

Electronic Supplementary Information

Preparation of non-isocyanate polyurethane from epoxy soybean oil: dual dynamic networks to realize mild self- healing and reprocessing conditions

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Experimental section

Materials

Epoxy soybean oil (ESO, AR, epoxy value = 6.121), 4,4'-Diaminodiphenyl methane (DDM, AR, 97%), 4,4'-diaminodiphenyldisulfide (DDS, AR, 99%), and tetrabutylammonium iodide (TBAI, AR, 99%) were obtained from Aladdin Chemical Co., Ltd. L-Ascorbic acid (AR, 99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. CO₂ was provided by Nanjing Max Special Gas Co., Ltd. Magnesium sulfate (MgSO₄, AR, 99%) and ethyl acetate were all purchased from Nanjing Chemical Reagent Co., Ltd. All chemicals and solvents were used as received without further purification. Distilled water was prepared by the laboratory.

Preparation of CSBO

The preparation method of CSBO is as reported in our previous work.¹ ESO, the catalyst TBAI, and the co-catalyst L-Ascorbic acid were incorporated into a pressure reactor. Then CO₂ was passed into the pressure reactor with an initial pressure of 3.5 MPa. The reaction was carried out at 80 °C for 2 d with magnetic stirring. After the temperature of the reactor was cooled to room temperature and the gas in the reactor was slowly released, a viscous crude produce CSBO was obtained. Subsequently, the crude CSBO was dissolved in ethyl acetate and then washed three times with saturated brine and deionized water, respectively. The original layer was then dried in anhydrous MgSO₄ and concentrated by rotary evaporation. The concentrated product was dried overnight at 40 °C in a vacuum oven to collect the purified CSBO.

Preparation of bio-based ESO–DDS, CSBO–DDM, and CSBO–DDS

The bio-based materials with different dynamic covalent bonds were prepared according to a one-pot method. The preparation of ESO–DDS was based on the reaction between the epoxy groups of ESO and the amino groups of DDS. Briefly, powdered DDS was dissolved in liquid ESO by stirring for 30 min at 60 °C, and the homogeneous mixture was poured into the molds and cured at 140 °C for 72 h to prepare the ESO–DDS. Similarly, DDM was added to the CSBO and stirring at 60 °C for 30 min to obtain the homogeneous mixture, which was poured into the molds and cured at 140 °C for 72 h to prepare CSBO–DDM. Moreover, DDS was incorporated in the CSBO and stirring at 60 °C for 30 min to obtain the mixture, which was poured into the molds and cured at 140 °C for 72 h to prepare CSBO–DDS. The formulas of the bio-based NIPUs are exhibited in Table S1.

Characterization

The structure of ESO, CSBO, DDM, DDS, ESO–DDS, CSBO–DDM, and CSBO–DDS was characterized by a Fourier transform infrared (FTIR) spectrometer (Nicolet Is50, Thermo Fisher Scientific, USA). ¹H NMR and ¹³C NMR spectra for ESO and CSBO were recorded on a AV400 spectrometer (Bruker, Germany) with frequency of 400.13 and 100.61 MHz, respectively. Deuteriochloroform (CDCl₃) was used as the solvent, with tetramethylsilane (TMS) as an internal standard.

The thermal stability of ESO–DDS, CSBO–DDM, and CSBO–DDS was measured using a thermogravimetric analyzer (209F1 TG, Netzsch, Germany), which heated from room temperature to 800 °C with a heating rate of 10 °C/min under a nitrogen atmosphere.

Tensile tests were carried out by a universal testing machine at 25 °C with a tensile rate of 5 mm/min (Shenzhen Sans Technology Co., Ltd., China), and all samples were measured 3 times to obtain the average value. The mechanical properties of CSBO–DDS with a size of 100 mm (length) × 20 mm (width) × 1 mm (thickness) was further measured by lifting a 200 g weight, and the film was strongly folded and then the weight was lifted again for the test.

The gel content of the cross-linked networks was estimated by immersing dry samples in boiling acetone with the Soxhlet apparatus. After extracting the samples with acetone for 24 h, the gel content was calculated according to the following equations:

$$Gel\ content\ (\%) = \frac{W_1}{W_0} \times 100\% \quad (S1)$$

where W_0 and W_1 are the weights of samples before and after the extraction, respectively. The final gel content values for each sample are the average value of three replicates.

