

**Electronic Supplementary Information for**  
**Mechanochromism of Dynamic Disulfide Bond for Chromophoric**  
**Indicator of Adhesion Strength for Epoxy Adhesive**

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## **Experimental**

### ***Materials***

4,4'-dithiodianiline (DTDA) and 4,4'-diaminodiphenylmethane (DDM) were purchased from the Tokyo Chemical Industry Co., Ltd. Diglycidyl ether of bisphenol A (DGEBA) (jER 825) was purchased from the Mitsubishi Chemical Corporation. Hexane, acetone, ethanol, sodium hydroxide, sodium carbonate and sodium dodecylbenzene sulfonate used in the surface treatment of aluminium substrates were purchased from Wako. Chemicals were used as received from suppliers. Aluminium alloy (6061-T6) was purchased from Standard-Testpiece Company.

### ***Characterizations***

Fourier transform - near infrared spectroscopy (FT-nIR) was employed by the equipment from JASCO 6100 spectrometer over the range of 4000 to 7500  $\text{cm}^{-1}$ . A spectrum of the ambient air was used as a background. (Figure 1 and S1)

The crosslinking density and gel fraction were confirmed by swelling test that was obtained through immersing all composition of epoxy resin into toluene in light shielding bottle at room temperature for 72 hours. Data presented in this experiment was the mean values of five measurements. (Figure S2)

The glass transition temperature ( $T_g$ ) was determined through differential scanning calorimetry (DSC) performing the equipment from Shimadzu DSC-60 plus. Temperature range was from 0 °C to 200 °C with heating and cooling rate 10 °C/min. Air was used as reference.  $T_g$  -value was evaluated from second heating cycle. (Figure S3)

The adhesion strength was evaluated through single lap shear tests using a Shimadzu autograph AG-X plus instrument with a crosshead speed of 1.0 mm/min. The reported values represent the averages of three samples along with the standard error. (Figure S4)

Electron spin resonance (ESR) was obtained by JEC-FA100 spectrometer from Joel with temperature controller and data-collection system. 200 milligrams of solid samples were ground into powder by ball-milling for 90 minutes and placed into quartz testing tubes immediately. All spectra were recorded at 9.1-9.2 GHz of frequency and 1mW microwave power. The  $g$ -value was calculated based on the equation:  $h \nu = g \beta B$ , where  $h$  is Planck's constant,  $\nu$  is frequency,  $\beta$  is Bohr magneton, and  $B$  is magnetic field. The  $g$ -value of thiyl radicals is 2.04.<sup>1</sup> (Figure S5)

Time-dependent UV-vis spectra were measured by equipment from JASCO V670. The epoxy resin powder was generated by sandpaper polishing and then confirmed immediately. Samples were tested with different lasting times ranged from 0 to 60 min. Spectra were collected from 400-800 nm with an interval of 1 nm at scanning speed of 400 nm/min. The intensity of absorption was transferred to Kubelka-Munk function (K-M function). (Figure 3 and 4)

### ***Synthesis of cross-linked aromatic disulfide epoxy-based resins***

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

### ***Preparations of adhesive joints***

Aluminium substrates (AA6061-T6) having dimensions of 100 (length)  $\times$  25 (width)  $\times$  2 (thickness) mm were prepared by mechanical surface polishing with 800 grit sandpaper followed by ultrasonic cleaning in ethanol, hexane, and acetone for 15 mins in each solvent. Each substrate was subsequently immersed in an alkaline degreasing solution at 70 °C for 10 mins (according to the standard procedure of ASTM D2651). Finally, each

substrate was washed with water for 5 min and then 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 fixed together using two clips. The overlapped area was 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 hr, 140 °C for 2 hr and 160 °C for 2 hr).

#### ***Calculation of swelling ratio and gel fraction based on swelling test***

The swelling ratio ( $Q$ ) was calculated based on the equation:  $Q = (M_2 - M_1) / M_1$ , where  $M_1$  is the initial weight before swelling and  $M_2$  is the swollen weight after swelling.

The gel fraction ( $X$ ) was calculated based on the equation:  $X = M_3 / M_1$ , where  $M_3$  is the weight of dried and swollen specimens.

