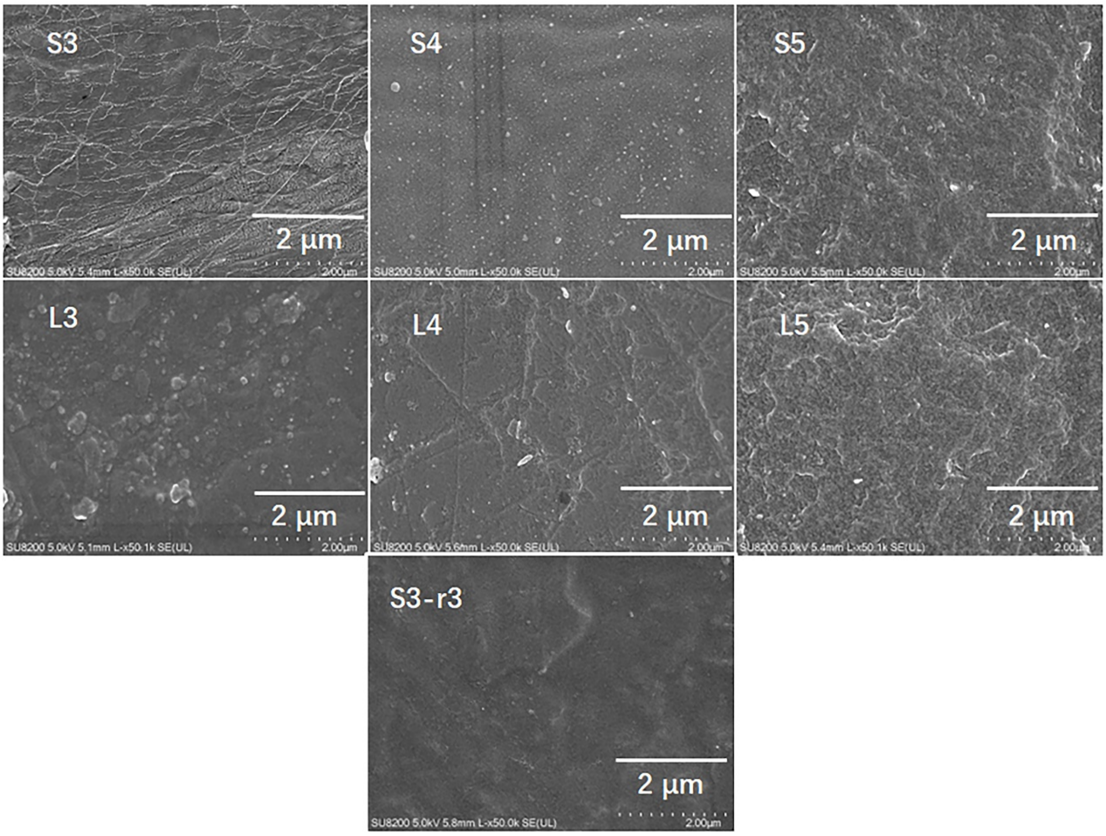

Figure S4 SEM images of vitrimer samples. Obtained on a scanning electron microscope (SU8220, Hitachi, Japan)

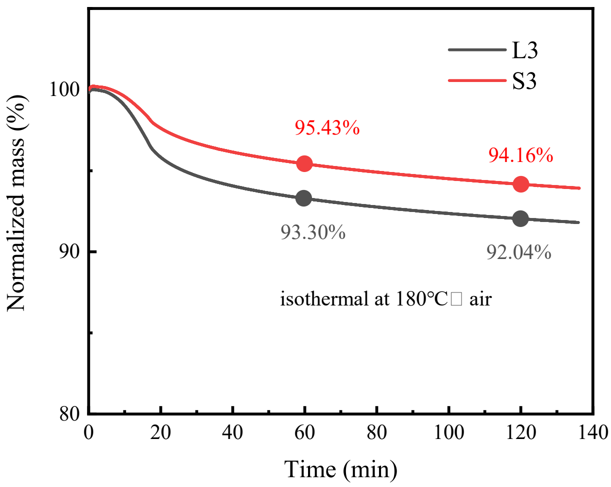

Figure S5 Isothermal TGA results for S3 and L3 vitrimers in air, with residual mass fractions at 1 h an 2 h marked.

