Electronic Supplementary Information for

Strengthening epoxy adhesives at elevated temperatures based on dynamic disulfide bonds

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Experimental

Materials

4′,4-diaminodiphenylmethane, dithiodianiline, bis(4-hydroxyphenyl) disulfide, diphenyl disulfide, epibromohydrin, sebacic acid and 1-methylimidazole were purchased from the Tokyo Chemical Industry Co., Ltd. Diglycidyl ether of bisphenol A (DGEBA) (jER 825) was purchased from the Mitsubishi Chemical Corporation. The anhydrous dimethylformamide, hexane, chloroform, methanol, acetone, ethanol, anhydrous potassium carbonate, anhydrous magnesium sulfate, citric acid monohydrate, sodium chloride, sodium hydroxide, sodium carbonate and sodium dodecylbenzene sulfonate used in the synthesis procedures or in alkaline cleaning of the aluminium substrates were purchased from Wako. Chemicals were used as received from suppliers. Aluminium alloy (6061-T6) was purchased from Standard-Testpiece Company.

Characterizations

^{1}H nuclear magnetic resonance spectra were collected using a JEOL-ESC 400 instrument at 400 MHz for CDCl3 solution of samples, and reported in ppm δ (ppm) from internal tetramethylsilane signal. (Fig. S1).

The efficiency of curing was assessed using Fourier transform infrared - near infrared spectroscopy, employing the JASCO 6100 spectrometer over the range of 4000 to 7000 cm^{-1}. A spectrum of the ambient air was used as a background (Fig. S2).

Dynamic mechanical analysis was performed using a Netzsch DMA242E instrument in the tensile test mode with sample dimensions of 10 × 5 × 0.2 mm over the temperature range from 25 to 250 °C at a heating rate of 3 °C/min. The oscillation frequency was maintained at 1 Hz (Fig. S3). Stress relaxation tests were carried out using the same

equipment in the tensile mode at different temperatures, allowing 30 extra min for thermal equilibration. To maintain straightness, a force of 0.006 N was applied to each sample. A strain of 1% was applied and this deformation was maintained during the measurement process (Fig. S4).

Single lap shear tests were performed using a Shimadzu autograph AG-X plus instrument with a crosshead speed of 0.1 mm/min. The sample temperature was controlled using an environmental chamber and the test temperatures were ambient, 50, 75, 100, 150 and 200 °C. A thermocouple was used to confirm that the internal chamber temperatures were correct. After attaining the desired temperature, the sample was held at that temperature for 1 h to allow for equilibration. The reported values represent the averages of three samples along with the standard error.

Synthesis of BGPDS (bis(4-glycidyloxyphenyl) disulfide)

The mixture of bis(4-hydroxyphenyl) disulfide (10 g, 40.0 mmol), anhydrous potassium carbonate (55.28 g, 400 mmol), epibromohydrin (54.79 g, 400 mmol), and dehydrated dimethylformamide (200 mL) was heated at 60˚C and stirred overnight under nitrogen atmosphere. The completion of the reaction was confirmed by TLC, and solid substrates were removed from the reaction mixture by a suction filtration. Then, 250 mL of water was added into the reaction mixture, and the mixture was extracted by chloroform/hexane solution (2/3 v/v) for three times. The combined organic phase was washed by water for three times and brine. The organic phase was dried by anhydrous magnesium sulfate and concentrated by rotary evaporation. The residue was recrystalized from methanol to afford the product as a white solid (10.8 g, 29.8 mmol, 75 %). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.40-7.36 (d, 4H, Ar-H), 6.87-6.84 (d, 4H, Ar-H), 4.25-4.20 (dd, 4H, $OCH_2CH(O)CH_2$), 3.96-3.90 (dd, 4H, $OCH_2CH(O)CH_2$), 3.37-3.32

(m, 2H, $OCH_2CH(O)CH_2$), 2.92-2.89 (dd, 4H, $OCH_2CH(O)CH_2$), 2.76-2.74 (dd, 4H, $OCH_2CH(O)CH_2$).[1] (fig. S1)

Synthesis of cross-linked aromatic disulfide epoxy-based resins (formula SS, SC, CS, and CC)

The epoxy monomer and diamine hardener were combined in a 2:1 molar ratio (see Table S1) in a glass vial and mixed at 90 °C for 30 min then rapidly poured into a Teflon mould. Each sample was cured in an oven at 120 °C for 2 h, 140 °C for 2 h and 160 °C for 2 h.

