

Electronic Supplementary Information

Natural glycyrrhizic acid: improving stress relaxation rate and glass transition temperature simultaneously in epoxy vitrimers

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The supporting information includes 14 pages, 5 tables and 9 figures.

Contents

1. Characterization	Page S3
2. DSC curves of DGEAC, GL and SA.....	Page S6
3. Thermal stability of DGEAC/SA/GL networks	Page S6
4. FTIR spectra analysis for curing reactions	Page S7
5. DSC curves of DGEAC/SA/GL networks after curing reactions.	Page S7
6. Gel contents and swelling tests of DGEAC/SA/GL networks	Page S8
7. Storage modulus of DGEAC/SA/GL networks.....	Page S8
8. Tensile test of DGEAC/SA/GL networks.....	Page S9
9. Stress relaxation of DGEAC/SA/GL networks	Page S10
10. Details of vitrimer samples in Fig. 3d.	Page S11
11. Topology freezing transition temperature of DGEAC/SA/GL networks	Page S12
12. Comparison of welding, reprocessing, repairing, recycling and chemical degrading of V4 with other reported epoxy vitrimers based on TERs.....	Page S13

1. Characterization.

Differential scanning calorimeter (DSC) test: Differential scanning calorimeter (DSC, TA-DSC 250) was used to investigate the curing behavior. The samples (~5 mg) were sealed in aluminum crucibles, and scanned at a heating rate of 5°C/min for curing samples and raw materials. For cured networks, the samples (~5 mg) were heated from -40°C to 200°C at a heating rate of 20°C/min.

Thermal stability test: Thermal stability was measured by using a thermogravimetric analyzer (TGA, TA-Q50). Samples (~5 mg) were loaded into alumina crucibles and scanned from room temperature to 700°C at a heating rate of 10°C/min under nitrogen atmosphere.

Fourier transform infrared spectroscopy (FTIR): Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a spectrophotometer (Nicolet iS5). The sample was grinded with potassium bromide (KBr, 100 mg) in a mortar, and the mixture was compressed into a disk using a mould. All samples were scanned from 4000 to 400 cm⁻¹.

Gel content tests: Dry sample (~30 mg, m_0) was immersed in 5 mL of dichloromethane (DCM) for 20 h. After 20 h, the samples were dried in a vacuum oven at 70°C and then weighted (m_1). The gel content was calculated according to the following equation:

$$\text{Gel contents (\%)} = \frac{m_1}{m_0} \times 100\% \quad (\text{S1})$$

Swelling tests: The swelling ratio was measured by immersing the sample (~30 mg, m_0) in dichloromethane (DCM) at room temperature. When the absorption reached equilibrium, the sample was taken out of the solution. The excessive surface solvent was removed with a filter paper, and the swollen sample was weighted (m_1). The swelling ratio was calculated according to the following equation:

$$\text{Swelling ratio (\%)} = \frac{m_1 - m_0}{m_0} \times 100\% \quad (\text{S2})$$

Dynamic mechanical analysis: Dynamic mechanical properties were measured by using a dynamic mechanical analyzer (DMA, TA-Q850) in tension mode. The sample with a dimension of 30 mm × 5 mm × 1 mm was scanned from -50 to 200°C at a heating rate of 5°C/min. The amplitude was set at 10 μm and the frequency was 1 Hz.

Tensile test: Tensile test was measured by a universal testing machine (MTS-CMT4304) according to ASTM D882 standard. Dumbbell-shaped samples were used for the test. The crosshead speed was 2 mm per min, and the gauge length was 17 ± 2 mm. At least five samples were tested for each vitrimer system.

Stress relaxation test: Stress relaxation was measured by using DMA (TA-Q800). The sample dimension was 30 mm × 5 mm × 1 mm. The sample was heated to the appointed temperature and soaked for 15 min with a static force (0.001 N). After that, an instantaneous strain of 2% was forced to the material. The stress and modulus was detected for several hours until it achieved equilibrium.

Thermodilatometry test: Thermodilatometry was measured using DMA (TA-Q850) in controlled force tension mode. The sample dimension was 30 mm × 5 mm × 1 mm. A constant force was added to stretch material which made the stress constant at 2 kPa. Sample was heated to 250°C as a heating rate of 5°C/min. The derivative of each curve was used to obtain the T_{mall} value.

