Electronic Supplementary Material

Rosin side chain type catalyst-free vitrimers with high cross-link density, mechanical strength, and thermal stability

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This supporting information contains methods, 4 Figures and 5 Tables.

Methods

The crosslink density of vitrimers were calculated by this equation:

$$d=\frac{E'}{3R(T_g+40)} \tag{S1}$$

The unit volume crosslink density was set to d (mol m^{-3}), E' denoted the storage modulus in the rubbery plateau region (T_g + 40 °C), R referred to the universal gas constant, and T_g was the glass transition temperature.

According to the method described in the literature, the shape memory properties of the material were characterized by single cantilever DMA mode. R_f and R_r were used to represent the shape fixation rate and shape recovery rate of each cycle, respectively, and were calculated by the following formula [1]:

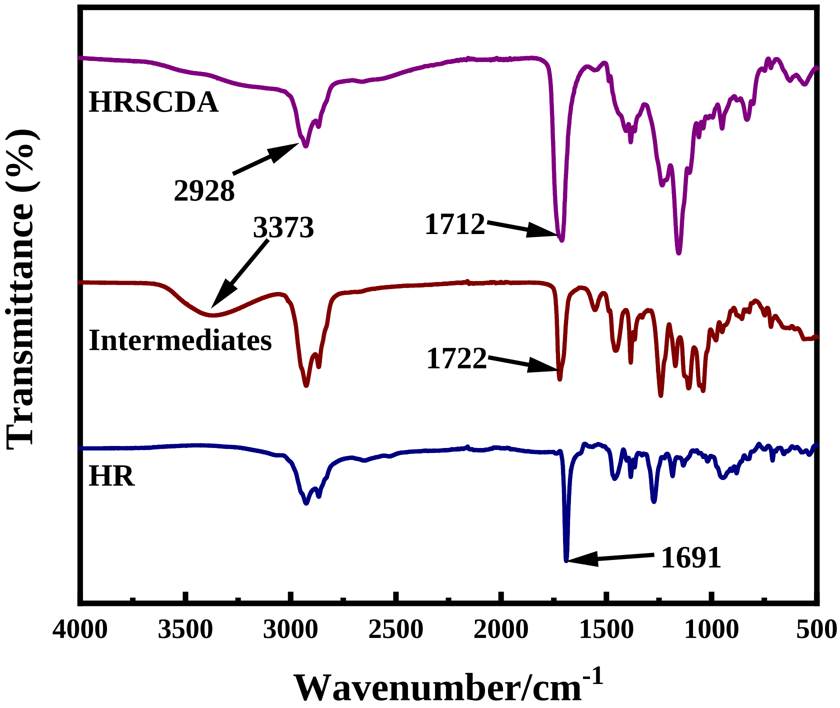
$$R_f=\frac{\sigma_d}{\sigma_l}\times 100\% \tag{S2}$$

