Supporting information

Preparation of a Lignin-based Vitrimer Material and Its Potential Use for Recoverable Adhesive

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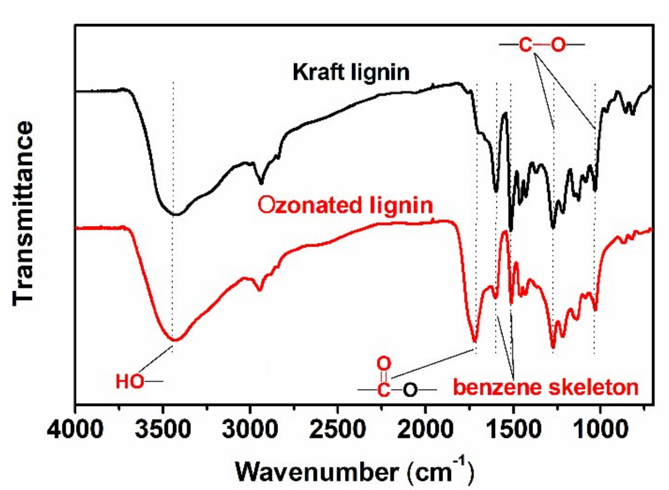

Fig. S1 FTIR spectra of Kraft lignin and ozonated lignin (Oz-L).

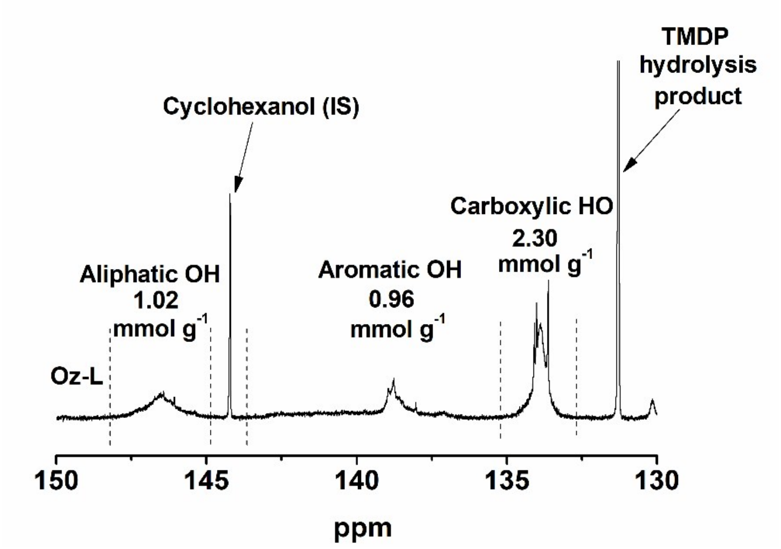

Fig. S2 ^{31}P-NMR spectra of Oz-L.

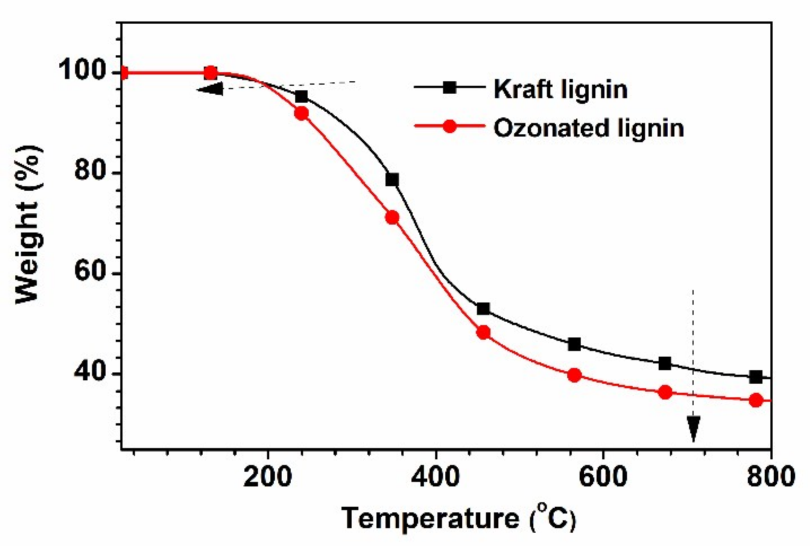

Fig. S3 TGA curves of Kraft lignin and Oz-L.

