Supporting Information

Eutectic Hardener from food-based chemicals to obtain fully bio-based and durable Thermosets

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Experimental Details

Nuclear Magnetic Resonance (NMR): High-temperature NMR spectra were recorded on a *Bruker AVANCE* III (400 MHz). ^{1}H-NMR chemical shifts are given in reference to the residual solvent peak of $CDCL_3$ at 7.26 ppm.

Fourier Transformed Infrared Spectroscopy (FTIR): A Bruker Tensor 27 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector and single-reflection diamond ATR device was used to record IR spectra. The curing at room temperature was studied by taking spectra of the same sample in time intervals. The spectrum of air was recorded as background before each measurement. A total of 128 scans with a resolution of 1 cm^{-1} were recorded for each sample.

Rheology: Isothermal curing studies and Frequency sweeps of the Eutectic mixtures were performed on a Thermo Scientific HAAKE MARS rheometer. Isothermal curing measurements were obtained in plate–plate geometry (25 mm diameter, 1 mm gap, 0.5 % Strain) at varying temperatures (24, 30, 35, 40, 45, 50, and 60 °C). Variations of complex viscosity, storage, and loss modulus with temperature were analyzed. The viscosity of the eutectic mixtures was determined with a frequency sweep (0.1 – 10 Hz, 1 % strain).

Dynamic Mechanical Thermal Analysis (DMTA): The dynamic mechanical properties were studied using a Mettler-Toledo DMA-1 in tensile mode. Samples were tested on temperature sweeps from−50 °C to 150 °C with a heating rate of 3 °C min^{-1}. Experiments were done in a single frequency oscillation mode with a frequency of 1 Hz, a force amplitude of 0.1 N and a displacement amplitude of 0.1 % in auto tension offset control.

Determination of Gel fraction: Pieces with m ~ 200 mg were placed in a 20 mL vial and covered with 5 mL of THF. After 7 days the swollen pieces were taken out of the vial, dried with a piece of paper, and weighed. These samples are then washed at least three times with isopropanol and dried in a vacuum oven (30 °C) until their weight was constant. The Swelling ratio was determined according to Equation S1:

$$Swelling\ ratio\ (\%) = \left(\frac{m_{swolen} - m_{initial}}{m_{initial}}\right) * 100\ \%$$ (eq. S1)

The gel fraction was determined according to equation S2:

$$Gel\ fraction\ (\%) = \left(\frac{m_{final}}{m_{initial}}\right) * 100\ \%$$ (eq. S2)

Differential scanning calorimetry (DSC): DSC measurements were performed with a Mettler-Toledo DSC823^e heat-flux instrument. STAR software was used for data analysis. Temperature, enthalpy, and tau lag calibrations were performed with indium and zinc standards. Eutectic and curing mixtures (5 – 10 mg) were placed in a 40 mL aluminum crucible and closed by a punctured pan lid. The experiments were done under air flow (80 mL min^{-1}). Eutectic mixtures were scanned from -90 C or -85 °C to 35 °C at 1 K min^{-1}.

The room temperature curing test were performed on an initially prepared mixture by preparing 15+ samples and storing them in the same environment at 24 °C. The development of the glass transition temperature T_g was monitored by scanning the sample from 24 °C to -50 °C to 100 °C. T_g was determined as the inflection point of the specific heat capacity (C_p) increment.

Tensile tests: Tensile tests were performed with a *Shimadzu* EZ-LX tensile tester equipped with a 1 kN load cell. The tests were performed on dog bones (l = 48 mm, w = 5.1 – 5.3 mm, t = 1.9 – 3.5 mm) cut from cured 19.6 x19.6 cm square slabs of the respective material. The exact sample dimensions were determined for each sample before testing. A grip-to-grip separation of 35.92 mm was used. The samples were prestressed to 0.1 N and then loaded with a constant cross-head speed of 20 mm min^{-1}.