Welding test: Welding property was studied using an oven at 130°C for 1 h. Two pieces were assembled into an “L” pattern with the help of EG at the interface. A glass slide was added on the sample to offer a small pressure.

Reprocessing test: Reprocessing property was studied using a long medicine spoon to fix in an oven at 130°C for 1 h.

Repairing test: Repairing property was studied using an optical microscope (UPT200I). The sample was cracked using a knife and repaired at an oven at 130°C. A drop of EG was added on the interface of each sample to help the repairing process. A glass slide was added on the sample to offer a small pressure.

Physical recycling: Physical recycling properties were studied using tensile test similar with the original samples. The sample pieces were gathered and put into a mould on a press vulcanizer at 130°C at 10 tons pressure to form two new films. The new films were used to prepare dumbbell-shaped samples with similar size to original ones.

Chemical degradable test: The chemical degradable property was investigated by using EG (5 mL) in vials at 130°C. The sample was cut into ~30 mg rectangular piece, and then immersed in EG at 130°C in an oven.

2. DSC curves of DGEAC, GL and SA.

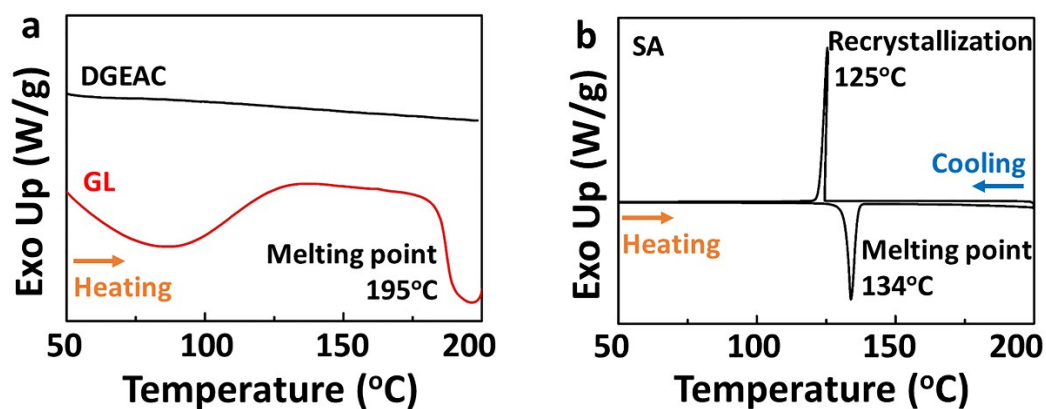


Fig. S1 (a) DSC curves of DGEAC and GL at a heating rate 5°C/min. (b) DSC curves of SA at a heating/cooling rate 5°C/min.

3. Thermal stability of DGEAC/SA/GL networks.

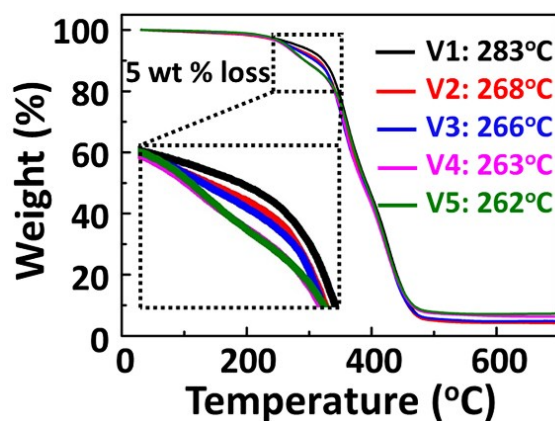


Fig. S2 TGA results of DGEAC/SA/GL networks after curing at N₂ atmosphere. The heating rate was 10°C/min.