Synthesis of cross-linked transesterification epoxy-based resins (formula CA)

To allow a comparison between various dynamic reaction mechanisms, a 1:0.45:0.45 mixture (on a molar basis) of epoxy monomer, citric acid monohydrate and sebacic acid was prepared in a glass vial. The catalyst 1-methylimidazole was added to catalyse the transesterification and epoxy-acid reactions. The mixing and curing procedures were the same as those reported in a previous publication.[2]

Preparations of adhesive joints

Aluminium substrates (AA6061-T6) having dimensions of 100 (length) × 25 (width) × 2 (thickness) mm were prepared by mechanical surface polishing with 800 grit sandpaper followed by ultrasonic cleaning in ethanol, hexane and acetone for 15 min in each solvent. Each substrate was subsequently immersed in an alkaline degreasing solution at 70 °C for 10 min (according to the ASTM D2651 standard procedure). Finally, each substrate was washed with water and dried at 70 °C. In each trial, an epoxy monomer and amine hardener were combined as Table S1 in a glass vial and mixed at 90 °C for 30 min, then immediately applied on the overlapped area of treated metal substrates. The adhesive joint was held together using two clips. The overlapped area was fixed at

25 × 12.5 mm and the thickness of the adhesive was controlled within 200-250 μm by adding 1 wt.% glass beads to the polymer. Finally, the adhesive joints were cured in an oven under the same conditions as applied to the bulk samples (that is,
120 °C for 2 h, 140 °C for 2 h and 160 °C for 2 h for the SS, SC, CS, and CC samples; 120 °C for 3 h and 160 °C for 6 h for the CA sample).

Rebonding Procedures

The adhesive joints were broken after the first single lap shear test. Following such tests, each detached specimen was hot-pressed at 200 °C under 20 kN of compressive force for 20 min (in the case of the SS, SC and CS specimens) or 160 °C under 20 kN for 60 min (for the CA specimen). After cooling to room temperature, these specimens were again subjected to single lap shear tests.[2–4]

Model reaction

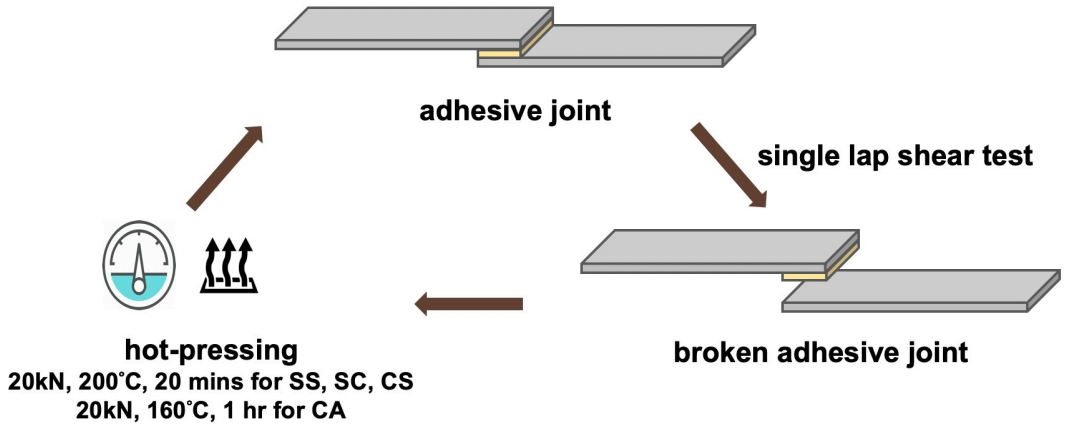
Solutions of diphenyl disulfide and 4,4'-dithiodianiline in DMSO-d_6 (0.45 M each), prepared separately, were mixed in 1:1 (v/v) ratio in an NMR tube covered with aluminium foil to shed the light. After the treatment of the sample at determined temperature for 2 hrs, the composition of the mixture was monitored by ^{1}H NMR (Fig S5).