$$R_r = \frac{\sigma_d - \sigma_r}{\sigma_d} \times 100\% \tag{S3}$$

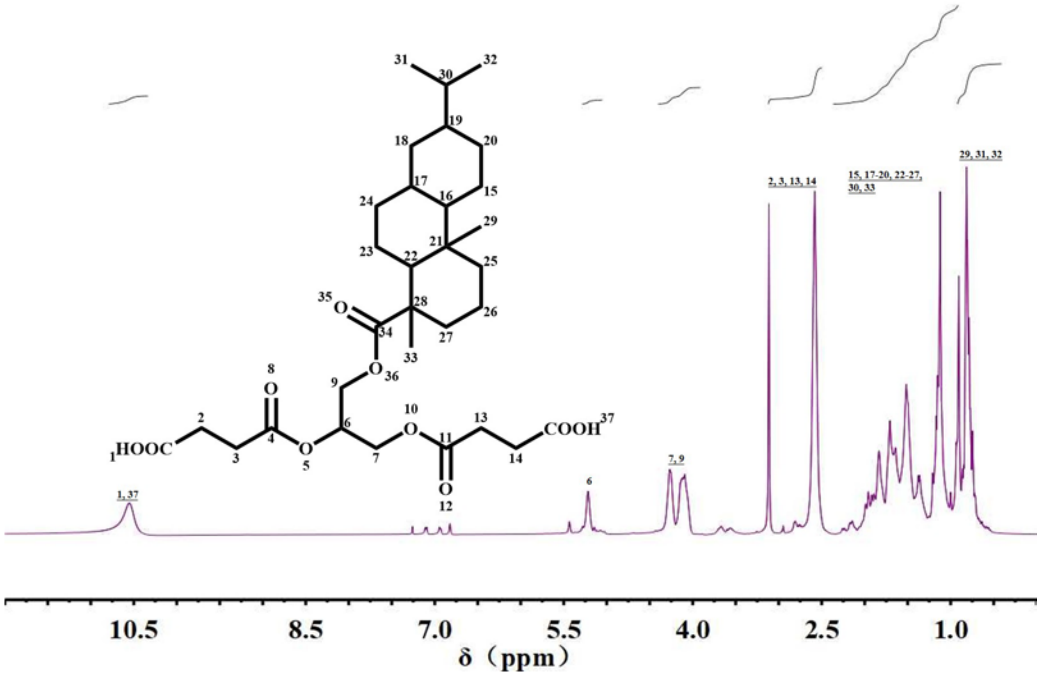
where σ_l represented the maximum deformation under load, while σ_d denoted the fixed deformation after cooling and load removal, and σ_r refered to the recovered deformation.

To study chemical recovery of HRSCDA-Epoxy$_{(x)}$ vitrimers, 5 g small pieces were inserted into a pressure reactor that contained 50 mL of ethanol. The reaction temperature was 160 °C and this process lasted 4 hours. Then the remaining ethanol was detached by a rotary evaporator. Then concentrated solution was gained and cured in a PTFE mold. Finally, chemically recovered vitrimers were obtained. The mechanical properties of the physically recovered and chemically degraded recovered vitrimers were investigated by uniaxial tensile test.

(A)



(B)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7, 9
6
2, 3, 13, 14
15, 17-20, 22-27, 30, 33
29, 31, 32
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COOH37
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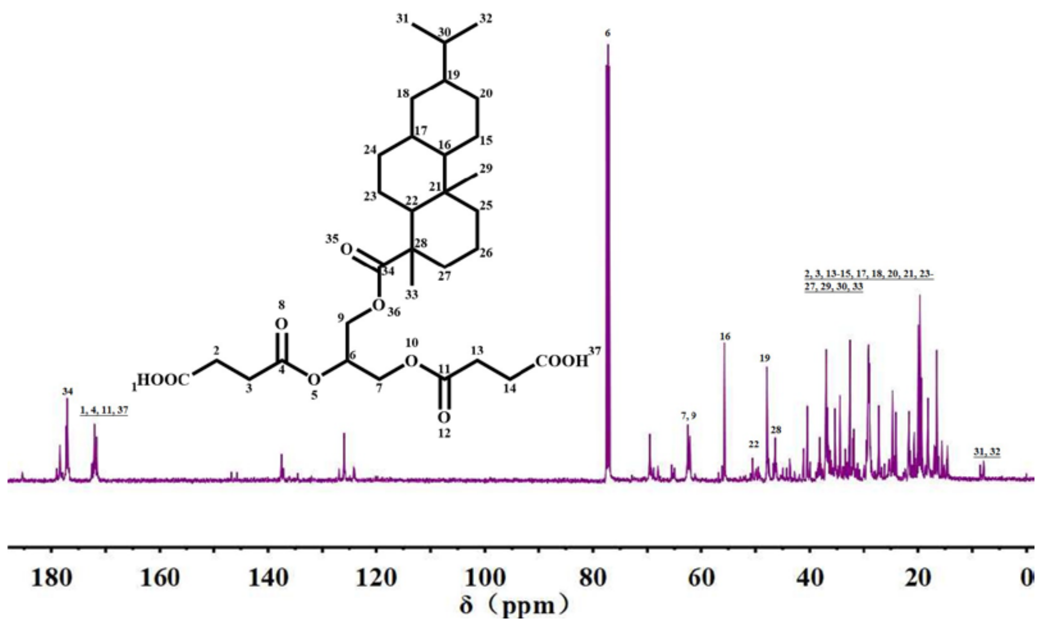
8.5
7.0
5.5
4.0
2.5
1.0
δ（ppm）