#### ***Calculation of crosslinking density based on swelling test***

The crosslinking density of each epoxy network was calculated based on Flory-Rehner equation: crosslinking density ( $C.D.$ ) =  $\ln [(1 - V_r) + V_r + \chi V_r^2] / 2 V_s (V_r^{1/3} - V_r / 2)$ , where  $V_r$  is the volume fraction of polymer in the swollen state at equilibrium,  $\chi$  is the polymer-solvent interaction parameter, and  $V_s$  is the molar volume of solvent.

$V_r$  is calculated based on equation:  $V_r = M_1 \rho_s / [M_1 (\rho_s - \rho_r) + M_2 \rho_r]$ , where  $M_1$  is the weight of polymer before swelling,  $M_2$  is the weight of polymer after swelling,  $\rho_s$  is the density of toluene (865 kg/m<sup>3</sup>),  $\rho_r$  is the density of polymer (1200 kg/m<sup>3</sup>).

$\chi$  is calculated based on equation:  $\chi = \beta_1 + (V_s / RT) (\delta_s - \delta_p)^2$ , where  $\beta_1$  is the lattice constant, usually about 0.34, R is the universal gas constant, T is the absolute temperature,

$\delta_s$  and  $\delta_p$  is solubility parameter for toluene ( $8.9 \text{ cal}^{1/2}\text{cc}^{-3/2}$ ) and polymer ( $13.0 \text{ cal}^{1/2}\text{cc}^{-3/2}$ ), respectively.

$V_s$  is calculated based on equation:  $V_s = M / \rho_s$ , M is the molecular weight of toluene ( $92.14 \text{ g/mol}$ )<sup>2-4</sup>

Table S1. Formulation of all epoxy networks

Network	Epoxy resin (DGEBA)		Diamine hardener (DTDA)	
	mol	g	mol	g
ERD-1	3	5	1	1.22
ERD-2	2	5	1	1.83
ERD-3	2	5	2	3.65
ERD-4	2	5	3	5.48
	Epoxy resin (DGEBA)		Diamine hardener (DDM)	
	mol	g	mol	g
Control Sample	2	5	1	1.46

Table S2. Summary of swelling ratio, gel fraction, crosslinking density, glass transition temperature ( $T_g$ ), and adhesion strength for control sample in this work.

Swelling ratio ( $Q$ ) (%)	Gel fraction (%)	Crosslinking density (mol/m <sup>3</sup> )	$T_g$ (°C)	Adhesion strength (MPa)
2.5 ± 0.3	98.6 ± 0.3	2561.2	181	15.7 ± 0.9