Table S1 Formulation of all epoxy networks

Network	epoxy monomer		diamine crosslinker		
	S-epoxy BGPDS (mol. ratio (g))	C-epoxy DGEBA (mol. ratio (g))	S-diamine DTDA (mol. ratio (g))	C-diamine DDM (mol. ratio (g))	
SS	2 (1)	-	1 (0.343)	-	
SC	2 (1)	-	-	1 (0.274)	
CS	-	2 (1)	1 (0.365)	-	
CC	-	2 (1)	-	1 (0.291)	
	epoxy monomer		acid crosslinker		catalyst
	C-epoxy DGEBA (mol. ratio (g)		citric acid monohydrate	sebacic acid	1-methylimidazole
CA [2]	1.1 (1)		0.5 (0.183)	0.5 (0.264)	0.055 (0.024)

Table S2 Summary of T_g, T_v, and activation energy for known dynamic covalent system

dynamic covalent system	T (˚C) $_g$	T (˚C) $_v$	activation energy (kJ/mol)
aromatic disulfide [3,4]	127 - 133	-18 - 86	38 - 55
transesterification [2,5,6]	45 - 65	105 - 120	88 - 119
imine exchange [7]	121	36	90
siloxane exchange [8] (not epoxy system)	123 - 125	47 - 117	81 - 174
transamination [9] (not epoxy system)	-77 - -51	22 - 35	52 - 80
transalkylation [10] (not epoxy system)	-11	98	140



Scheme S1 Rebonding procedure for dynamic adhesive (SS, SC, CS, and CA)