(C)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31, 32
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COOH37
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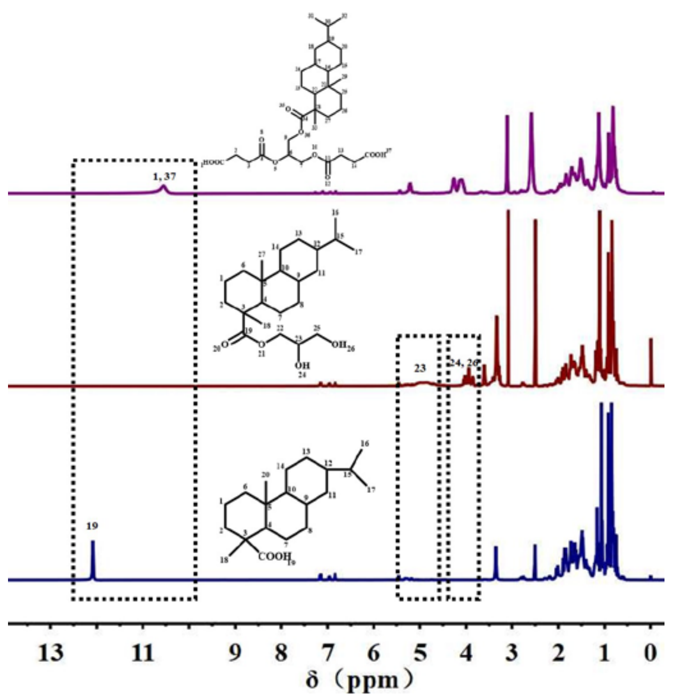
160
140
120
100
80
60
40
20
0
δ（ppm）

(D)



(E)

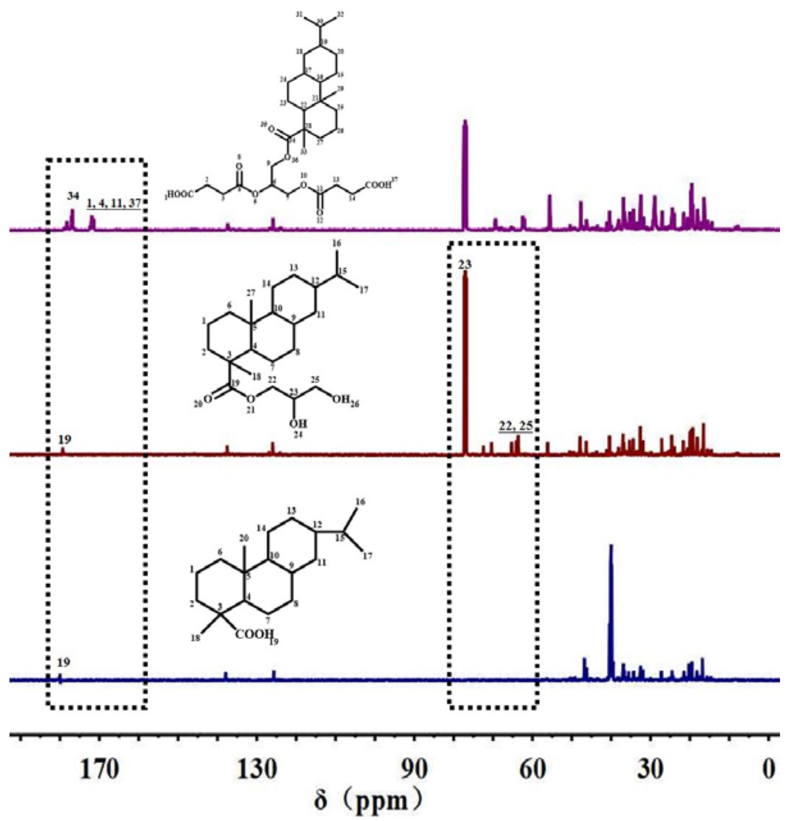


Figure S1. (A) FT-IR spectra of HR, Intermediates, and HRSCDA, (B) ^{1}H NMR and (C) ^{13}C NMR spectra of HRSCDA, (D) ^{1}H NMR and (E) ^{13}C NMR spectra of HR, Intermediates and HRSCDA.