Dynamic mechanical properties of the bio-based polymers with different raw materials were determined by a dynamic mechanical analyzer (DMA Q800, TA Instruments, USA). All samples were prepared as a rectangle of 25 mm × 5 mm × 1.5 mm and tested using the film tension mode with a heating rate of 3 °C/min from –25 to 100 °C under the frequency of 1 Hz.

Stress relaxation tests of different bio-based NIPUs were also characterized by DMA Q800 (TA Instruments, USA) in the linear viscoelastic region at different temperature (100 °C, 120 °C, 140 °C, 160 °C, 180 °C) with a constant strain of 3%.

Then the changing trend of the module as a function of time was recorded. The activation energy (E_a) of stress relaxation was calculated according to the Maxwell model between relaxation time and temperature.

The self-healing properties of ESO–DDS, CSBO–DDM, and CSBO–DDS were observed using an optical microscope (Axioscope 5, ZEISS, Germany). The samples scratched by a knife were placed in an oven at 50 °C or 150 °C, and the changes of the scratches were observed using a microscope after different periods of time. In addition, the self-healing behavior under UV light has also been explored by the microscope after different periods of time. The UV healing experiments were performed in a UV chamber (IntelliRay 400, Uvitron International, United States) at a wavelength of 365 nm for 60 min under irradiation intensity 30 mW/cm².

The reprocessing of ESO–DDS, CSBO–DDM, and CSBO–DDS was performed using a hot-pressing machine (Dongguan Zhenggong Electromechanical Equipment Technology Co., Ltd., China). The samples were chopped into small pieces and the hot-pressing at 140 °C for 8 h with a constant press of 8 MPa. After the samples were cooled to room temperature and released from the press, the recyclable NIPUs were obtained.

Calculations of CSBO–DDS for activation energy (E_a)²

Equation obtained from Arrhenius law: $y = 8.9274x - 16.4137$ ($R^2 = 0.9949$)

Which corresponds to: $\ln(\tau) = 8.9274 \times 1000/T - 16.4137$

Identifying this to the experimental equation: $E_a/R = 8.9274 \times 1000$

$E_a = 8.9274 \times 1000 \times 8.314 = 74.22 \text{ kJ mol}^{-1}$

Calculations of ESO–DDS for activation energy (E_a)

Equation obtained from Arrhenius law: $y = 9.8046x - 18.1182$ ($R^2 = 0.9997$)

Which corresponds to: $\ln(\tau) = 9.8046 \times 1000/T - 18.1182$

Identifying this to the experimental equation: $E_a/R = 9.8046 \times 1000$

$$E_a = 9.8046 \times 1000 \times 8.314 = 81.51 \text{ kJ mol}^{-1}$$

Calculations of CSBO–DDM for activation energy (E_a)

Equation obtained from Arrhenius law: $y = 10.7229x - 18.3925$ ($R^2 = 0.9853$)

Which corresponds to: $\ln(\tau) = 10.7229 \times 1000/T - 18.3925$

Identifying this to the experimental equation: $E_a/R = 10.7229 \times 1000$

$$E_a = 10.7229 \times 1000 \times 8.314 = 89.15 \text{ kJ mol}^{-1}$$

Characterization of ESO and CSBO

The NMR characterizations have been performed to confirm the successful conversion of ESO to CSBO. In the ^1H NMR spectra (Figure S1), the proton signals appeared at 2.7-3.0 ppm corresponding to the epoxy groups of ESO is shifted to 4.4-4.8 ppm due to the newly formed cyclic carbonate group. In addition, compared with the ^{13}C NMR spectrum of ESO (Figure S2), a new peak is observed at 153.8 ppm in the ^{13}C NMR spectrum of CSBO ascribed to the carbonyl in the cyclic carbonate. The signals at 53 ppm in the ESO spectrum shifts to 82 ppm in the CSBO spectrum due to the epoxy group is converted to cyclic carbonate groups. The results of NMR confirmed the successful conversion of the ESO to CSBO. Moreover, the conversion rate of ESO to CSBO was calculated via ^1H NMR by comparing the integrals of the two diastereotopic protons in the epoxy groups (protons at positions a and b in Figure S1, 2.7-3.0 ppm) of starting material and the carbamate groups (protons at positions c and d in Figure S1, 4.4-4.8 ppm) of the products.³ The conversion rate was determined according the equation S2 below.

$$\text{Conversion rate (\%)} = \frac{I_{c,d}}{I_{a,b} + I_{c,d}} \quad (S2)$$

where $I_{a,b}$ is the integral of the protons at 2.7-3.0 ppm in ^1H NMR of CSBO and $I_{c,d}$ is the integral of the protons at 4.4-4.8 ppm in ^1H NMR of CSBO. According to the above method, the conversion rate can be calculated as 76.4%.