4. FTIR spectra analysis for curing reactions.

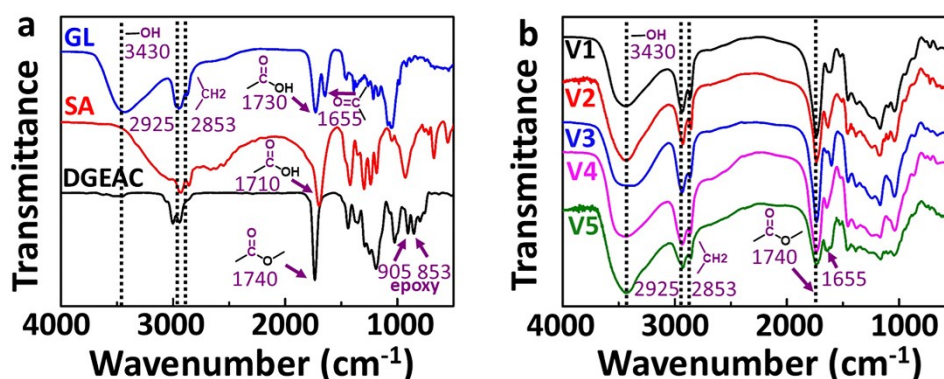


Fig. S3 (a) FTIR spectra of DGEAC, SA, and GL monomer ranging from 500 to 4000 cm⁻¹. The signals at 1740 and 905/853 cm⁻¹ were assigned to ester bonds and epoxy groups from DGEAC, and the signals at 2925/2853 and 1710 cm⁻¹ were assigned to methylene and carboxyl groups from SA, while the signals at 3430, 2925/2853, 1730 and 1655 cm⁻¹ were assigned to hydroxyl, methylene, carboxyl and ketone groups from GL. (b) FTIR spectra of DGEAC/SA/GL (V1 to V5) ranging from 500 to 4000 cm⁻¹. The signals at 3430, 2925/2928, 1740, and 1655 cm⁻¹ were assigned to hydroxyl groups, methylene groups, ester bonds and ketone groups, respectively.

5. DSC curves of DGEAC/SA/GL networks after curing reactions.

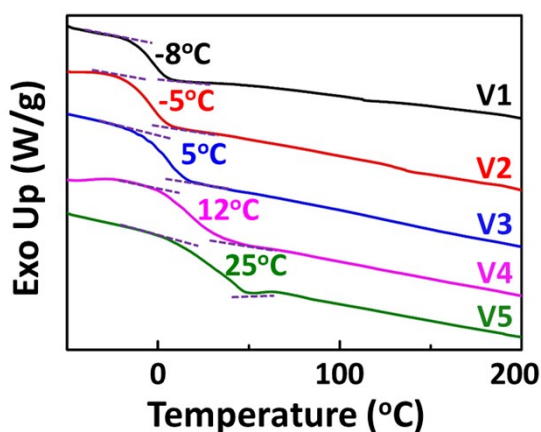


Fig. S4 DSC curves of DGEAC/SA/GL networks (V1, V2, V3, V4, V5) at a heating rate 20°C/min.

6. Gel contents and swelling tests of DGEAC/SA/GL networks.

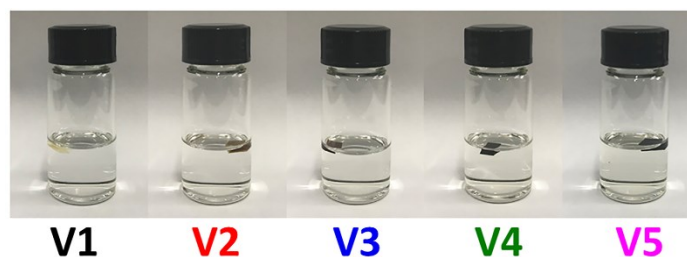


Fig. S5 Digital photo of gel contents and swelling tests after 20 h in DCM.

Table S1. Gel content and swelling ratio of DGEAC/SA/GL networks in DCM.

	V1	V2	V3	V4	V5
Gel Content (%)	90 ± 1.8	92 ± 1.8	90 ± 0.9	94 ± 2.0	99 ± 1.0
Swelling Ratio (%)	74 ± 4.1	71 ± 2.5	63 ± 2.5	60 ± 1.9	61 ± 0.4