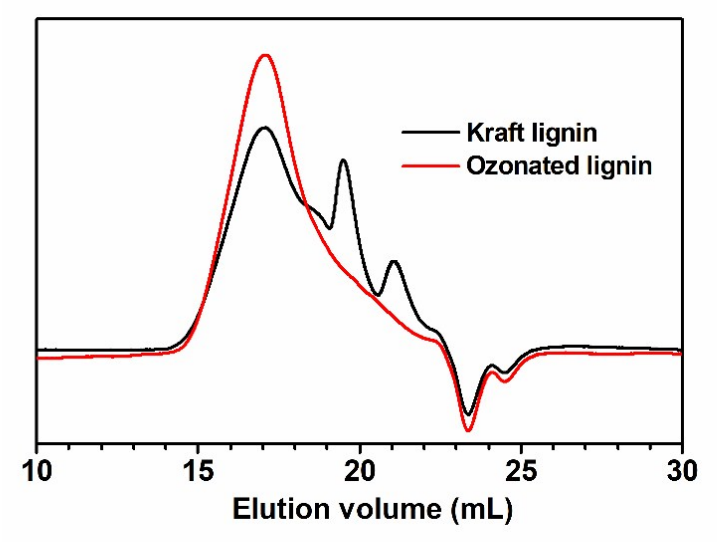

Fig. S4 GPC curves of Kraft lignin and Oz-L.

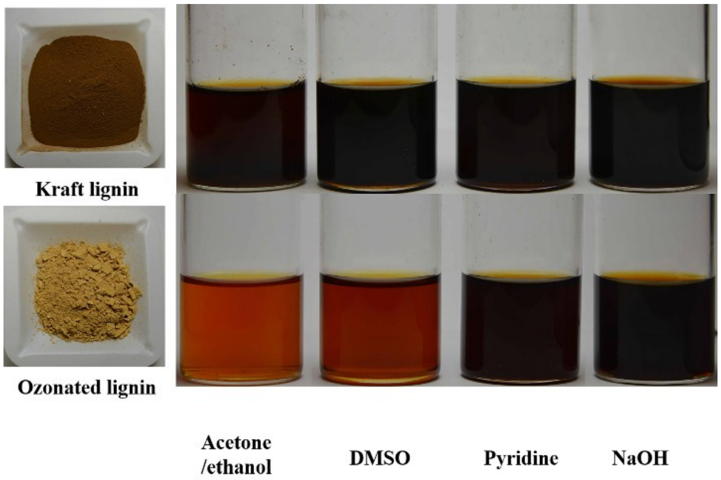

Fig. S5 Dissolution tests of Kraft lignin and Oz-L in acetone/ethanol (1:1, v/v), DMSO, pyridine and 2% NaOH.