Supplement Table and Figures

Table. S1 Formulations of polymer networks

Sample	CSBO (g)	ESO (g)	DDS (g)	DDM (g)
CSBO-DDS	6	/	2.019	/
CSBO-DDM	6	/	/	1.611
ESO-DDS	/	6	2.019	/

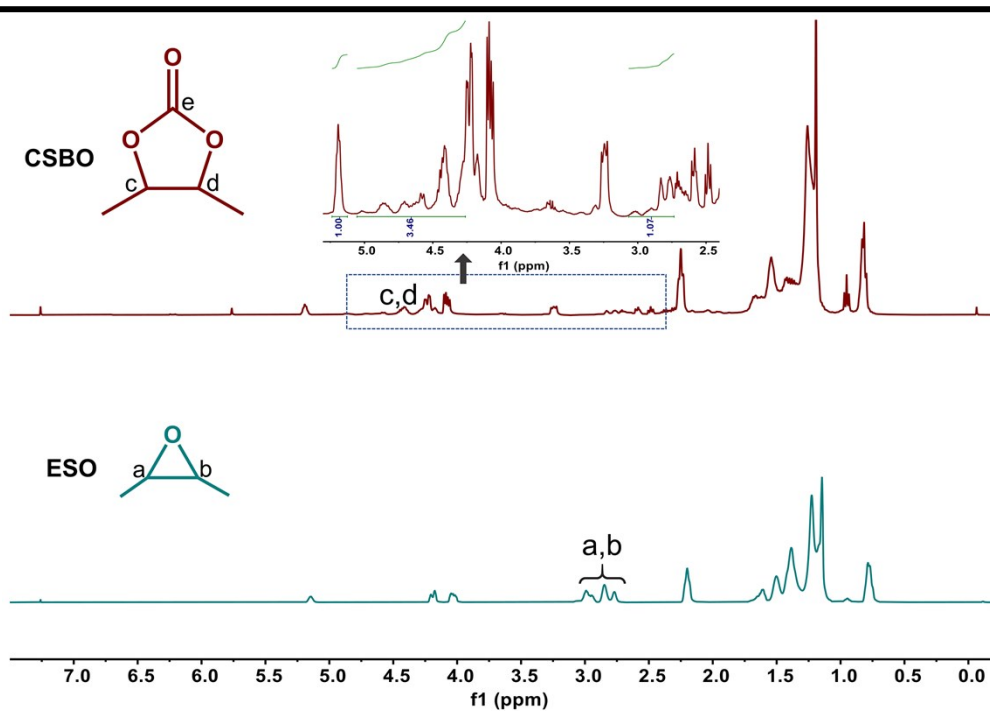


Figure S1. ¹H NMR of ESO and CSBO.