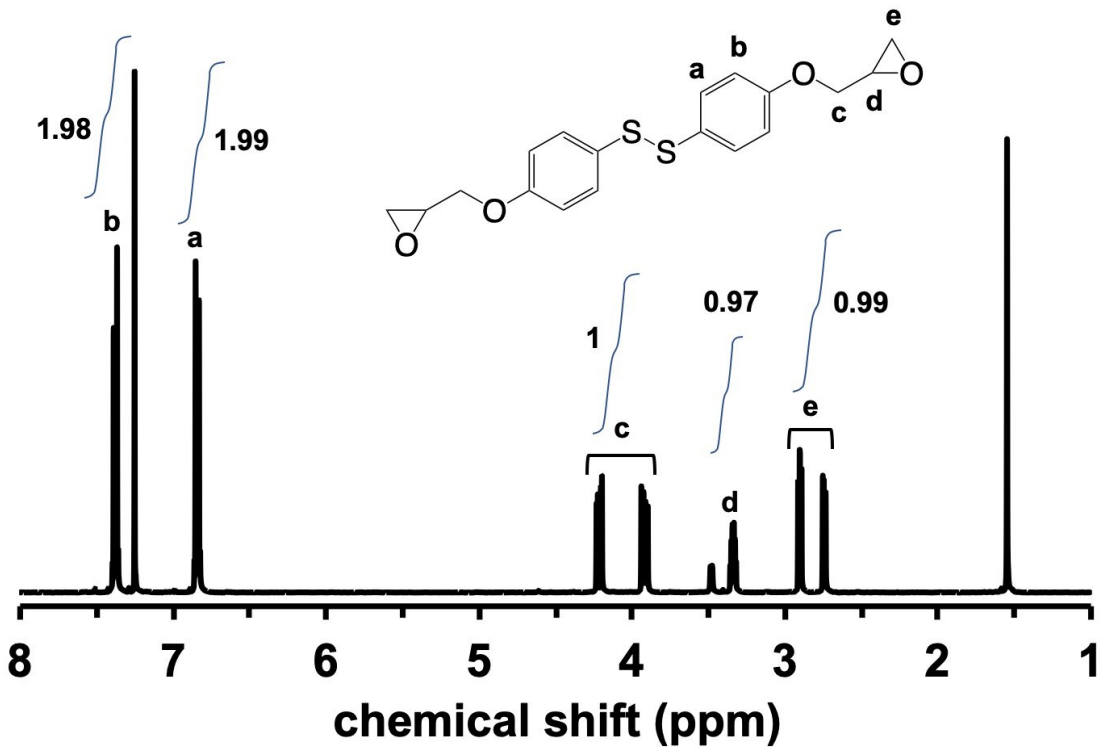


Figure S1 ^{1}H-NMR spectrum for bis(4-glycidyloxyphenyl) disulfide

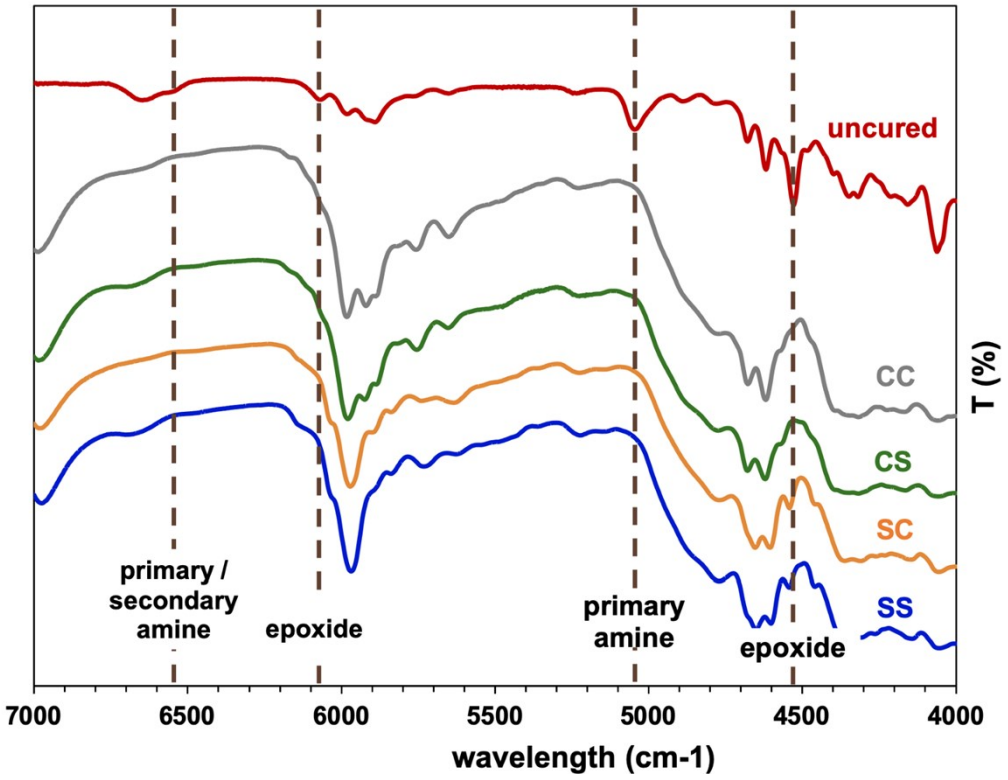


Figure S2 FTIR-nIR spectra of all epoxy