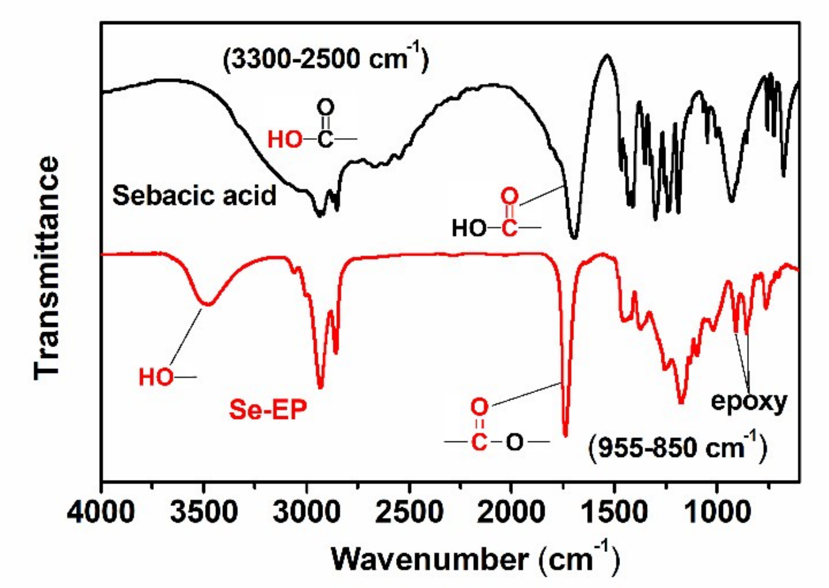

Fig. S6 FTIR spectra of sebacic acid (Se) and its epoxide (Se-EP).

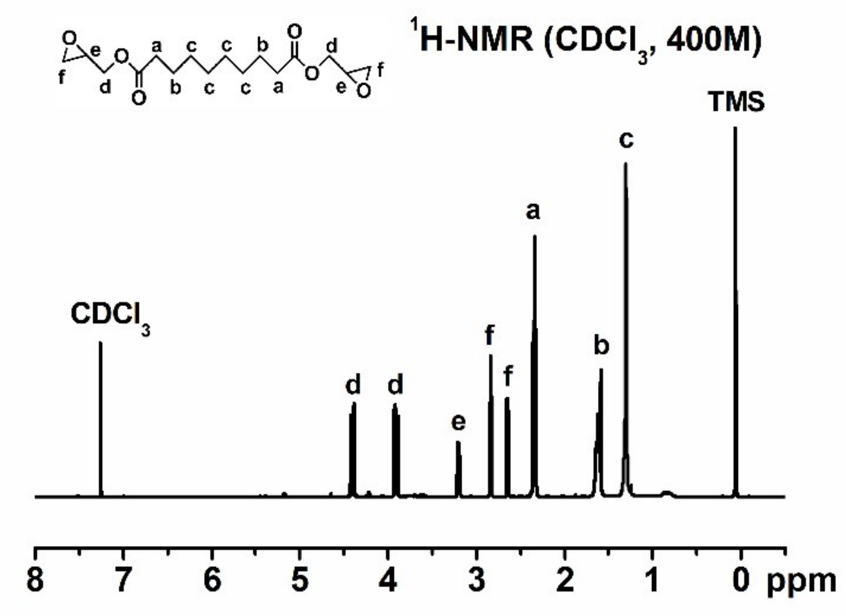

Fig. S7 ^{1}H-NMR spectrum of Se-EP.

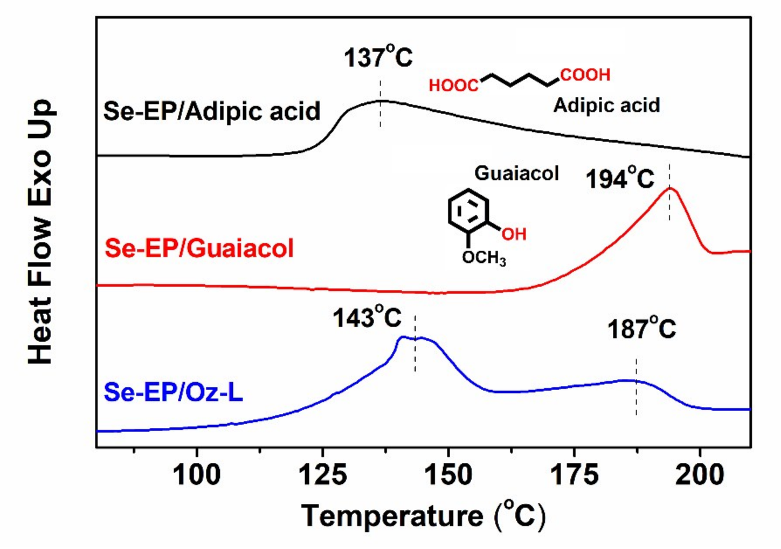

Fig. S8 DSC non-isothermal thermograms of Se-EP/adipic acid, Se-EP/guaiacol and Se-EP/Oz-L (R=1:1) were scanned at a heating rate of 5 ºC min^{-1} under nitrogen atmosphere.