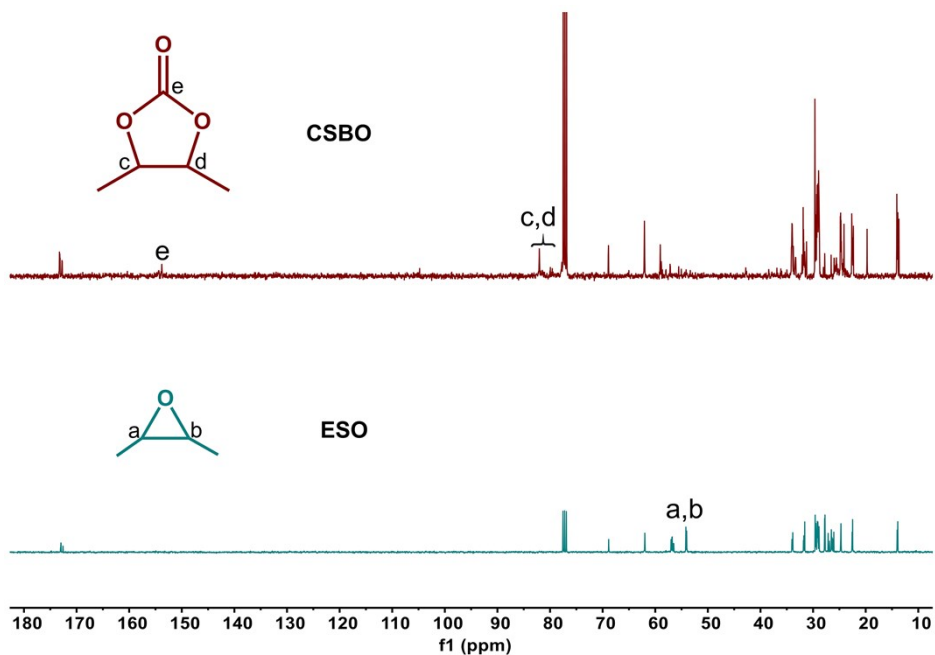


Figure S2. ^{13}C NMR of ESO and CSBO.

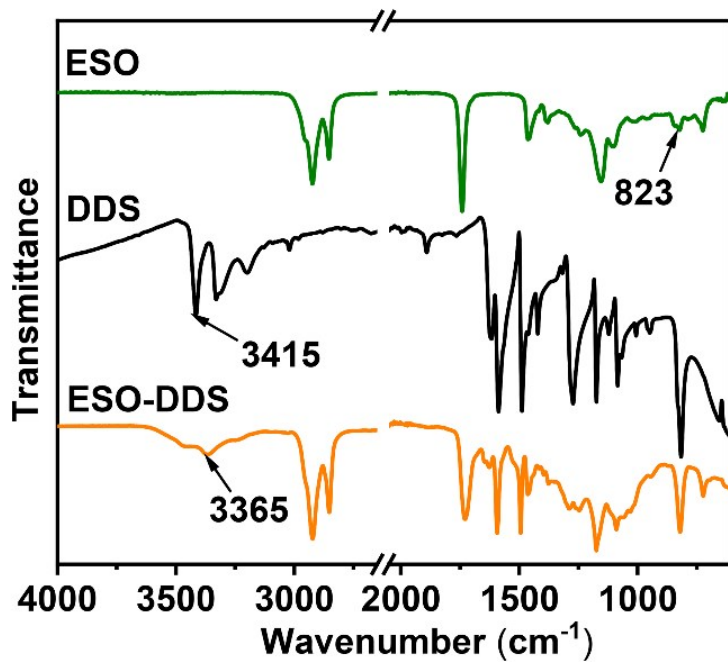


Figure S3. FTIR spectra of ESO, DDS, and ESO-DDS.

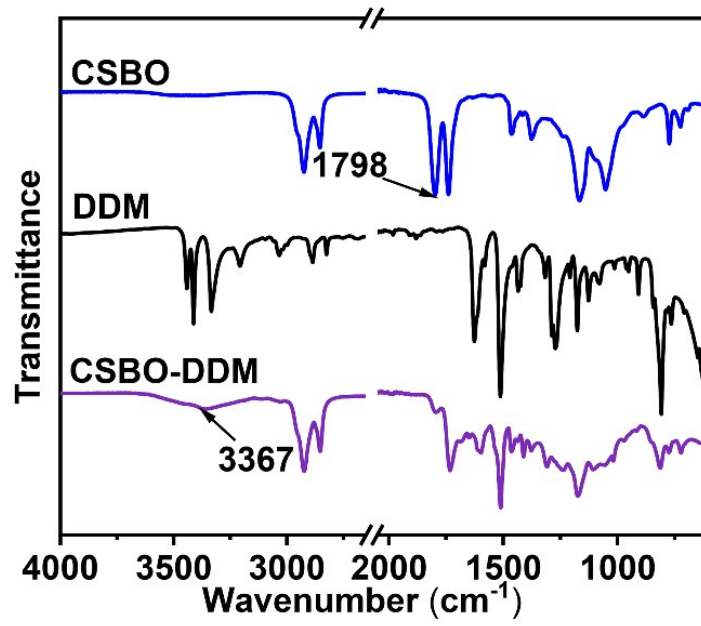


Figure S4. FTIR spectra of CSBO, DDM, and CSBO-DDM.