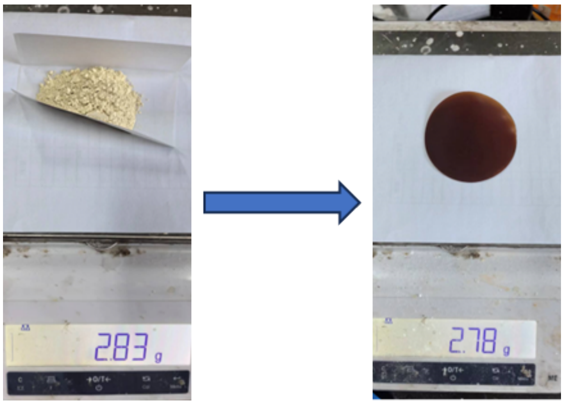

Figure S6 Photos of the L4-r2 vitrimer powder and the recycled L4-r3 sample. The loss ratio of recycling was 1.77%.

Figure S7 Adhesive test results. a) equipment for lap-shear test; b) a photo of failed Q235 steel plates bonded using L5 glue. Clear adhesive failure can be observed; c) lap-shear strength of ELO-based vitrimers.

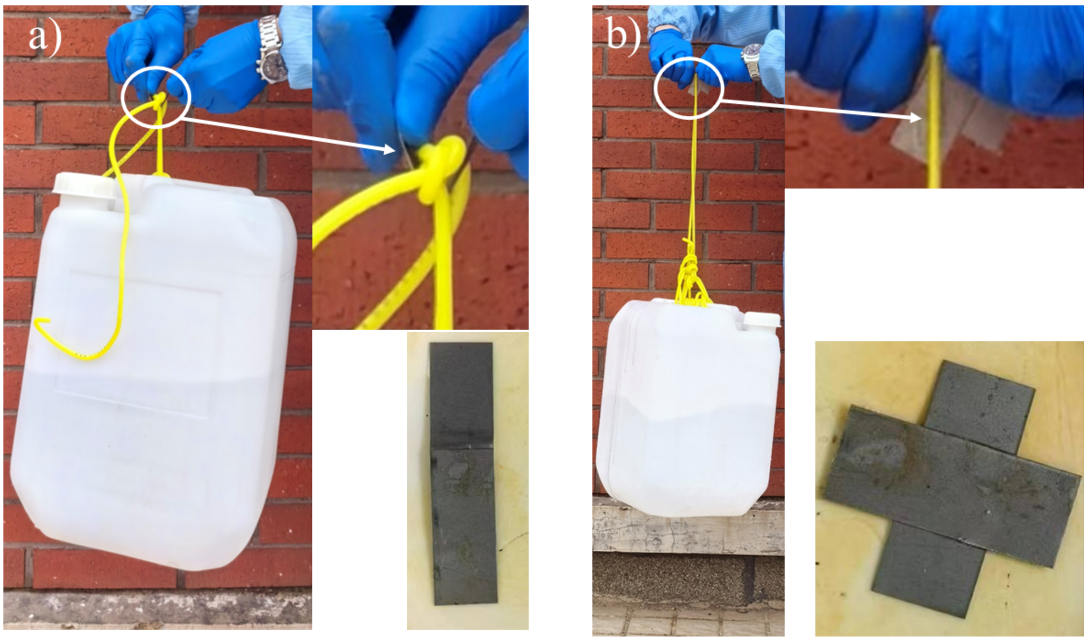

Figure S8 Bonded Q235 steel plates using 2~3 drops of L5 glue can afford a bucket weighing 11.2 kg. The size of steel plates was 2 cm × 5 cm.