networks at 4000 to 7000 cm^{-1}

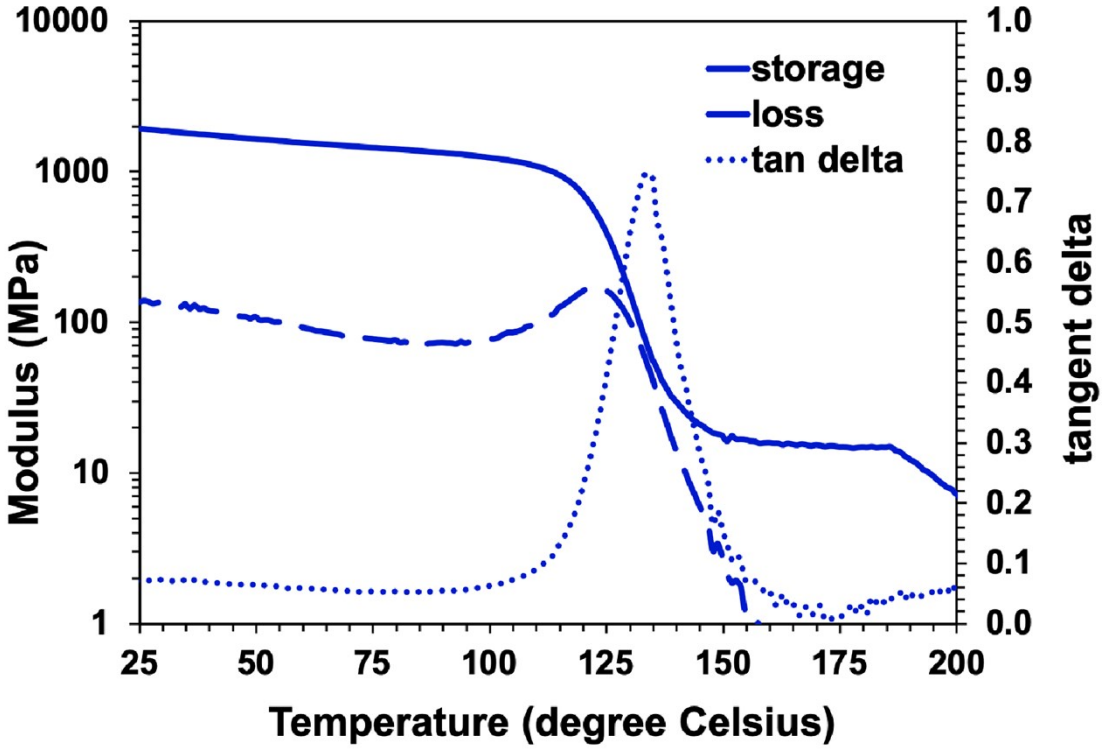


Figure S3 (a). DMA curve of dynamic epoxy networks SS

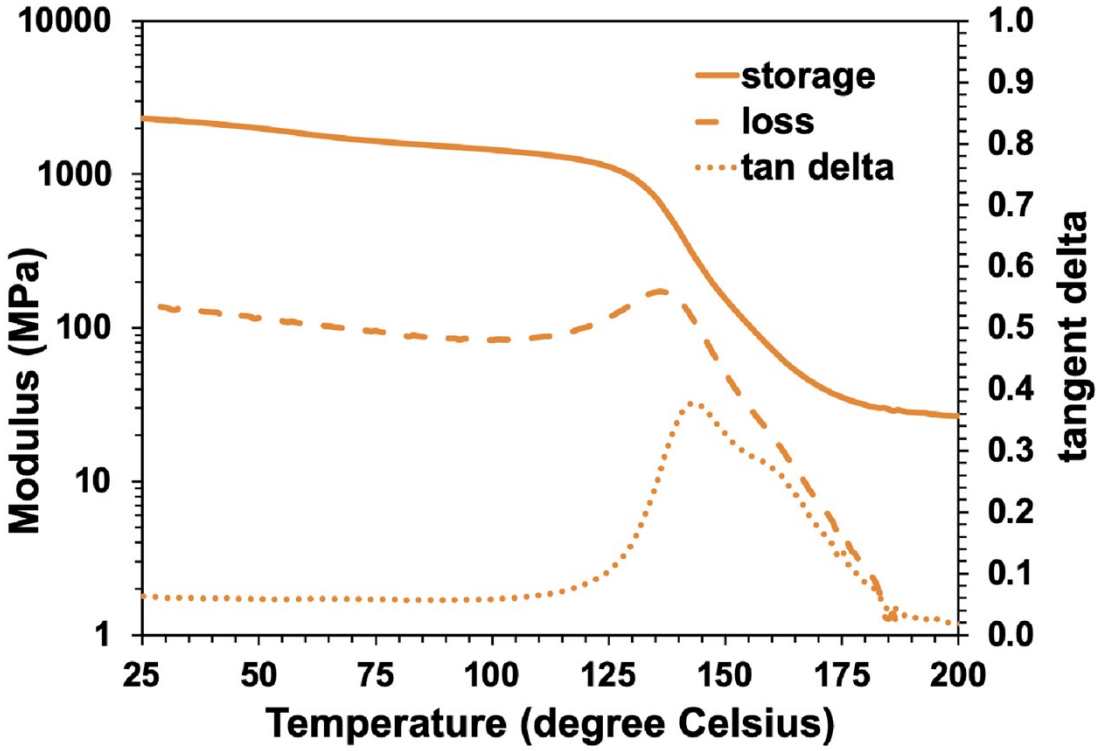