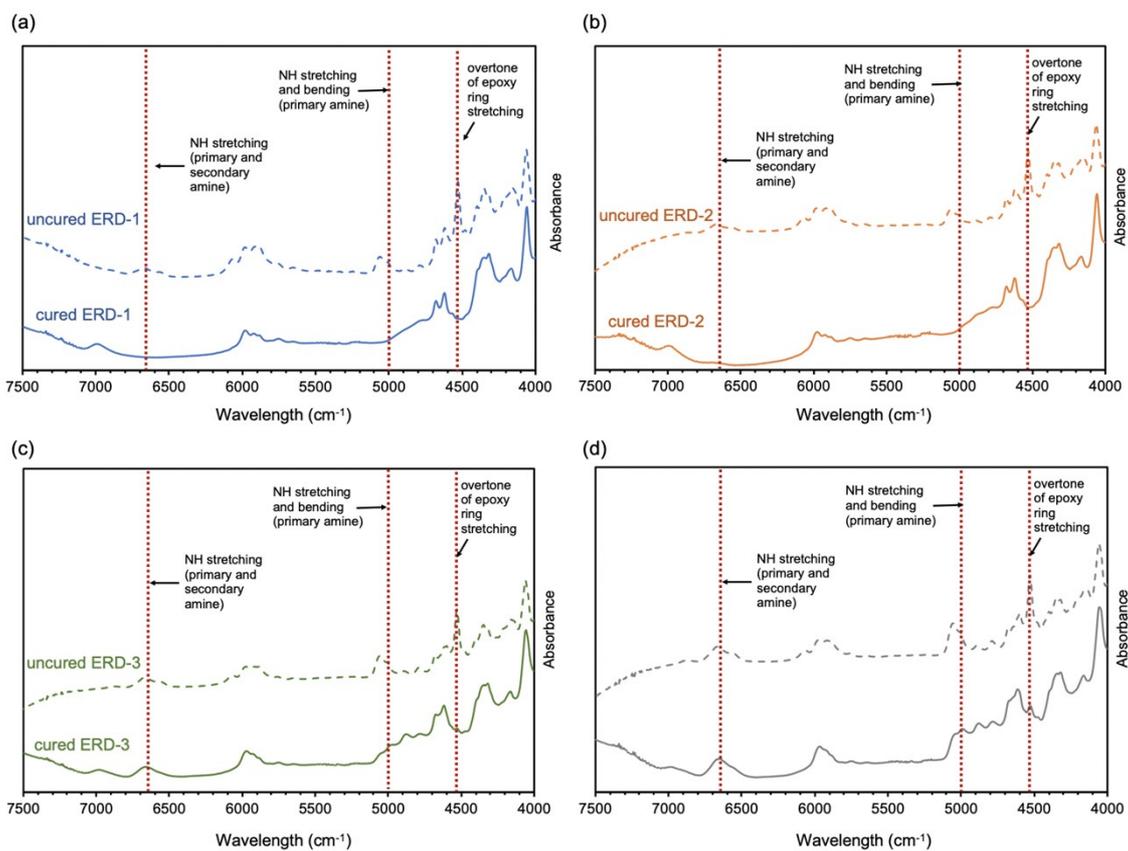


Figure S1. FT-nIR spectra for uncured and cured epoxy networks (a) ERD-1, (b) ERD-2, (c) ERD-3, and (d) ERD-4

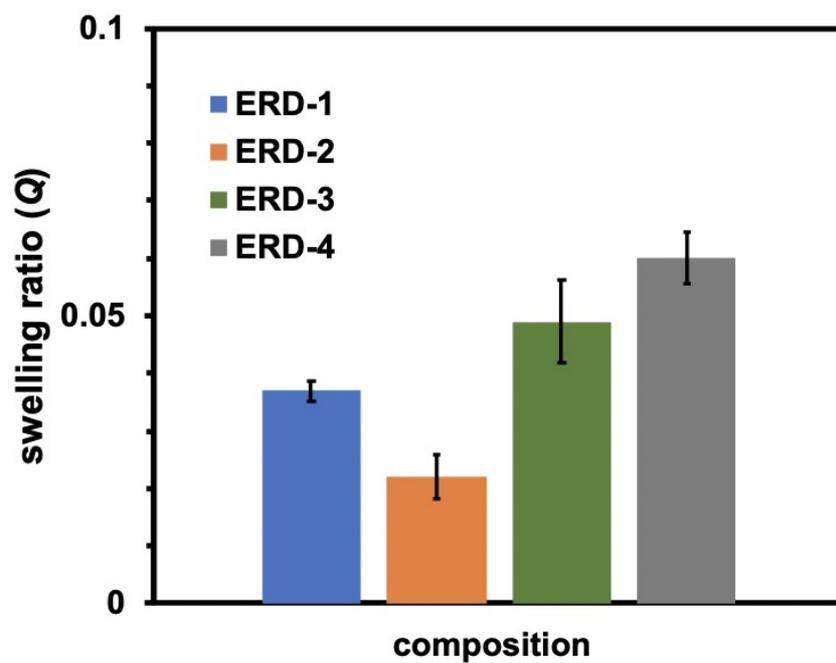


Figure S2. Swelling ratio ( $Q$ ) for all epoxy networks in toluene at room temperature for 72 hours in this work