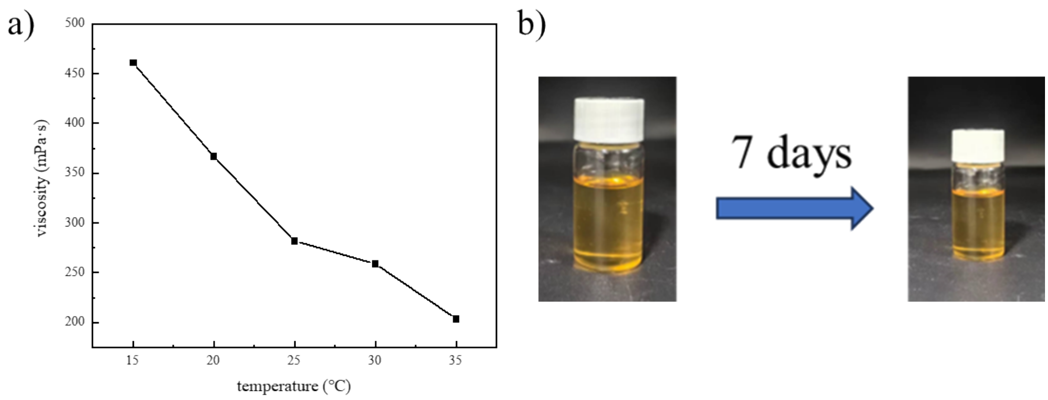

Figure S9 a) viscosity of L5 vitrimer glue. Obtained on a Ubbelohde Viscometer equipped with a 2# rotor, 6 rpm; b) photos of L5 vitrimer glue. It kept stable at 10°C for at least 7 days.

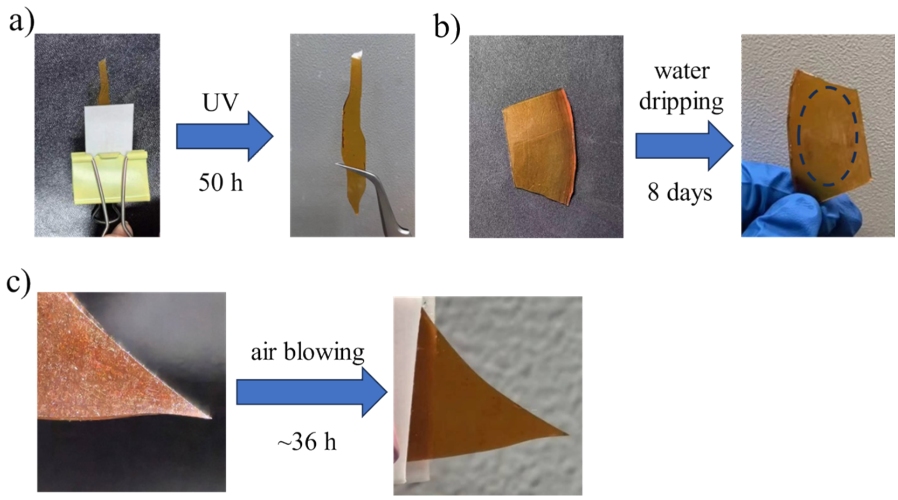

Figure S10 Weather resistance tests using an L3 vitrimer piece. a) UV exposure (365 mm, 24 W) for 50 h; b) water dripping for 8 days (1 drop per second); c) hot air blowing for 36 hours.

Table S6 Comprehensive comparison of reported EVO vitrimers (ref.1~8 and this work), other epoxy vitrimers (ref.9~13) and regular EVO thermosets (ref.13~17)

Ref. NO.	Tensile strength (virgin)/ MPa	Reprocessing condition	Tensile strength (1st recycled) /MPa	Epoxy resin	Dynamic covalent bond	Catalyst
1	37.4	190°C/20 MPa/5 min	~33	ESO	Schiff base	none
2	3.49	180°C/20 MPa/10 min	~2.5	ESO	disulfide	none
3	16.62	160°C/10 MPa/1 h	~14	ESO	DTE	$Zn(acac)_2$
4	3.1	200°C/20 MPa/135 min	1.4	ESO	DTE	TBD
5	0.6	Not reported	--	ESO	DTE	none
6	23	160°C/3 ton/10 min	19	ELO	boronic ester	none
7	1.8	130°C/10 MPa/15 min	~1.5	ESO	DTE	none
8	7.4	160°C/10 MPa/3 h	8.9	ESO	DTE	none
L5	52.4	170°C/20 MPa/2 h	28.9	ELO	DTE	none
L4	47.2		35.6			
L3	51.6		36.9			
S5	21.9	160°C/15 MPa/2 h	20.5	ESO		
S4	27.7		24.9			
S3	35.2		31.3			
9	~70	200°C/10 MPa/2 h	~70	bisphenol A epoxy	DTE	none
10	~55	240°C/3 min	~50	bisphenol A epoxy	DTE	$Zn(acac)_2$
11	10.98	100°C/60 min	9.07	isosorbide-derived epoxy	disulfide	none
12	0.18	100°C	~0.18	catechol-derived epoxies	DTE	$Zn(acac)_2$
13	94.1	Not reported	--	bisphenol A epoxy	DTE	none
14	28.7			ESO		
15	23			ESO		
	40			ELO		
16	0.68			ESO		
17	7.85			ESO		

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