Materials: *Epoxidized Linseed oil* (ELO) was kindly provided by Valtris Chemicals (molecular weight of 980 g.mol^{-1} and average of 5.5 epoxy groups per molecule) and used as received. The amount of Epoxy groups in ELO was determined by NMR (Figure S1). The integration of the single Glycerol CH was set as 1, which allows one to determine the number of Epoxy groups per molecule according to Equation S3 (eq. S3):

$$N_{epoxy} = \left(\frac{\int}{2}\right) = \frac{6.01 + 3.72 + 1.36}{2} = 5.545$$ (eq. S3)

and the average molecular weight of ELO according to Equation S4 (eq. S4)

$$M_{ELO} = M_{glycidyl\ ester} + \left(\frac{M_{-C=C-} * \int -C=C-}{N_{Proton}}\right) + \left(\frac{M * \int}{N_{Proton}}\right) + \left(\frac{M_{-CH_3} * \int -CH_3}{N_{Proton}}\right) + \left(\frac{M_{-CH_2-} * \int -CH_2-}{N_{Proton}}\right)$$

$$M_{ELO} = 173.1\frac{g}{mol} + \left(\frac{26.038\frac{g}{mol} * 0.215}{2}\right) + \left(\frac{42.037\frac{g}{mol} * 11.09}{2}\right) + \left(\frac{15.035\frac{g}{mol} * 9}{3}\right) + \left(\frac{14.072\frac{g}{mol} * 69.75}{2}\right) \frac{g}{mol}$$

(eq. S4)

Example formulation calculated for $R_{Eutectic} = 1$ and $R_{ELO} = 0.8$: To obtain the desired thickness of ~3 mm inside a 196 x 196 mm we found that starting with 80 g ELO is appropriate. The rest of the material required is calculated based on that. The amount of required CA is calculated as follows (eq S5):

$$m_{CA} = \left(\frac{m_{ELO}}{M_{ELO}}\right) * N_{Epoxy} * R_{ELO} * \left(\frac{M_{CA}}{N_{COOH}}\right) \quad \text{(eq. S5)}$$

$$m_{CA} = \left(\frac{80\ g}{944.86\ g\ mol^{-1}}\right) * 5.545 * 0.8 * \left(\frac{192.123}{3}\right) = 24.053\ \text{g}$$

The required amount of EL is then calculated as follows (eq S6)

$$m_{EL} = \left(\frac{m_{CA}}{M_{CA}}\right) * R_{Eutectic} * M_{EL} \quad \text{(eq. S5)}$$

$$m_{EL} = \left(\frac{24.053\ g}{192.123\ g\ mol^{-1}}\right) * 1 * 118.13 = 14.790\ g$$

To obtain a homogenous and liquid mixture of CA and EL they are heated together at 140 °C until they become fully liquid and cooled to 60°C in an oven. Since the melting point of the combined chemicals is well below room temperature, the obtained eutectic mixture stays liquid during curing conditions. Before mixing with the Hardener, ELO is kept at roughly 60 °C to melt residual crystals (ELO tends to partially crystallize at room temperature with time). Then, ELO and Hardener were mixed using a spatula at 60 °C, poured into a rectangular mold, and cured in an oven at 60 °C for 1 h. This pre-curing step ensured that air bubbles were taken out of the system. In order to get reproduce ability between samples, the time in the oven was carefully monitored so that each sample has been subjected to an identical thermal treatment. Then, a post curing step at 160 °C was carried out for 2 h, ensuring full consumption of oxirane groups. Using

this methods, rectangular slabs with $R_{Eutectic}$ of 0.5, 1, and 2 were prepared. For room temperature curing, the hardener was allowed to reach room temperature, then mixed with ELO (ELO was previously molten and also allowed to reach room temperature) and left to cure inside the same rectangular molds used for high temperature curing.