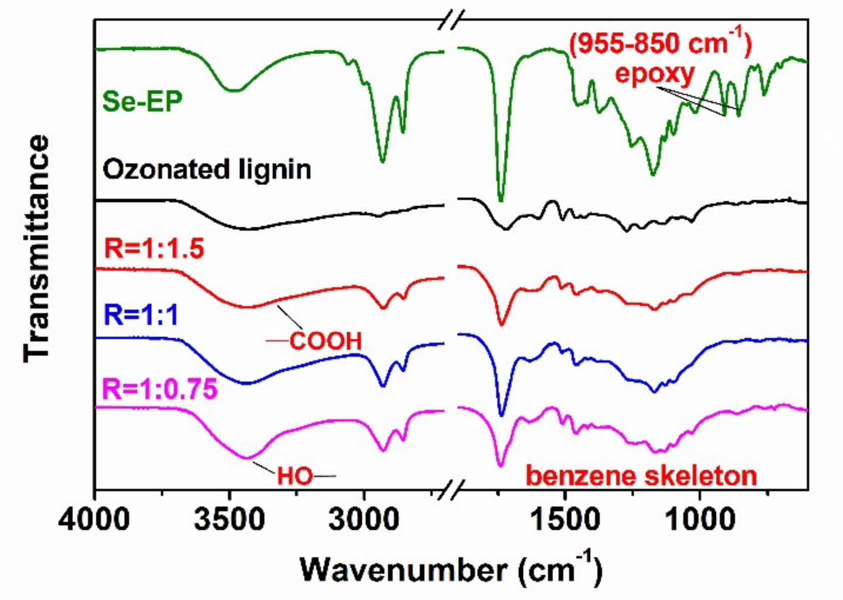

Fig. S9 FTIR spectra of the cured Se-EP/Oz-Ls with different stoichiometry ratios (R). R is based on ratio of epoxy versus the sum of phenolic OH and carboxylic acid groups.

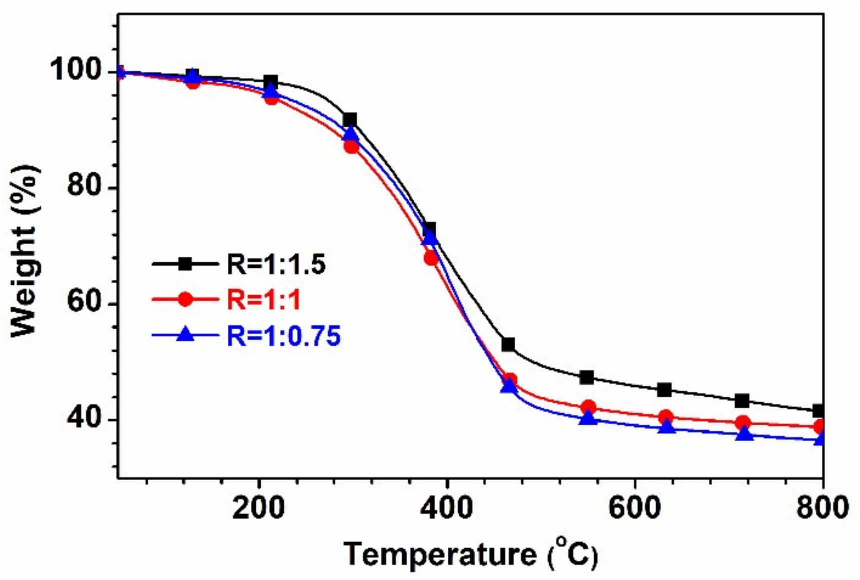

Fig. S10 TGA curves of the cured Se-EP/Oz-Ls with different R ratios.