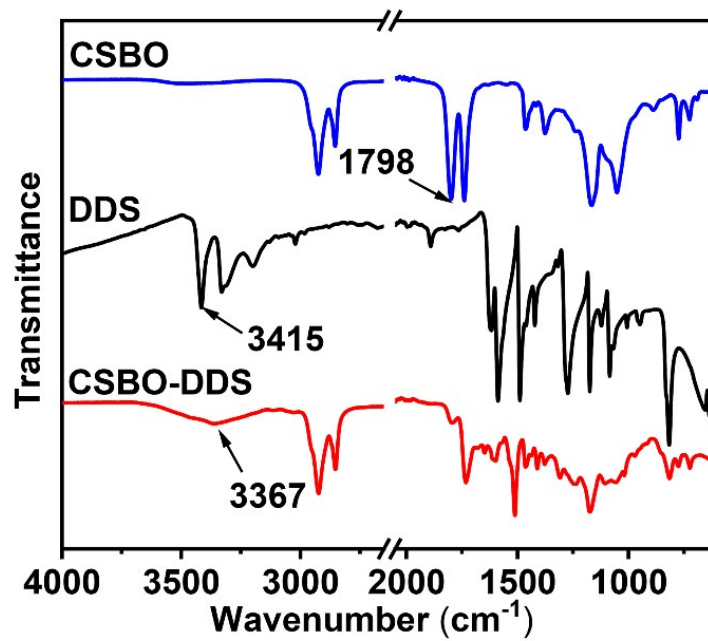


Figure S5. FTIR spectra of CSBO, DDS, and CSBO-DDS.

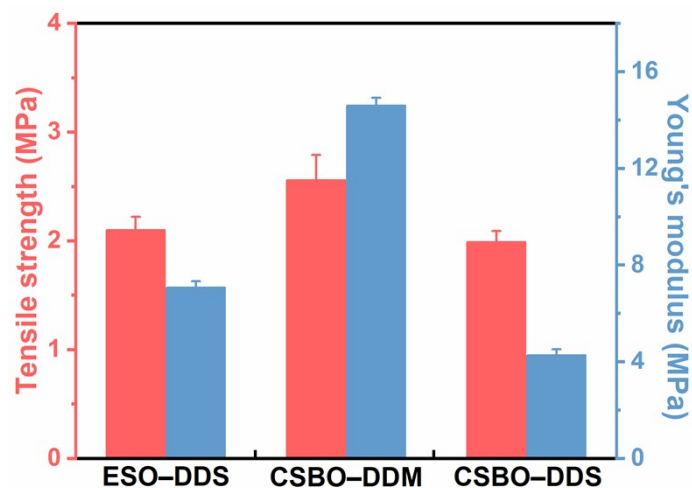


Figure S6. Tensile strength and young's modulus of ESO-DDS, CSBO-DDM, and

CSBO-DDS.

