Supporting Information

Direct-Ink-Writing Printing of Shape Memory Cross-Linked Networks from Biomass-Derived Small Molecules

Dan Liu, Di Wu, Yi Xiao, Rui Zhan, Xin-Rong Zeng and Ke-Ke Yang *

The Collaborative Innovation Center for Eco-Friendly and Fire-Safety Polymeric Materials (MoE), National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), State Key Laboratory of Polymer Materials Engineering, College of Chemistry, Sichuan University, Chengdu 610064, China; 1097088853@qq.com (D.L.); 1346990135@qq.com (D.W.); xiaoyi@stu.scu.edu.cn (Y.X.); m19942331358@163.com (R.Z.); zxr18997@163.com (X.-R.Z.)

* Corresponding author. E-mail: kkyang@scu.edu.cn (K.-K.Y.)

Characterization

Dynamic rheology test

Dynamic viscosity testing was performed using a Discovery HR-2 dynamic rheometer (TA Instruments, USA) to analyze the rheological properties of the 'ink'. The mold used was a parallel plate (Peltier steel) with a diameter of 40 mm. The frequency was set at 1.0 Hz, and the plate gap at 1.0 mm. Steady shear experiment was conducted under the 'Flow Sweep' mode at 25 °C, with the shear rate ranging from 1.0 to 1000 s^{-1}. The viscosity at a shear rate of 10 s^{-1} was recorded as the initial viscosity. Oscillatory shear experiment was performed under the 'Oscillation Time' mode at 25 °C, alternating between high and low strain. The low strain was maintained at 1.0%, while the high strain was set at 1000%, with each stage lasting 2 min. Changes in storage modulus (G') and loss modulus (G'') were monitored throughout the process. UV-assisted oscillatory shear experiment was carried out under the 'Oscillation Time' mode at 25 °C, with a fixed strain of 1.0% and a test time of 2 min. The fluctuations in G' and G'' with UV irradiation time were recorded.

Swelling Test

The swelling test was conducted to assess the cross-linking of the samples: The specific procedure involved cutting the sample into small pieces, measuring its original weight (m_0), immersing it in DCM at room temperature for 24 h, measuring the wet weight of the sample (m_1), allowing the swelled sample to volatilize solvent in a fume hood, drying it in an oven at 60 °C until a constant weight is achieved, and then measuring the final weight of the sample (m_2). The gel content (G) and swelling ratio (S) of the sample were calculated using equations (S1) and (S2), respectively.

$$G = \frac{m_2}{m_0} \times 100\% \quad \text{(S1)}$$

$$S = \frac{m_1}{m_2} \times 100\% \quad \text{(S2)}$$

Shape memory tests

Shape memory tests utilize a dynamic mechanical analyzer, Q800 (TA Instruments, USA) to quantitatively assess shape memory performance under controlled force mode. The specific procedure involves heating the specimen to 40 °C and applying stress to stretch it into a rectangular shape. Subsequently, the specimen is rapidly cooled to -40 °C to fix the temporary shape and held for 10 min, resulting in a strain denoted as ε_d (N). The stress is then removed to determine the fixed strain, denoted as ε_f (N). The specimen is heated back to 40 °C and held for 10 min to recover its shape, resulting in a strain denoted as ε_p (N). It is important to note that the "N" represents the number of cycles. The shape fixity ratio, R_f, and the shape recovery ratio, R_r, can be calculated using equations (S3) and (S4) respectively.

$$R_{f(N)} = \frac{\varepsilon_{d(N)} - \varepsilon_{p(N-1)}}{\varepsilon_{f(N)} - \varepsilon_{p(N-1)}} \times 100\% \quad \text{(S3)}$$

$$R_{r(N)} = \frac{\varepsilon_{f(N)} - \varepsilon_{p(N)}}{\varepsilon_{f(N)} - \varepsilon_{p(N-1)}} \times 100\% \quad \text{(S4)}$$