Figure S3 (b). DMA curve of dynamic epoxy networks SC

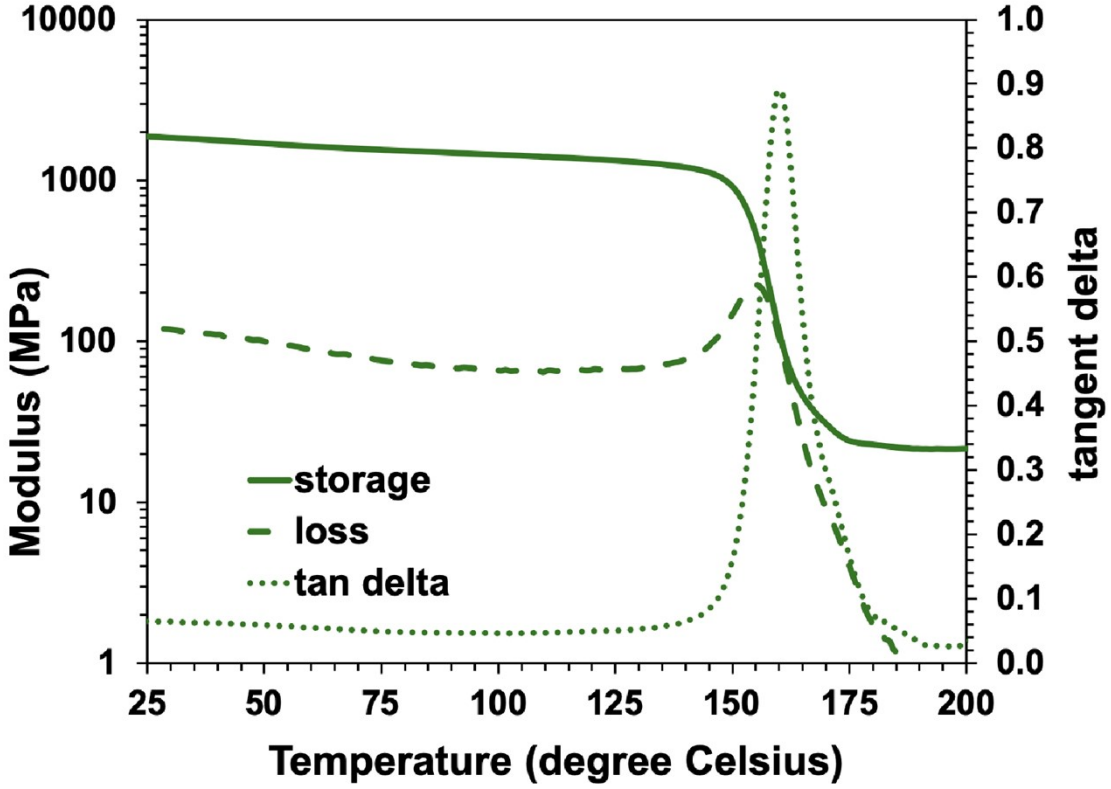


Figure S3 (c). DMA curve of dynamic epoxy networks CS

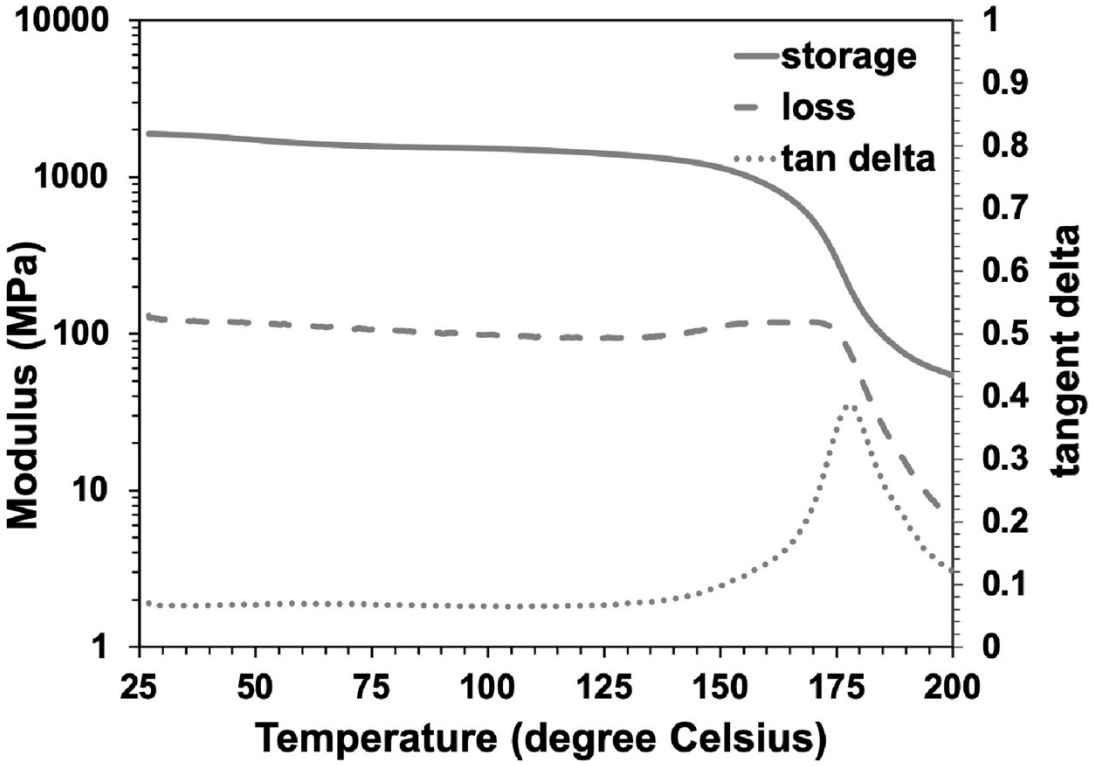