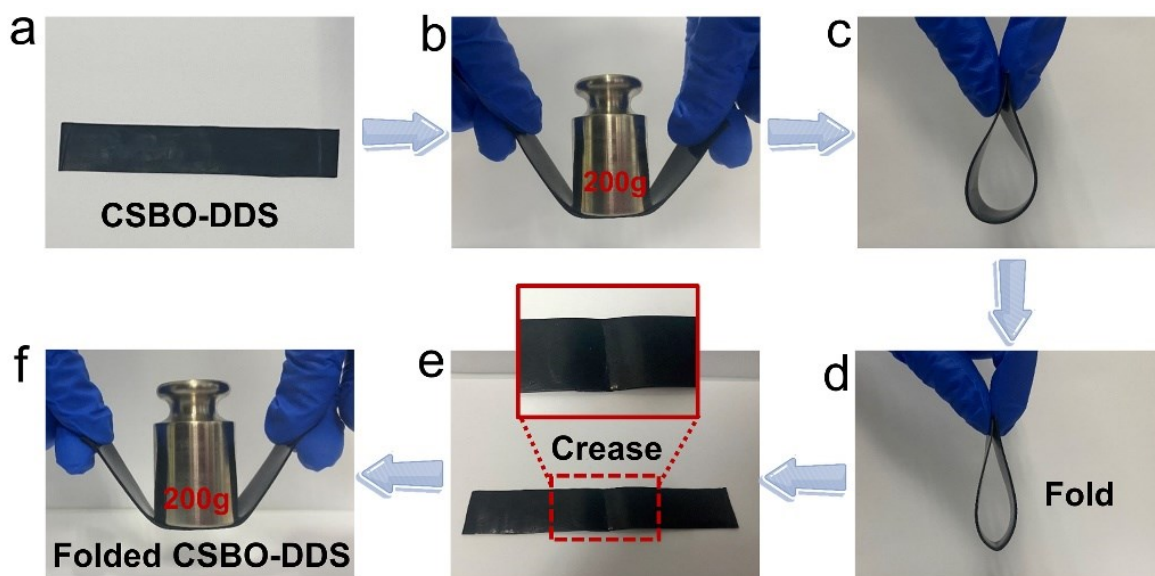


Figure S7. (a) The image of CSBO-DDS (10 cm×1.8 cm×0.1 cm); (b) the sample after folding lifted a 200 g weight; (c) and (d) the image of folded CSBO-DDS; (e) folded CSBO-DDS with obvious crease; (f) folded CSBO-DDS lifted 200 g weight.

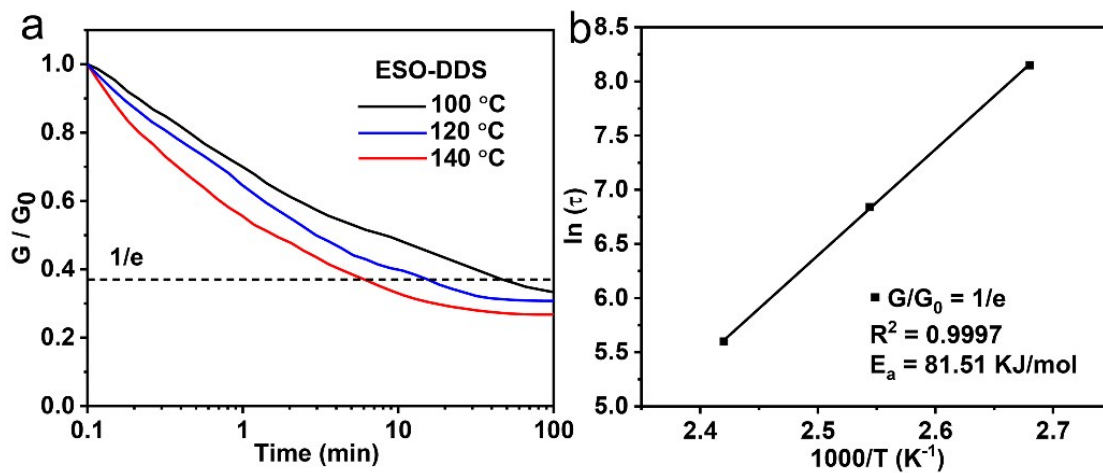


Figure S8. (a) Stress relaxation curves of ESO–DDS at different temperatures. (b) The linear fitting curve of ESO–DDS is based on the Arrhenius equation for activation energy calculation.