7. Storage modulus of DGEAC/SA/GL networks.

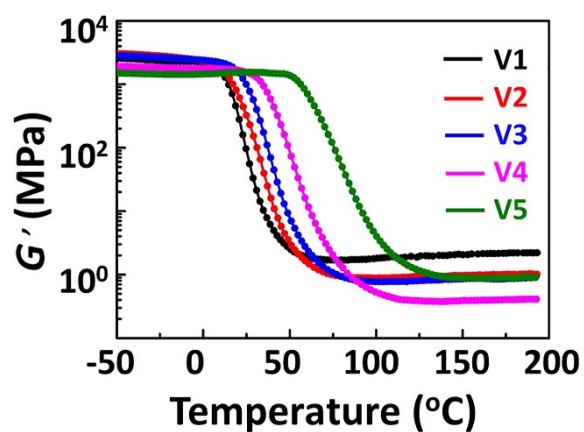


Fig. S6 Storage modulus of DGEAC/SA/GL networks using DMA at a heating rate of 5°C/min.

8. Tensile test of DGEAC/SA/GL networks.

Table S2. Tensile strength and modulus of DGEAC/SA/GL networks.

Sample	Strength (MPa)	Modulus (MPa)
V1	0.56 ± 0.02	2.37 ± 0.27
V2	0.55 ± 0.03	2.68 ± 0.11
V3	0.63 ± 0.07	17.20 ± 3.29
V4	2.52 ± 0.24	147.67 ± 14.59
V5	11.28 ± 1.00	542.26 ± 63.65
Recycled V4 ^[a]	1.48 ± 0.59	83.81 ± 0.57
Recycled V4 ^[b]	2.44 ± 0.35	131.96 ± 13.86

[a] Recycled V4 by 10 tons pressure at 130°C for 1 h. [b] Recycled V4 by 10 tons pressure at 130°C for 5 h.

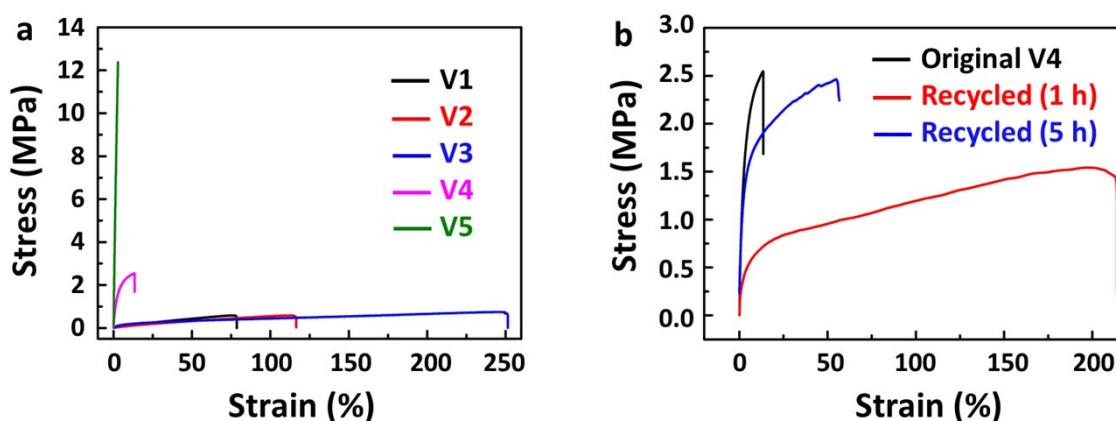


Fig. S7 (a) Stress-strain curves of DGEAC/SA/GL networks (V1 to V5) from tensile tests. (b) Stress-strain curves of original V4 and recycled V4 from tensile tests. The red line and blue line represented recycled sample after 130°C for 1 h and 5 h, respectively.