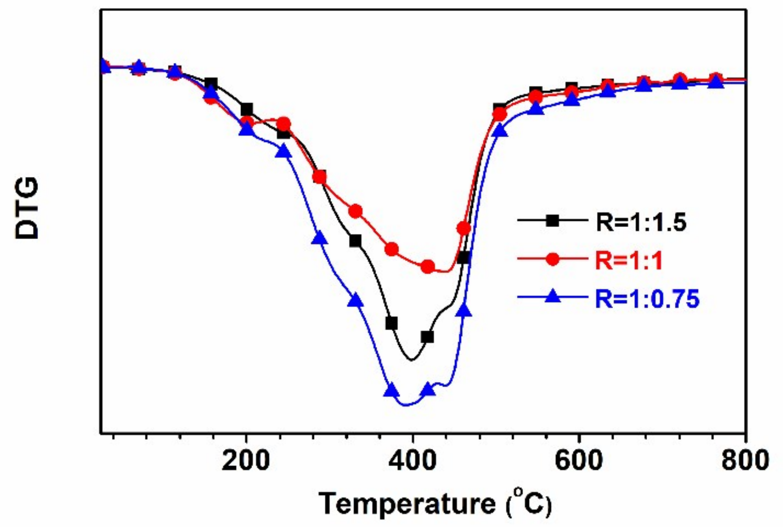

Fig. S11 DTG curves of the cured Se-EP/Oz-Ls with different R ratios from TGA test.

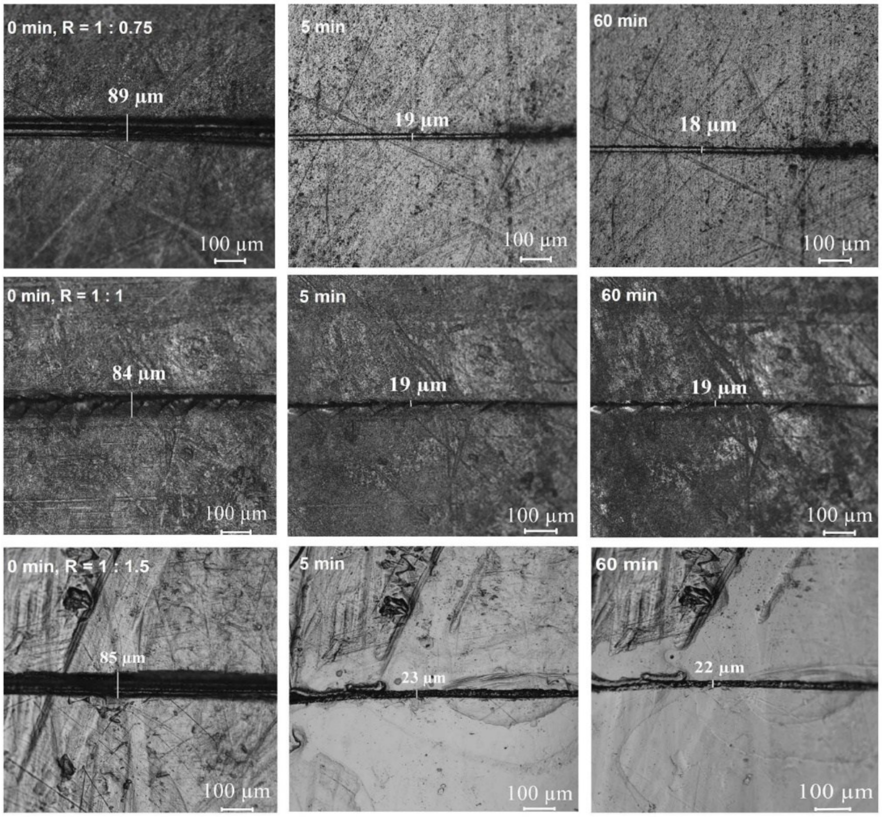

Fig. S12 Thermal repairing of Se-EP/Oz-Ls with R = 1:0.75, 1:1 and 1:1.5. The width of scratches versus time is recorded at the same position for each sample.