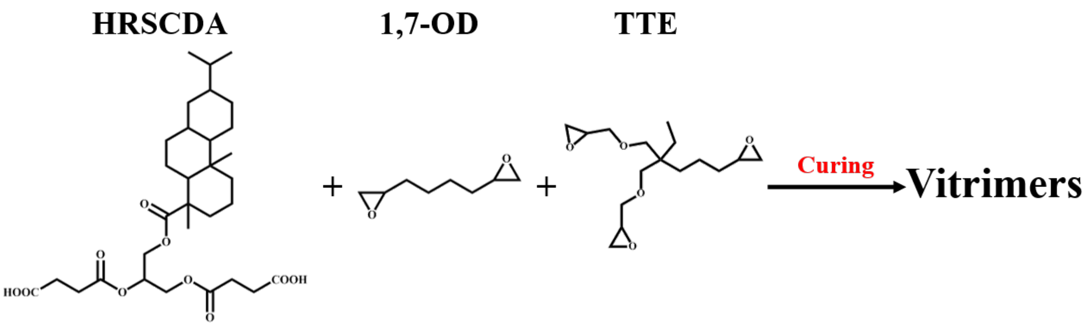


Figure S2. The HRSCDA-TTE$_{(x)}$ vitrimers' curing reaction.

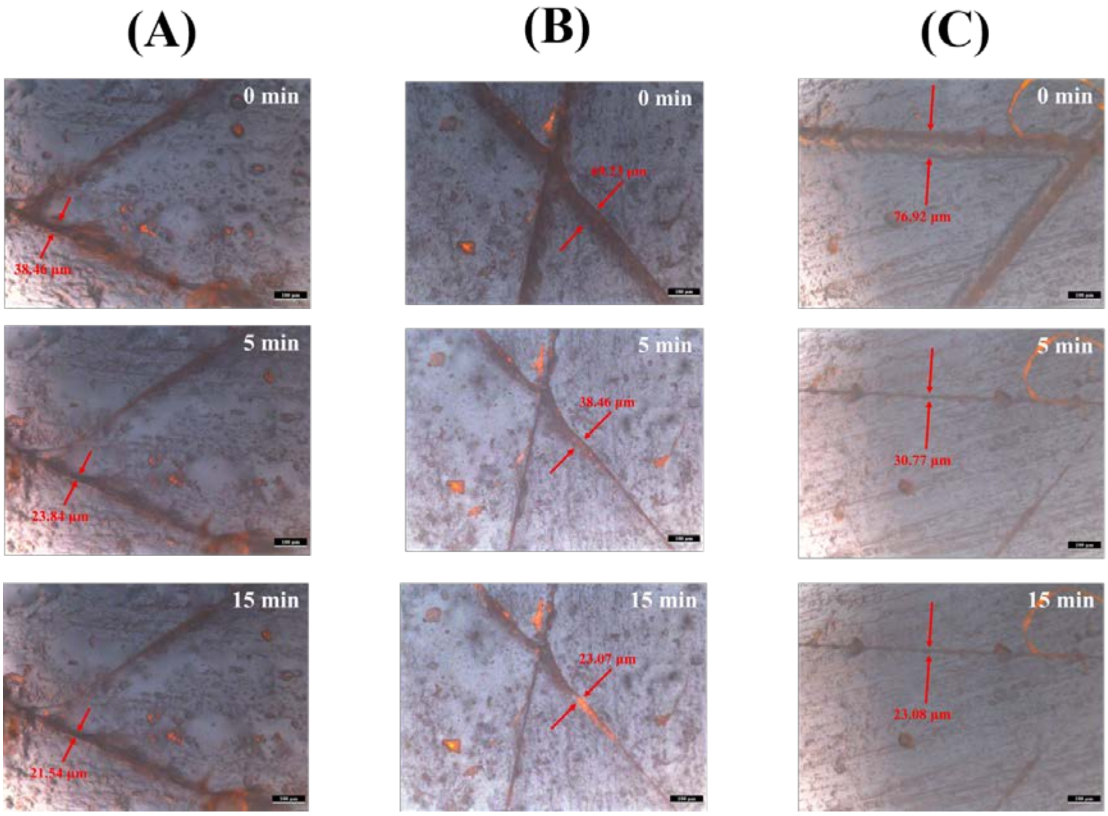


Figure S3. Healing of (A) the HRSCDA-TTE$_{(20)}$, (B) the HRSCDA-TTE$_{(50)}$ and (C) the HRSCDA-TTE$_{(80)}$ vitrimers with different heating times.