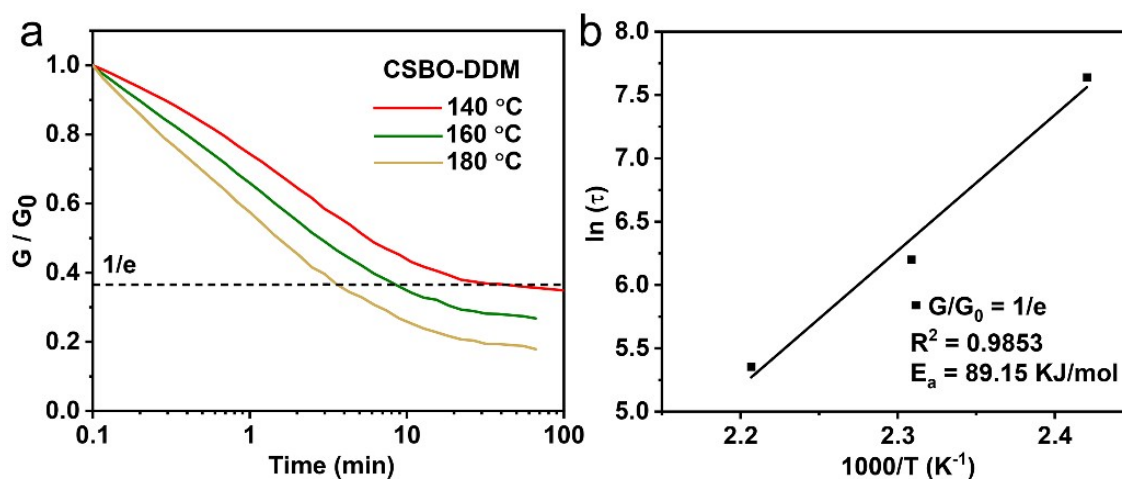


Figure S9. (a) Stress relaxation curves of CSBO–DDM at different temperatures. (b) The linear fitting curve of CSBO–DDM is based on the Arrhenius equation for activation energy calculation.

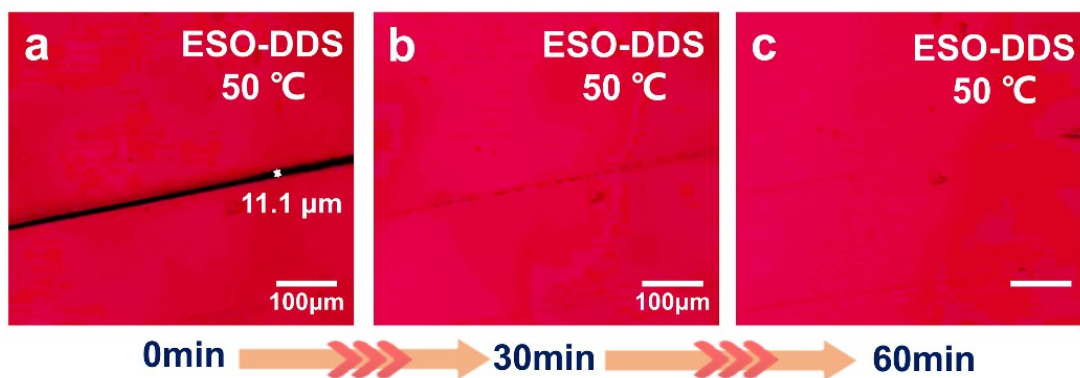


Figure S10. Self-healing of ESO-DDS with different heating times.

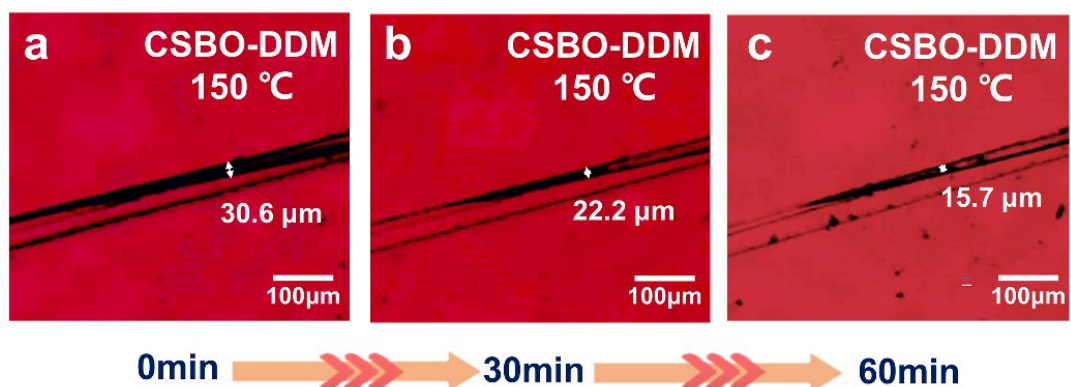


Figure S11. Self-healing of CSBO-DDM with different heating times.