9. Stress relaxation of DGEAC/SA/GL networks.

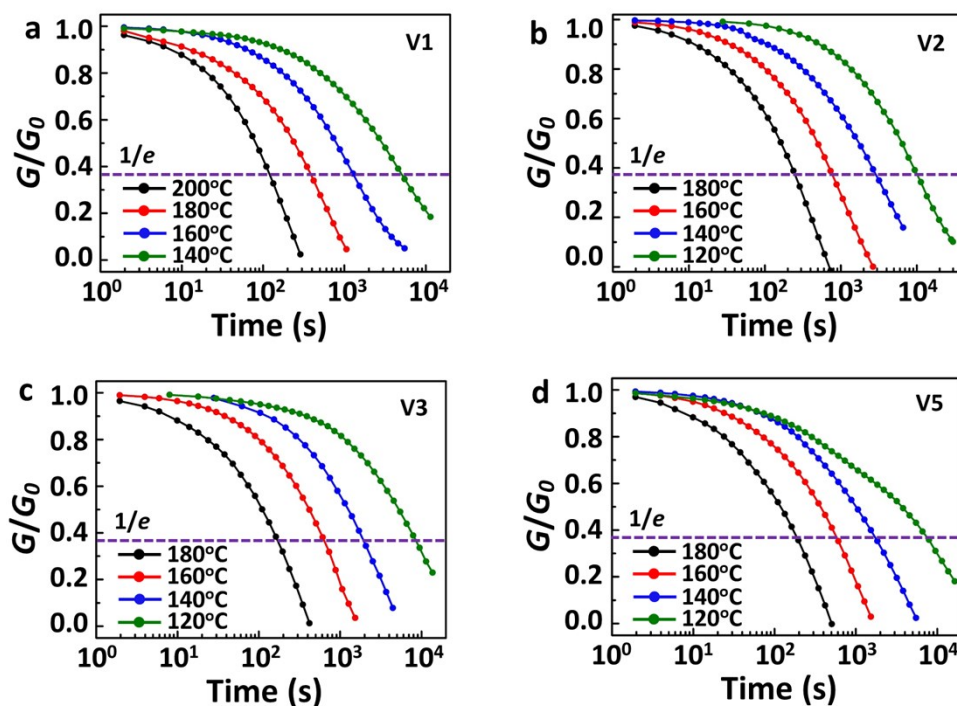


Fig. S8 Stress relaxation of DGEAC/SA/GL networks (V1, V2, V3 and V5) at different temperatures using DMA tension mode with a strain of 2%.

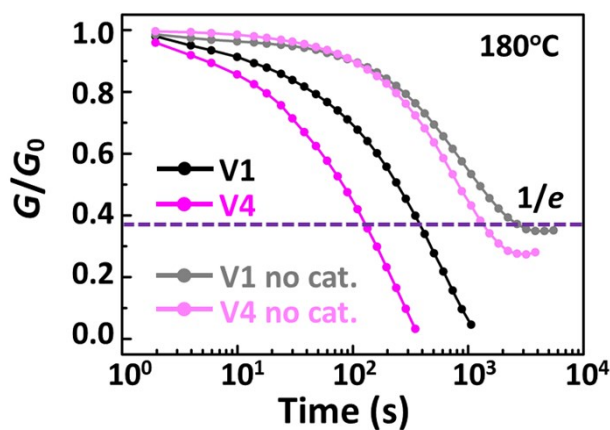


Fig. S9 Stress relaxation of V1 and V4 with and without catalyst TBD at 180°C using DMA tension mode with a strain of 2%.

10. Details of vitrimer samples in Fig. 3d.

Table S3. Detail of vitrimer samples in Fig. 3d.

Entry	Sample	Catalyst contents	Reference
1	100H 5CAT 75H 5CAT 60H 5CAT	TBD: 5 mol% of the epoxy groups	[28]
2	CL-PE-310	Zn(OAc) ₂ : 20 mol% of the carboxyl groups	[48]
3	Single ester vitrimer	TBD: 5 mol% of the carboxyl groups	[46]
4	Cross-linked PDMS	Zn(OAc) ₂ : 5 mol% of the carboxyl groups	[42]
5	Epoxy 1	Zn(Ac) ₂ : 5 mol% of the epoxy groups	[26]
6	Nanoclay-CANs	Zn(Ac) ₂ : 2.24%	[23]
7	ESO/GL (R = 0.5, TBD 5 mol%)	TBD: 5 mol% of the carboxyl groups	[41]
8	HBE-2/SA-CAT	Zn(acac) ₂ : 5 mol% of the carboxyl groups	[32]
9	ESO-FPA _{1.0}	Zn(acac) ₂ : 3.33 mol% of the carboxyl groups	[33]
10	PAB-POSS vitrimer	Zn(Ac) ₂ : 10 mol% of the carboxyl groups of poly(acrylonitrile-co-butadiene)	[43]

11. Topology freezing transition temperature of DGEAC/SA/GL networks.

The topology freezing transition temperature (T_v) of V4 was calculated as the following process:

Initially, equation S3 was obtained from Arrhenius law as shown in Fig. 3b:

$$y = 11.42x - 20.37 \quad (R = 0.9997) \quad (S3)$$

The Maxwell relation (equation S4) below is used to calculate T_v which is defined as the point at the viscosity $\eta = 10^{12}$ Pa S. The shear modulus G was estimated from tensile modulus (E') as measured by DMA with the relation (equation S5). E' of the sample was calculated as the average modulus at temperature ranging from 150 to 180°C from the modulus-temperature curves (Fig. S6). The average plateau modulus of the sample is 0.39 MPa. The Poisson's ratio ν is chosen as the value 0.5, which is usually used for rubbers.

$$\eta = G\tau^* \quad (S4)$$

$$G = \frac{E'}{2(1 + \nu)} \quad (S5)$$

Consequently,

$$G = 0.39 / (2 \times 1.5) = 1.3 \times 10^5 \text{ Pa},$$

$$\tau^* = \eta / G = 10^{12} / (1.3 \times 10^5) = 7.65 \times 10^6 \text{ s},$$

$$\ln \tau^* = \ln (7.65 \times 10^6) = 15.85.$$

$$\text{Using equation S3, } 15.85 = 11.42x - 20.37, x = 3.17$$

$$\text{Thereby, } 1000/T_v = 3.17, T_v = 315.46 \text{ K} = 42^\circ\text{C}.$$

According to the above calculation, the T_v of DGEAC/SA/GL networks (V1 to V5) were obtained and listed in Table S3.

Table S4. The T_v of DGEAC/SA/GL networks.

Sample	V1	V2	V3	V4	V5
T_v (°C)	73	54	52	42	49

12. Comparison of welding, reprocessing, repairing, recycling and chemical degrading of V4 with other reported epoxy vitrimers based on TERs.

Table S5. Comparison of welding, reprocessing, repairing, recycling and chemical degrading of V4 with other reported epoxy vitrimers based on TERs.

Entry	Sample	Welding	Reprocessing	Repairing	Recycling	Chemical degrading	Reference
1	Epoxy CANs (5 mol % catalyst)					180°C (160 min)	[S1]
2	Epoxy CANs (5 mol % catalyst)	180°C (180 min)		180°C (180 min)	180°C (220 min)	180°C (190 min)	[S2]
3	Epoxy CANs (7 mol % catalyst)	180°C (180 min)			180°C (220 min)	140°C (440 min) 180°C (190 min) 220°C (60 min)	[S2]
4	Nanoclay-CANs					180°C (360 min)	[S3]
5	ESO/GL (R = 0.5, TBD 5 mol %)	200°C (15 min)		200°C (60 min)	200°C (135 min)	180°C (720 min)	[S4]
6	Cross-linked PDMS				180°C (40 min)	180°C	[S5]
7	TEP-1	220°C (60 min)		220°C (5 min)			[S6]
8	HBE-1/SA	150°C (60 min)		150°C (30 min)			[S7]
9	PEG-epoxy/L-COOH (R = 1 : 2)					190°C (15 min)	[S8]
10	Se-EP/Oz-L (R = 1 : 1)		190°C (60 min)	190°C (5 min)			[S9]
11	Eu-EP/SAs (R = 1 : 0.5)		200°C (60 min)	190°C (60 min)	160°C (60 min)	160°C (420 min)	[S10]
12	EVS, EVC ₂ S ₈ and EVC ₄ S ₆				170°C (10 min)		[S11]
13	ESO-FPA _{1.0}		160°C (30 min)	180°C (30 min)		140°C (120 min)	[S12]
14	CL-PE-310	160°C (60 min)	160°C (120 min)	180°C (5 min)	160°C		[S13]
15	EP-CA-40		150°C (120 min)		170°C (10 min)		[S14]
16	CS11 vitrimer		160°C (60 min)				[S15]
17	CNT-vitrimer	230°C (3 min)		180°C (60 min)			[S16]
18	ACAT-vitrimer	200°C	200°C	180°C (10 min)	200°C (10 min)		[S17]
19	DGEAC/SA/GL (V4)	130°C (60 min)	130°C (60 min)	130°C (120 min)	130°C (60 min)	130°C (300 min)	<i>This work</i>

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