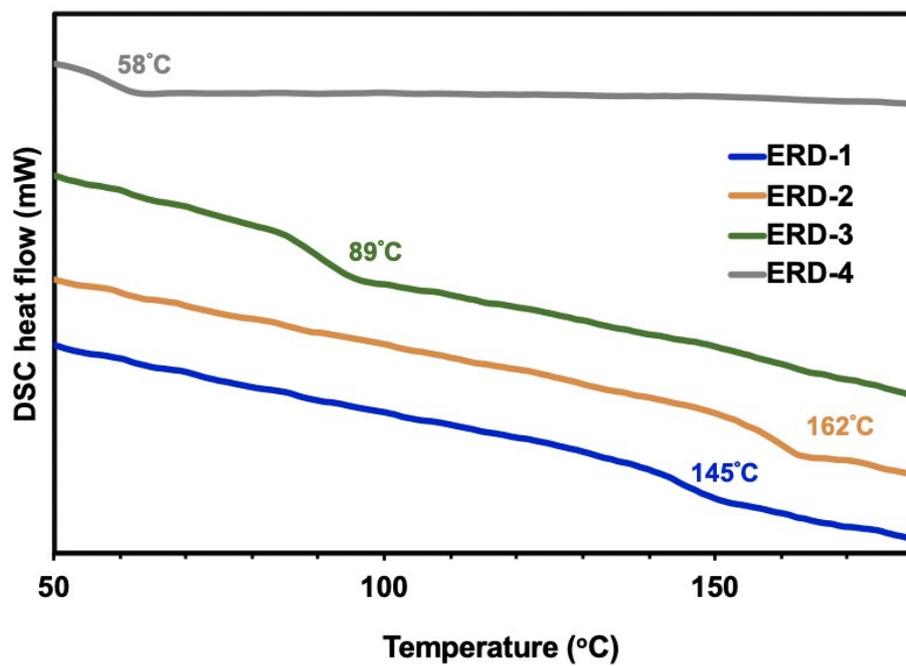


Figure S3. Differential scanning calorimetry (DSC) curve and glass transition temperature ( $T_g$ ) for all epoxy networks in this work

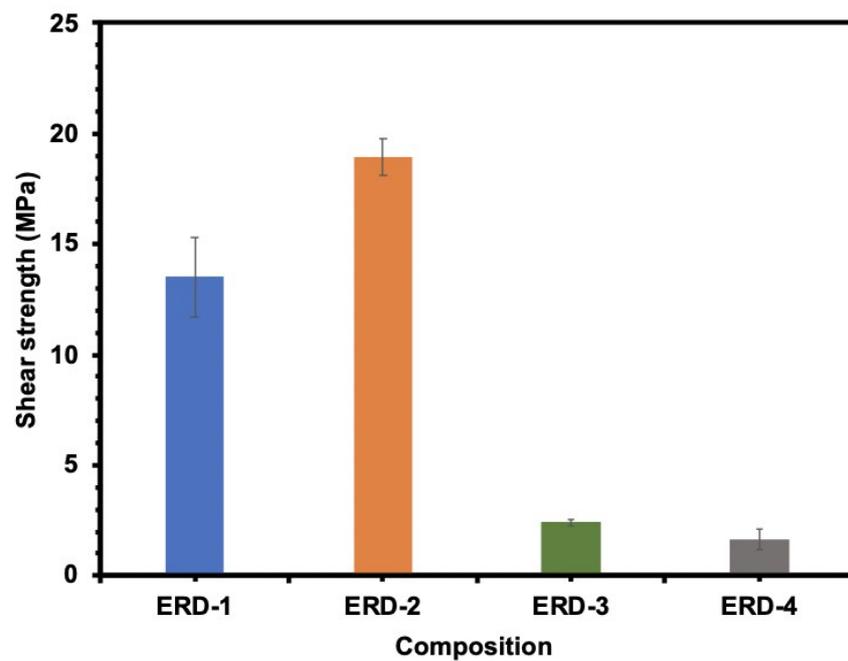


Figure S4. Adhesion strength based on single lap shear test for all epoxy networks in this work