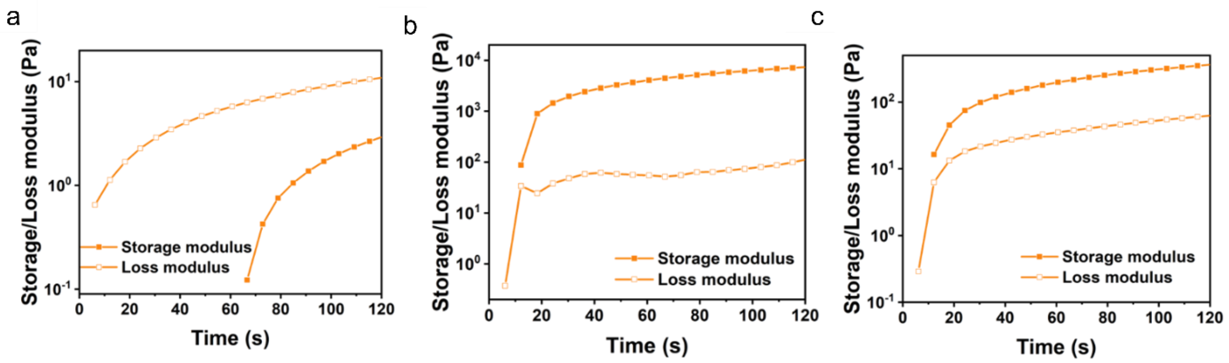

Figure S1 UV-assisted dynamic rheological testing of MO-TTMP with different ratios of thiol-ene (r): 0.5 (a); 1.2 (b); 1.5 (c) (UV intensities (P)= 30 mW/cm^2; concentrations (c)=1.5 g/mL; BAPO contents (w_{BAPO}) =2.0%).

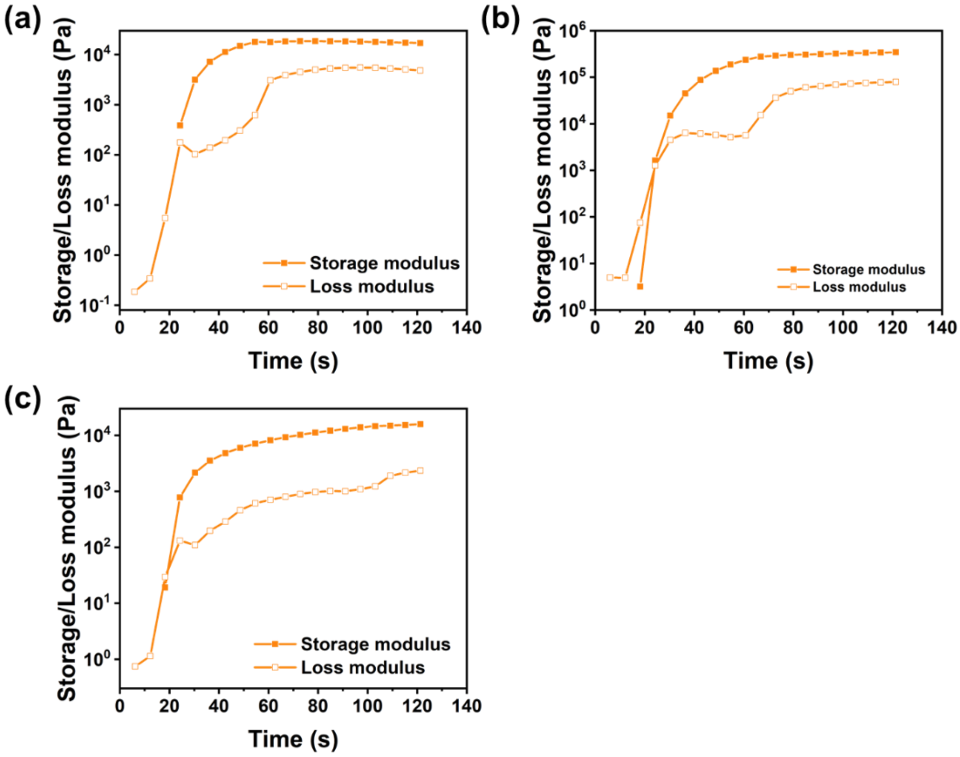

Figure S2 UV-assisted dynamic rheological testing of MO-TTMP with different concerntrations: 0.8 g/mL (a); 0.9 g/mL (b); 1.1 g/mL (c) (P= 30 mW/cm^2; r =1; w_{BAPO}=2.0%).