Fig. S13 Physical recycling of the cured Se-EP/Oz-Ls (R = 1:1). The fragments were pressed at 190 °C for 2 h.

Table S1. The summary of shape fixity (R_f) and shape recovery (R_r) for the cured Se-EP/Oz-Ls in each cycle.

R[a]	R_f[b] (%)			R_r[c] (%)		
	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3
1:0.75	91.81	92.25	92.30	97.28	97.12	96.88
1:1	93.49	93.65	94.64	95.44	95.05	93.60
1:1.5	93.19	93.29	95.07	91.10	86.72	83.59

[a]R represents the ratio of epoxy versus the sum of phenolic OH and carboxylic acid groups; [b]R_f represents the shape fixity; [c] R_r represents the shape recovery.

EXPERIMENTAL SECTION

Materials

Sebacic acid (Acros Organics, 98%), zinc acetylacetonate hydrate ($Zn(acac)_2$, Aldrich, 99.995%), tetra-n-butylammonium bromide (TBAB, TCI, 98%), Kraft lignin (Ingevity), potassium carbonate (Fisher, 99.8%), potassium iodide (J.T. Baker, 99%), allyl bromide (Acros Organics, 99%), pyridine (Aldrich, anhydrous, 99.8%), chloroform-d (Aldrich, 99.8% atom D), cyclohexanol (Aldrich, 99%), chromium acetylacetonate (Aldrich, 99.99%), 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, Aldrich, 95%) and phenolphthalein indicator (BICCA) were used as received. Bio-epichlorohydrin (bio-ECH) was supplied by Advanced Biochemical (Thailand) Co., Ltd. All the solvents (GR grade) were used without further purification.

Kraft lignin ozonolysis and characterization

Ozonolysis of Kraft lignin was performed based on Lee et al.[1] and Bule et al.[2] with a slight modification. Under magnetic stirring, Kraft lignin (8 g) was dissolved in 1,4-dioxane/water solution (9:1, 400 mL). Ozone was generated by a L11-L24 ozone generator (Pacific Ozone, California). The ozonation reaction was carried out with ozone (5.3%, w/w) at a flow rate of 1 L min^{-1} for 60 min in a 600 mL glass column reactor. After ozonation, the soluble segments were obtained by vacuum filtration, and the solvents were removed and recycled using a rotary evaporator. The resulting crude product was washed twice by water. The purified ozonized lignin was dried in a vacuum oven at 50 ºC for 48 h.

Synthesis of sebacic acid-derived epoxy (Se-EP)

Sebacic acid (10 g, 1 *equiv.*) and TBAB (0.05 *equiv.*) were dissolved in epichlorohydrin (20 *equiv.*) in a 500 mL round bottom flask. The reaction was performed at 117 ºC for 3 h with a reflux under magnetic stirring. After the reaction temperature was cooled down to 50 ºC, a 30% NaOH (1.1 *equiv.*) aqueous solution was added dropwise into the mixture within 4 h. The resulting solution was further reacted at 50 ºC for 2 h. After reaction, the solution was washed with hot water to remove the salts. The organic phase was collected, and the solvent (ECH) was removed and recycled using a rotary evaporator. The concentrated mixture was dried in a vacuum oven at 70 ºC. The received product, diglycidyl sebacate, was directly used for curing without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 4.42 (dd, 2H), 3.91 (dd, 2H), 3.19-3.23 (m, 2H), 2.85 (t, 2H), 2.65 (dd, 2H), 2.35 (t, 4H), 1.60-1.65 (m, 4H), 1.25-1.31 (m, 8H).

Preparation of Se-EP/ozonated lignin vitrimer

The cured Se-EP/Oz-L materials were prepared with different R ratios. R is the stoichiometry ratio of epoxy versus the sum of phenolic OH and carboxylic acid groups. $Zn(acac)_2$ was used as catalyst at an amount of 10 mol% on the basis of active hydrogen groups (both COOH and phenolic OH) in Oz-L. A small amount of ethanol was used to assist the mixing of the three components, and the solvent was removed in a vacuum oven at 50 ºC after the mixture was loaded on a Teflon sheet. Curing reaction was carried out at 150 ºC for 1 h and 190 ºC for 2 h in a hot press.