Figure S3 (d) DMA curve of conventional epoxy networks CC

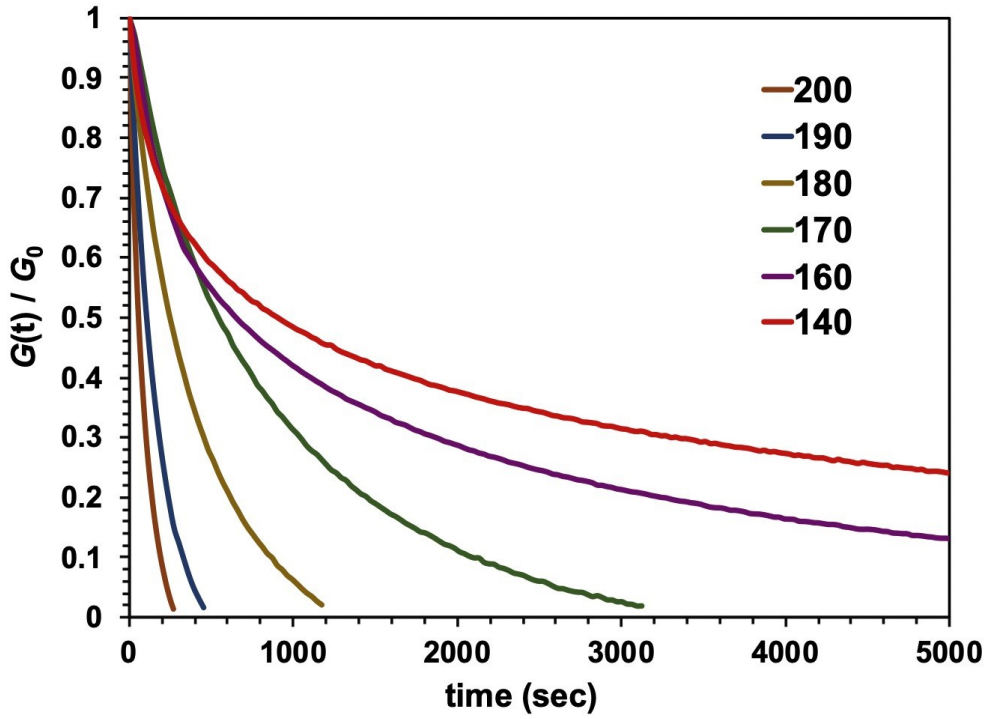


Figure S4 (a) Normalized stress relaxation curves of dynamic epoxy networks SC at different temperatures