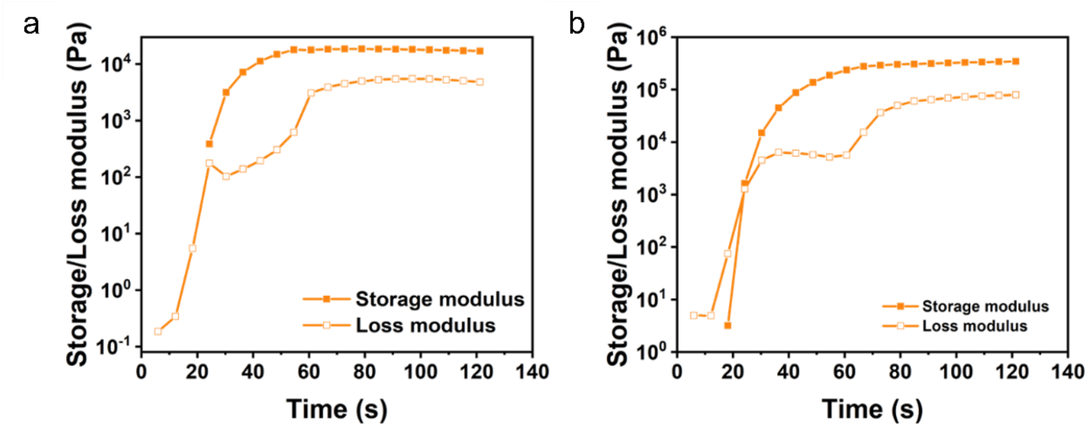

Figure S3 UV-assisted dynamic rheological testing of MO-TTMP with different w_{BAPO}: 0.8% (a); 1.0% (b); (P= 30 mW/cm^2; r =1; c=1.5 g/mL).

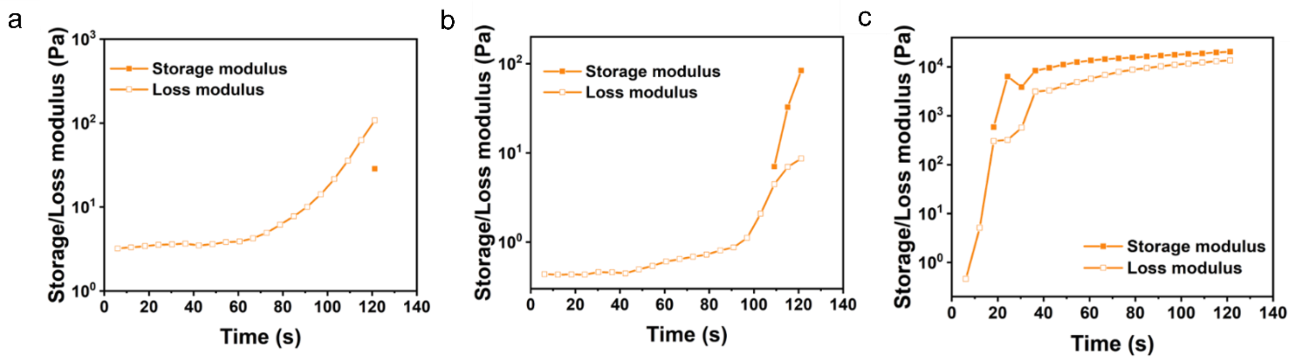

Figure S4 UV-assisted dynamic rheological testing of MO-TTMP with different P: 5 mW/cm^2 (a); 10 mW/cm^2 (b); 15 mW/cm^2 (c); (w_{BAPO}=1.5%; r =1; c=1.5 g/mL).