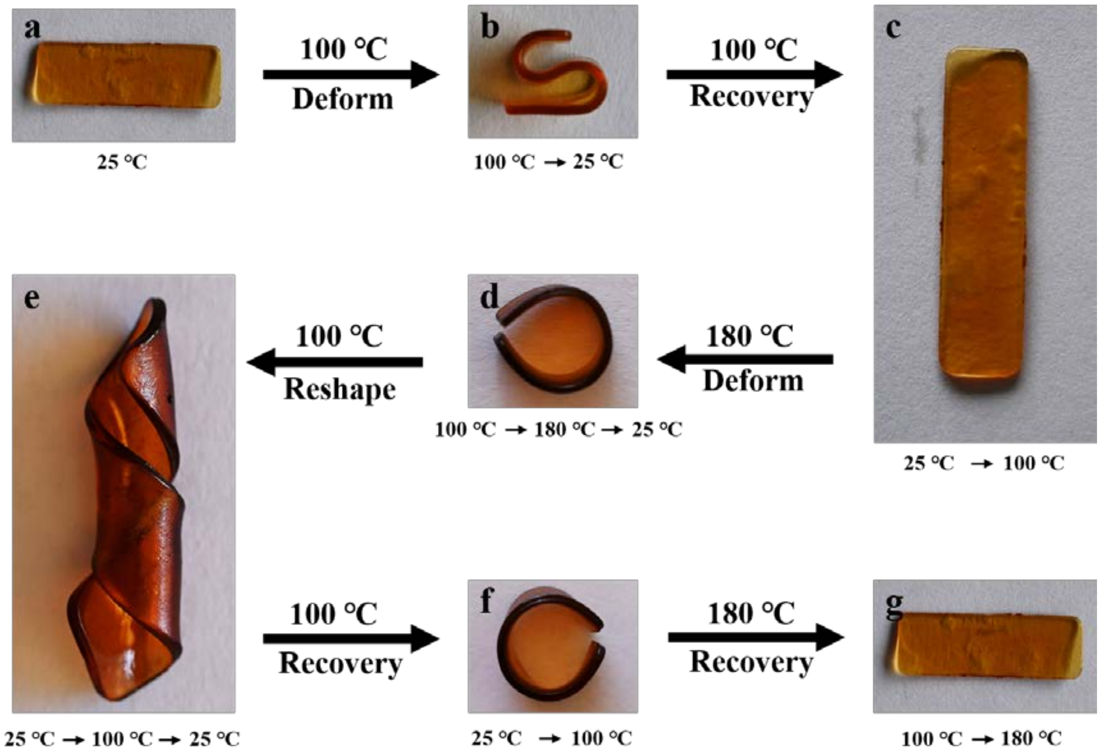


Figure S4. Shape memory digital photograph of the HRSCDA-Epoxy$_{(80)}$ vitrimers: (a–c) Double-shape memory of the the HRSCDA-Epoxy$_{(80)}$ vitrimers using the glass transition temperature (T_g) to fix in an ‘S’-shape, and their recovery upon heating; (c–g) triple-shape memory of the vitrimer using the topology freezing transition temperature (T_v) to fix the ‘O’-shape, and the T_g to fix the spiral shape, and their sequential recovery upon heating.

Table S1. Formulations of the HRSCDA-$TTE_{(x)}$ vitrimers

Samples	ᵃR	HRSCDA/ g	Carboxyl group/ mol	1,7-OD/ g	Epoxy group 1/ mol	TTE/ g	Epoxy group 2/ mol	Total epoxy group/ mol
HRSCDA-$TTE_{(20)}$	1:1	5.40	0.021	1.19	0.017	0.60	0.004	0.021
HRSCDA-$TTE_{(50)}$	1:1	5.40	0.021	0.75	0.010	1.50	0.011	0.021
HRSCDA-$TTE_{(80)}$	1:1	5.40	0.021	0.30	0.004	2.40	0.017	0.021

"x" in HRSCDA-$TTE_{(x)}$ represents the percentage of the number of TTE to the total number of epoxy groups.