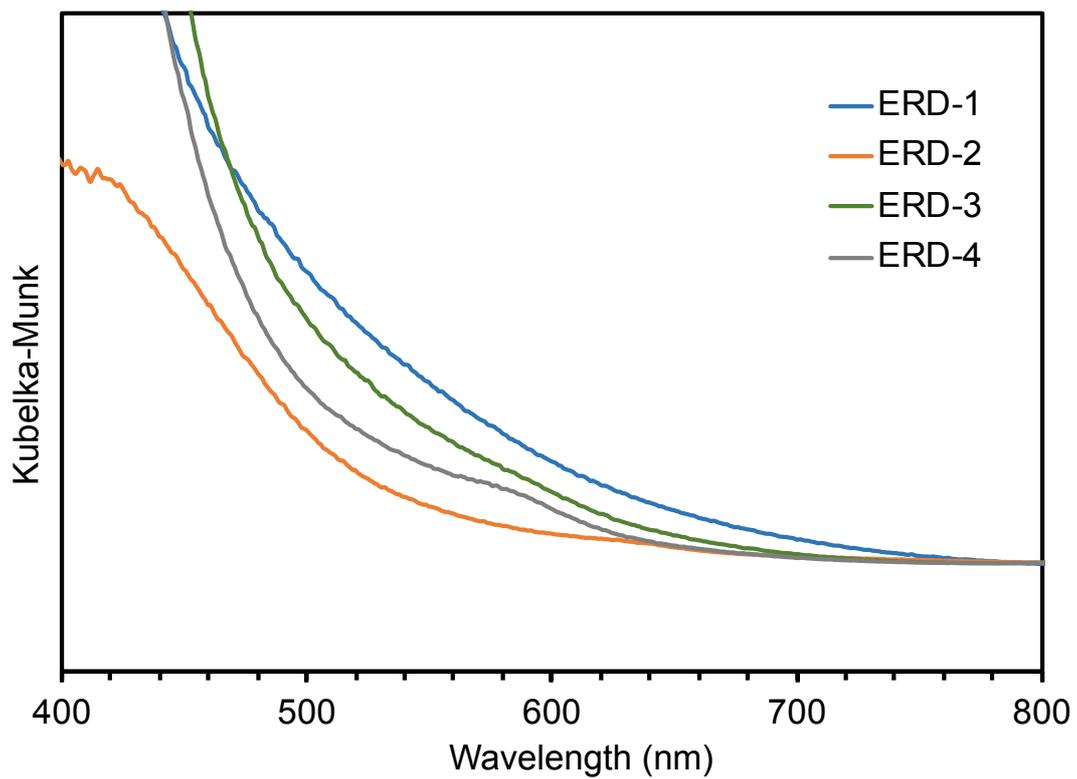


Figure S5. Kubelka-Munk absorbance of UV-vis spectra in solid state for ERD-1, ERD-2, ERD-3, and ERD-4 in the form of bulk epoxy network before polishing.

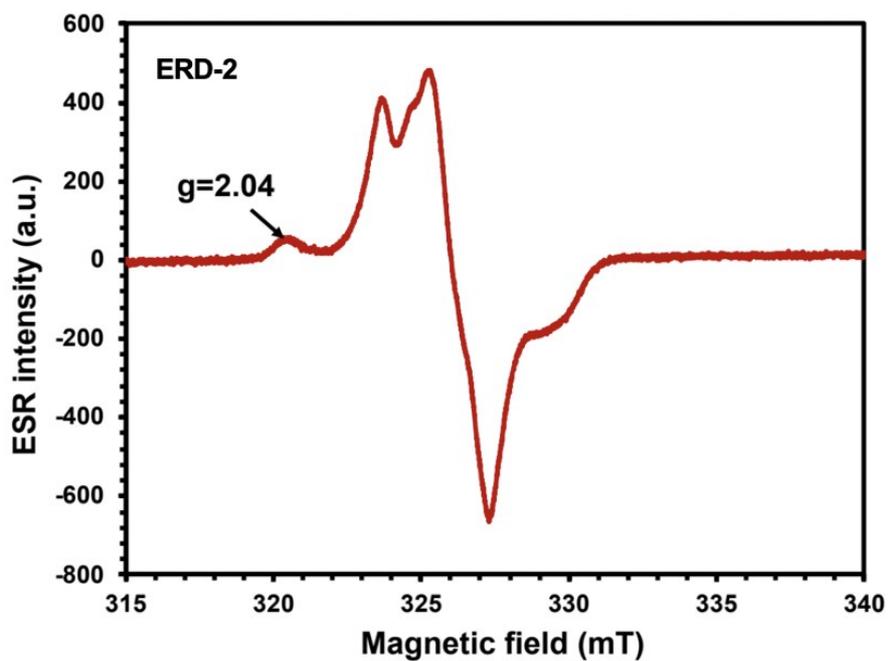


Figure S6. Electron spin resonance (ESR) spectrum for ERD-2. The sample was examined immediately after ball-milling into powder. The g-value of thiyl radical ( $-S \cdot$ ) is 2.04.

Reference:

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