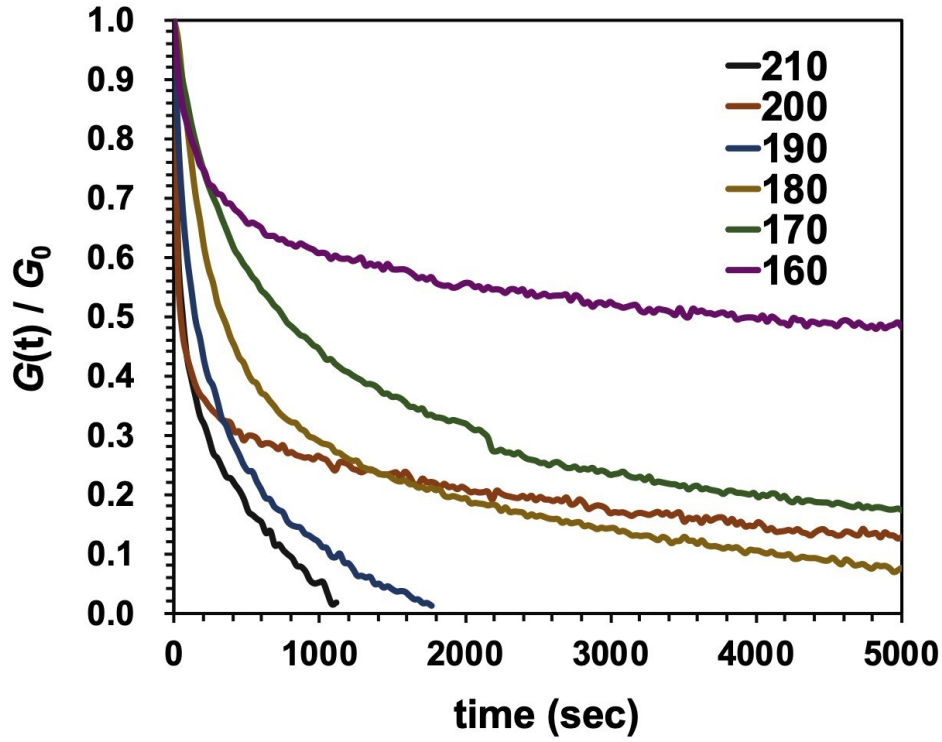


Figure S4 (b) Normalized stress relaxation curves of dynamic epoxy networks CS at different temperatures

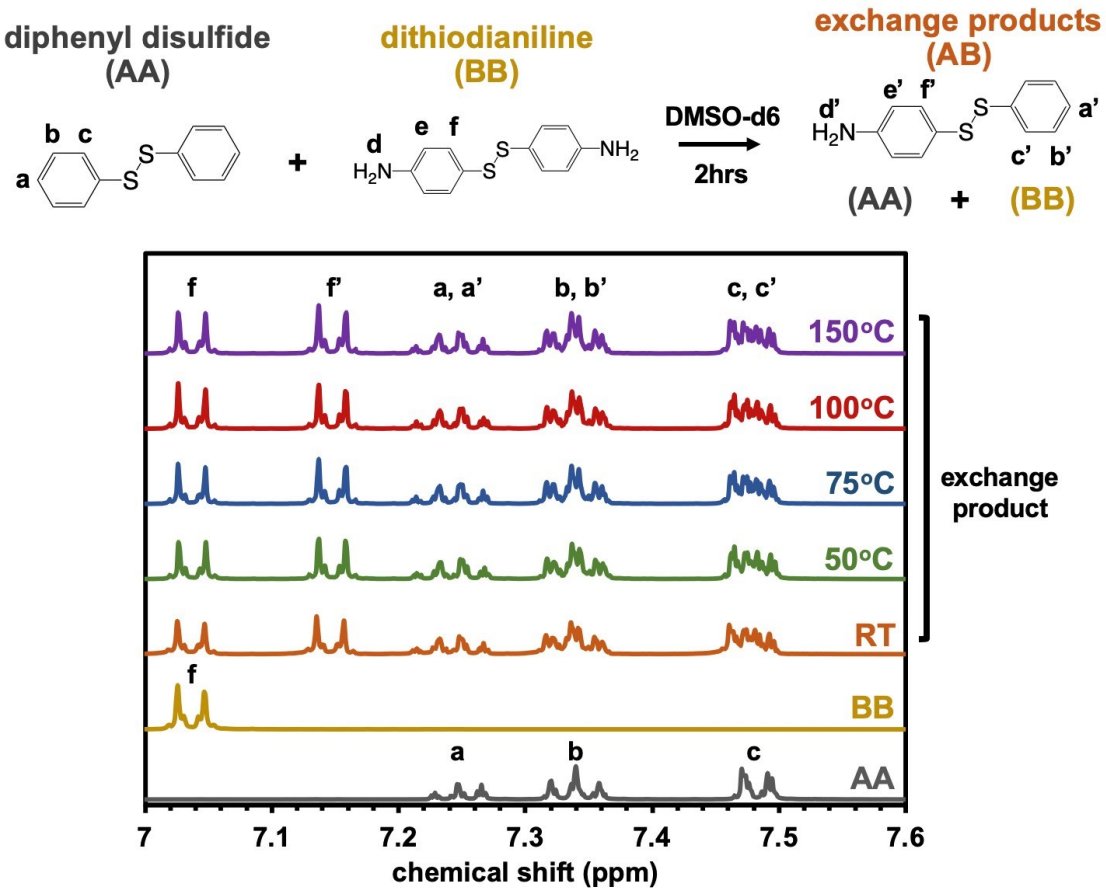


Figure S5 NMR spectra for disulfide-exchange model compounds at different temperatures located at the range of 7-7.6 ppm. After the treatment of the mixture at each temperature (room temperature to 150 °C) for 2 h, all the samples showed the identical spectra which exhibit the composition of the mixture is AA:BB:AB = 1:1:2. These results indicated the efficient exchange reaction of S-S bond in a solution even at room temperature, by which the equilibrium reaches the statistical distribution.

Reference

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