[a]R = carboxyl group content/epoxy group content.

Table S2. Physical properties of the HRSCDA-Epoxy$_{(x)}$ vitrimers

Sample	**Gel/ %**	**T$_d$/ ℃**	**T$_g$ DSC/ ℃**	**T$_g$ DMA/ ℃**	**Storage Modulus at 25 ℃/ MPa**	**Storage Modulus at 150℃/ MPa**	**d/ mol m^{-3}**	**τ/ s**	**Tensile Strength/ MPa**	**Strain at break/ %**
HRSCDA-Epoxy$_{(0)}$	88.09 ± 0.36	324	34.4	50.6	2.8	4721	2.08	80.50	12.25 ± 1.75	1.05 ± 0.30
HRSCDA-Epoxy$_{(20)}$	93.86 ± 1.43	359	38.9	51.6	3.2	6360	2.78	65.58	15.25 ± 12.75	1.31 ± 0.97
HRSCDA-Epoxy$_{(50)}$	95.24 ± 1.39	354	49.1	56.7	5.4	6794	2.81	55.50	20.63 ± 3.37	1.49 ± 0.07
HRSCDA-Epoxy$_{(80)}$	98.39 ± 0.89	352	60.5	73.2	12.4	8474	3.00	50.50	40.19 ± 6.56	3.92 ± 0.72

Table S3. Comparison of the mechanical performance between other rosin-based vitrimers and our HRSCDA-Epoxy$_{(x)}$ vitrimers

Material system	Tensile strength/ MPa	Elongation at break/ %	Ref
Epoxidised soybean oil, fumaropimaric acid	~ 16.6	~ 88.9	[2]
C-FPAE, BDB	~ 39.5	~ 9.1	[3]
PWMPA, HDI, DBTDL	~ 16.8	~ 61	[4]
HRSCDA, ZT-5190, 1,7-OD	~ 40.2	~ 3.9	This work

Table S4. The change in scratch width of the HRSCDA-Epoxy$_{(x)}$ vitrimers

Sample	Scratch width at 200 ℃/ μm					
	0 min	Rate	5 min	Rate	15 min	Rate
HRSCDA-Epoxy$_{(0)}$	14.29	0	12.21	14.6%	10.14	29.0%
HRSCDA-Epoxy$_{(20)}$	35.71	0	28.57	20.0%	21.43	40.0%
HRSCDA-Epoxy$_{(50)}$	121.43	0	64.29	47.1%	52.34	56.9%
HRSCDA-Epoxy$_{(80)}$	101.43	0	53.57	47.2%	42.86	57.7%

Table S5. The change in scratch width of the HRSCDA-TTE$_{(x)}$ vitrimers

Sample	Scratch width at 200 ℃/ μm					
	0 min	Rate	5 min	Rate	15 min	Rate
HRSCDA-TTE$_{(20)}$	38.46	0	23.84	38.0%	21.54	43.9%
HRSCDA-TTE$_{(50)}$	69.23	0	38.46	44.4%	23.07	66.7%
HRSCDA-TTE$_{(80)}$	76.92	0	30.77	60.0%	23.08	70.0%

References

1. Xu Y, Fu P, Dai S, Zhang H, Bi L, Jiang J, Chen Y. Catalyst-free self-healing fully bio-based vitrimers derived from tung oil: Strong mechanical properties, shape memory, and recyclability. Industrial Crops and Products, 2021, 171: 113978.
2. Yang X, Guo L, Xu X, Shang S, Liu H. A fully bio-based epoxy vitrimer: Self-healing, triple-shape memory and reprocessing triggered by dynamic covalent bond exchange. Materials & Design, 2020, 186: 108248.
3. Zeng Y, Li J, Liu S, Yang B. Rosin-based epoxy vitrimers with dynamic boronic ester bonds. Polymers, 2021, 13(19): 3386.
4. Li J, Yang W, Ning Z, Yang B, Zeng Y. Sustainable polyurethane networks based on rosin with reprocessing performance. Polymers, 2021, 13(20): 3538.