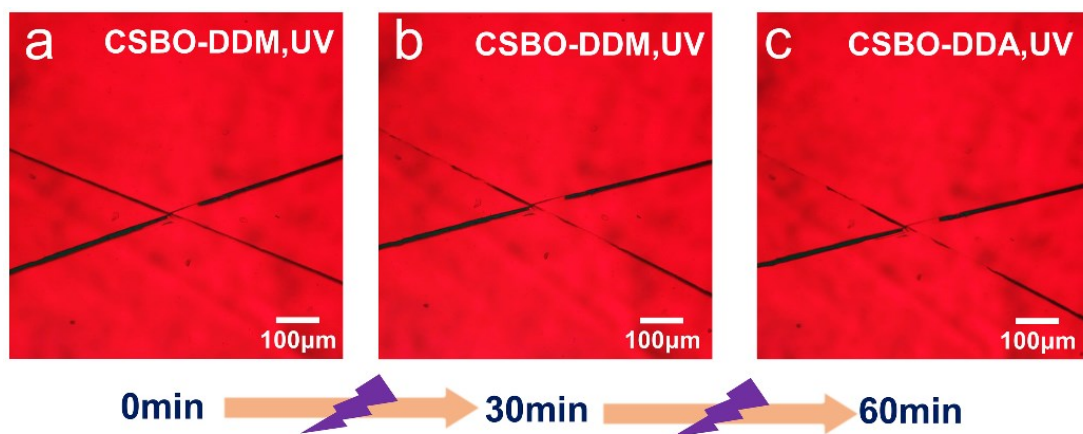


Figure S12. Self-healing of CSBO-DDM under UV irradiation.

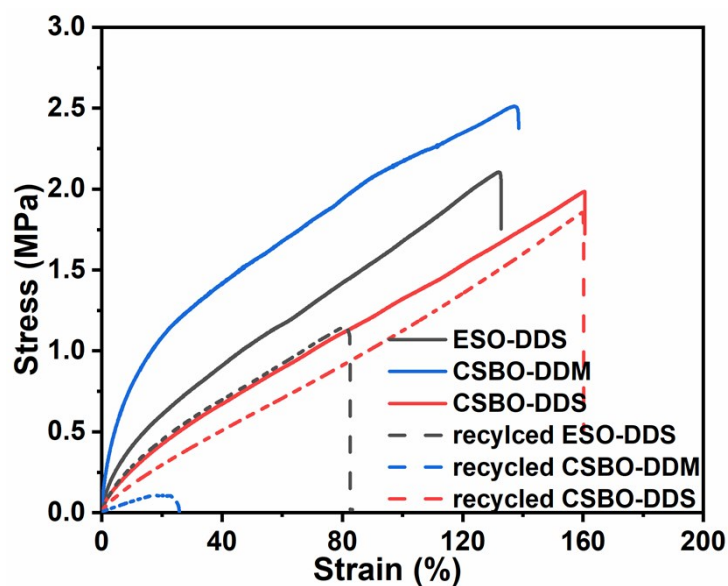


Figure S13. Stress-strain curves of the samples before and after the hot-pressing.

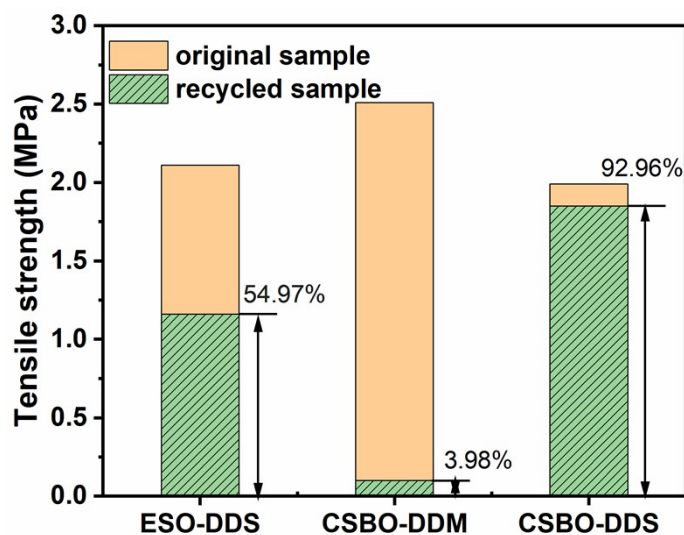


Figure S14. Comparative tensile strength of three samples before and after the hot-pressing.

References

1. X. Liu, X. Yang, S. Wang, S. Wang, Z. Wang, S. Liu, X. Xu, H. Liu and Z. Song, *ACS Sustainable Chemistry & Engineering*, 2021, **9**, 4175-4184.
2. S. Dhers, G. Vantomme and L. Avérous, *Green Chemistry*, 2019, **21**, 1596-1601.
3. S. Arayachukiat, C. Kongtes, A. Barthel, S. V. C. Vummaleti, A. Poater, S. Wannakao, L. Cavallo and V. D'Elia, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 6392-6397.