Characterizations

The molecular weight of Kraft lignin and Oz-L were measured using a Viscotek gel permeation chromatography (GPC) system equipped with a GPCmax™ pulp and a TDA 305 multi-detector. The columns used for GPC separation were two AM GPC gel columns (500 Å, 5 μm) in series. Tetrahydrofuran (THF) was used as eluent. To improve the solubility of sample in THF, all lignin samples were modified by allyl bromide following a method in the literature.[3]

Fourier transform infrared spectroscopy (FTIR) analysis was performed on NICOLET iS50 FTIR spectrophotometer. The sample was scanned for 64 times from 4000 to 400 cm^{-1} with a resolution of 4.0 cm^{-1}. Nuclear magnetic resonance (NMR) analysis was carried out on a Varian 400-NMR spectrometer (400 MHz). $CDCl_3$ was used as deuterated solvent for dissolving the samples.

The epoxy equivalent weight (EEW, mol/100 g) of Se-EP was determined by titration following a hydrochloric acid (HCl)-acetone method. The HCl-acetone solution was prepared by adding 2 mL HCl solution (37%, wt/wt) into 80 mL acetone solution. A sample of ~ 0.2 g (accurate to 0.0002 g) was reacted with 10 mL HCl-acetone solution in darkness for 30 min at room temperature. Then, 3-5 drops of phenolphthalein indicator were added into flask, and the solution was titrated with a ~0.15 N NaOH (C_{NaOH}) standard solution. Until the color of solution was changed to light pink color and did not fade within 30 s, the consumption volume of NaOH standard solution was recorded as V_1. The epoxy equivalent weight of Se-EP was calculated as the following equation,

$$EEW = \frac{(V_0 - V_1) \times C_{NaOH}}{10W}$$

V_0 represents the consumption volume of NaOH standard solution in blank; V_1 represents the consumption volume of NaOH standard solution in experiment section; W represents the weight of sample.

The amount of active hydrogen groups (carboxylic acid and phenolic hydroxyl groups) was titrated according to the following method. The dry ozonated lignin of ~0.2 g (accurate to 0.0002 g) reacted with 25 mL ~0.1 N NaOH standard solution in a 100 mL flask in darkness for 30 min at room temperature. The solution was titrated with a ~0.1 N HCl standard solution. The pH value was monitored by a pH meter. Until the pH value turn to ~7.0, the consumption volume of HCl standard solution was recorded.

The amount of phenolic and carboxylic acid groups in Oz-L was determined by ^{31}P-NMR based on the method of Granata et al[4] with a slight modification. The dried Oz-L of ~20 mg (accurate to 0.1 mg) was dissolved into 550 μL of a mixture solvent of pyridine and deuterated chloroform (1.6:1, v/v) containing cyclohexanol (internal standard, 0.11%, w/v) and chromium acetylacetonate (relaxation agent, 0.098%, w/v) in a 1 mL vial. The TMDP (70 μL) was then added into the vial. The vial was shaken for ~ 20 s to achieve the complete phosphitylating reaction. The ^{31}P-NMR spectrum was measured on a NMR spectrometer (600 MHz). Samples were scanned for 64 times with a 25 s delay between 90° pulses.

Differential scanning calorimeter was used to distinguish the relative reactivity of phenolic and carboxylic acid groups in Oz-L. The samples (~5 mg) were scanned from -20 to 220 °C at a heat rate of 5 K min^{-1} under nitrogen atmosphere.

Thermal stability was determined using a TGA/DSC1 thermo-gravimetric analyzer (TGA). A sample of ~10 mg was loaded into a ceramic crucible and scanned from 25 to 800 ºC at a heating rate of 10 K min^{-1} under nitrogen atmosphere.