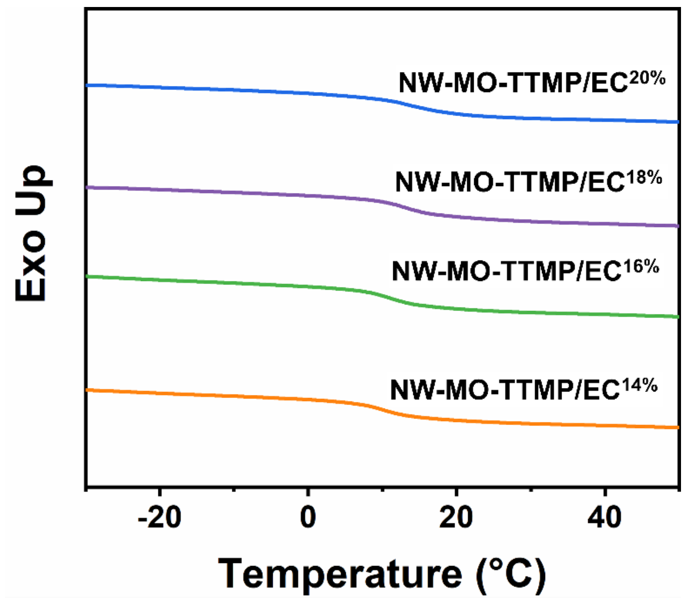

Figure S5 DSC curves of NW-MO-TTMP/EC.

Table S1 Tensile relevant data of elastomers with different cross-linking agents and unsaturated biomass small molecules

Sample	n(SH): n(C=C)	w_{BAPO} (%)	P (mW/cm^2)	c (g/mL)	σ (MPa)	ε (%)
NW-CSO-TTMP	1.2	1.0	20	1.5	0.8±0.0	49±6
NW-CSO-DODT	1.2	1.0	20	1.5	0.4±0.0	47±2
NW-MO-TTMP	1.2	1.0	20	1.5	2.7±0.1	378±7
NW-NE-TTMP	1.2	1.0	20	1.5	0.7±0.0	50±1

Table S2. Tensile and swelling data of NW-MO-TTMP with different *r*, *c*, w_{BAPO} and *P*

entry	n(SH): n(C=C)	c (g mol^{-1})	w_{BAPO} (%)	P (mW/cm^2)	G (%)	S (%)	σ (MPa)	ε (%)
1	0.5	1.5	2.0	30	/	/	/	/
2	0.8	1.5	2.0	30	82.7±1.5	298±67	0.9±0.1	174±10
3	1.0	1.5	2.0	30	95.6±1.5	311±23	2.6±0.3	215±26
4	1.2	1.5	2.0	30	85.2±0.3	416±33	1.0±0.01	219±16
5	1.5	1.5	2.0	30	53.6±0.7	531±93	/	/
6	1.0	1.1	2.0	30	94.8±3.0	303±4	2.2±0.2	208±24
7	1.0	0.9	2.0	30	94.9±0.7	376±27	1.9±0.2	244±10
8	1.0	0.8	2.0	30	94.2±1.6	303±20	1.3±0.1	251±30
9	1.0	1.5	0.8	30	89.5±2.5	304±5		
10	1.0	1.5	1.0	30	91.0±2.0	304±5		
11	1.0	1.5	1.5	30	94.8±0.3	271±6		
12	1.0	1.5	1.5	5	91.1±2.4	309±51		
13	1.0	1.5	1.5	10	91.5±1.8	295±28		
14	1.0	1.5	1.5	15	92.4±0.6	275±29		
15	1.0	1.5	1.5	20	91.8±1.1	328±19		

Table S3. The results of tensile tests and swelling tests for NW-MO-TTMP/ECs

Sample	σ (MPa)	ε (%)	G (%)	S (%)
NW-MO-TTMP/EC$^{9\%}$	9.4±0.5	383±23	97.0±0.6	302±17
NW-MO-TTMP/EC$^{14\%}$	16.6±0.8	254±5	93.7±4.4	332±39
NW-MO-TTMP/EC$^{16\%}$	17.4±1.9	252±12	95.9±3.9	354±64
NW-MO-TTMP/EC$^{18\%}$	18.2±0.9	259±4	94.6±0.3	340±45
NW-MO-TTMP/EC$^{20\%}$	20.6±1.1	229±12	95.9±0.1	368±44

Table S4. DSC and SMEs data of NW-MO-TTMP/ECs

Sample	T_g (°C)	R_f (%)	R_r (%)
NW-MO-TTMP/EC$^{14\%}$	9.7	99.7±0.0	99.4±3.4
NW-MO-TTMP/EC$^{16\%}$	11.2	99.7±0.0	99.6±0.4
NW-MO-TTMP/EC$^{18\%}$	12.5	99.7±0.1	98.6±0.1
NW-MO-TTMP/EC$^{20\%}$	13.2	99.8±0.0	99.4±0.3