Dynamic mechanical properties were measured using a dynamic mechanical analyzer (DMA) (Q800, Thermal Instrument) in tension mode. The film with a dimension of 20 mm x 5 mm x 0.3 mm was scanned from -60 to 180 ºC at the heating rate of 5 K min^{-1}. The amplitude was set at 15μm, and the frequency was 1 Hz.

Tensile properties were measured on DMA in tension mode at room temperature. The strain rate was 0.5% min^{-1}. The sample with a dimension of 20 mm x 5 mm x 0.3 mm was used for the test.

The swelling ratio of the cured Se-EP/Oz-Ls was measured by immerging the sample (~0.5 g, W_1) in a mixture solvent of ethanol/acetone (1:1, v/v) at 50 ºC. After the absorption of the sample for solvent reached equilibrium, the samples were removed from the solution. The excessive surface solvent was removed with a filter paper, and the swollen samples were weighted (W_2). The swelling ratio was calculated according to the following equation,

$$Swelling\ ratio\ (\%) = \frac{W_2 - W_1}{W_1} \times 100\%$$

Gel content of the cured Se-EP/Oz-L was determined by the solvent extraction method.[5] The pre-weighted dry sample (~0.5 g, W_1) was extracted in 100 mL mixture solvent of ethanol/acetone (1:1, v/v) for 48 h in a 500 mL round bottom flask equipped with a Soxhlet extractor. After extraction, the samples were dried in a vacuum oven at 50 ºC for 24 h and weighted (W_2). The gel content was calculated according to the following equation,

$$Gel\ content\ (\%) = \frac{W_1 - W_2}{W_1} \times 100\%$$

Shape memory property was characterized using a dynamic mechanical analyzer (DMA) (Q800, Thermal Instrument) in the single cantilever mode. The dimension of the sample was 20 mm x 5 mm x 0.3 mm. First, the sample was equilibrated at 80 ºC (above T_g) for 40 min. Subsequently, a constant force of 0.1 N was applied to the sample and the temperature was decreased to 10 ºC (below T_g) at a cooling rate of 5 K min^{-1}. When the temperature reached to 10 ºC, the constant force was removed, and the sample was heated back to 80 ºC at a heating rate of 5 K min^{-1}. These above steps were repeated for three times, and the displacements were recorded during the test.

Stress relaxation test was performed on a discovery HR-2 hybrid rheometer with 8 mm parallel plates. The film sample with uniform thickness was heated to the test temperature and equilibrated for 10 min. A constant axial force (2 N) was applied to the sample in order to keep a good touch of sample with parallel plates, and the relaxation modulus versus time under a constant strain of 1.5% was recorded.

Lap shear test was carried out on a universal testing machine (Instron 4466) according to the ISO 4587:2003 standard. Aluminum sheets (4215BC, 0.025Ga) with a dimension of 100 mm x 25 mm x 1 mm were polished using 240-grit sand paper and then cleaned by soapy water, distilled water and 2-propanol successively. In the presence of zinc catalyst, Se-EP/Oz-L mixture (R = 1:1, adhesive loading of 208 g m^{-2}) was sandwiched between the polished aluminum sheets with an overlapping area of 12.5 mm x 25 mm. The aluminum sheets were bonded by hot press with the same aforementioned curing conditions. The lap shear test was conducted with a constant cross head speed of 5 mm min^{-1} at room temperature. At least five repeat tests were performed for each sample.

Creep test was conducted on DMA in the film tension mode. The bonded aluminum sheets (20 mm x 5 mm x 1 mm) were subjected to creepage at 190 ºC for 20 min under a constant load of 2 MPa. The adhesive used for bonding the aluminum sheets was the Se-EP/Oz-L (R = 1:1, adhesive loading of 208 g m^{-2}).

Reference

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2 M. V. Bule, A. H. Gao, B. Hiscox and S. Chen, *Journal of agricultural and food chemistry*, 2013, **61**, 3916-3925.

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4 A. Granata and D. S. Argyropoulos, *Journal of Agricultural and Food Chemistry*, 1995, **43**, 1538-1544.

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