Supporting Figures

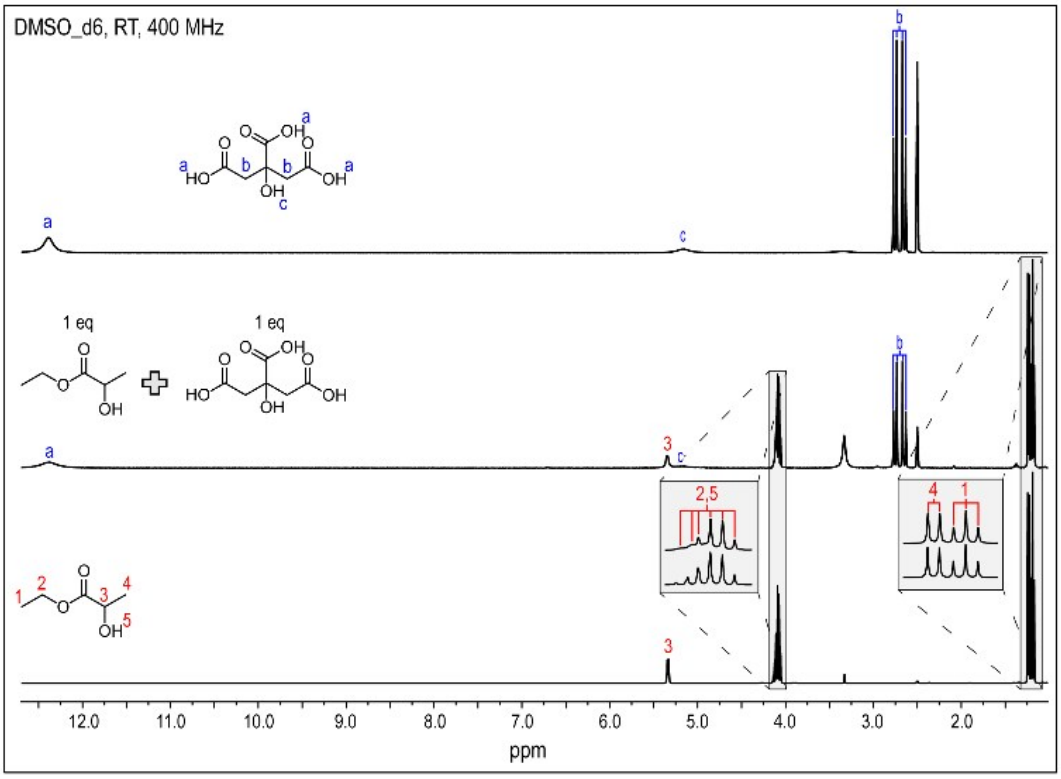

Figure S1. NMR spectrum (DMSO_d6, RT, 400 MHz) of a 1:1 mixture of CA and EL heated for 5 minutes at 140 °C.

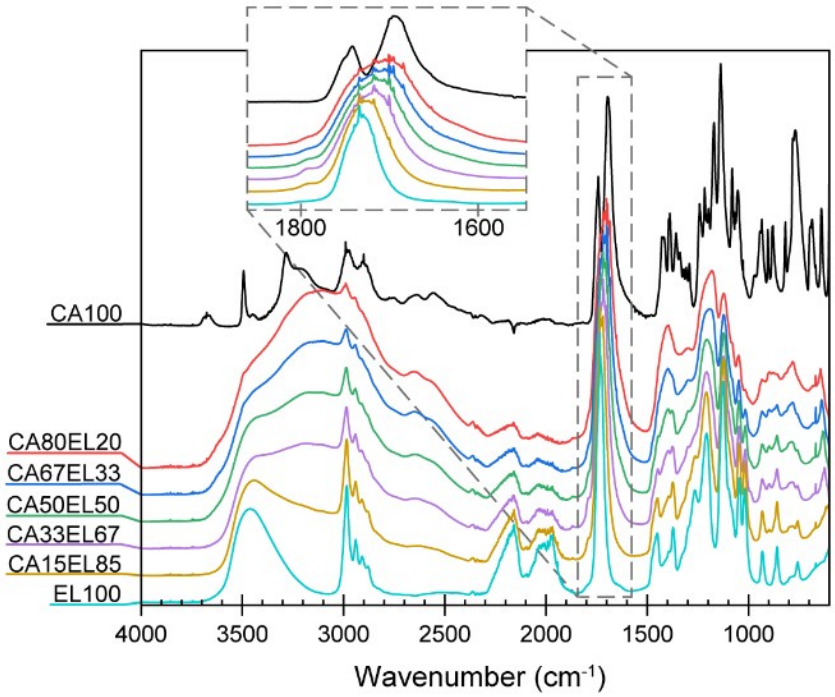

Figure S2. IR spectra of CA100, EL100, and Eutectic mixtures of the two in varying ratios, as denoted in the figure (The number refers to their fraction in mol%).

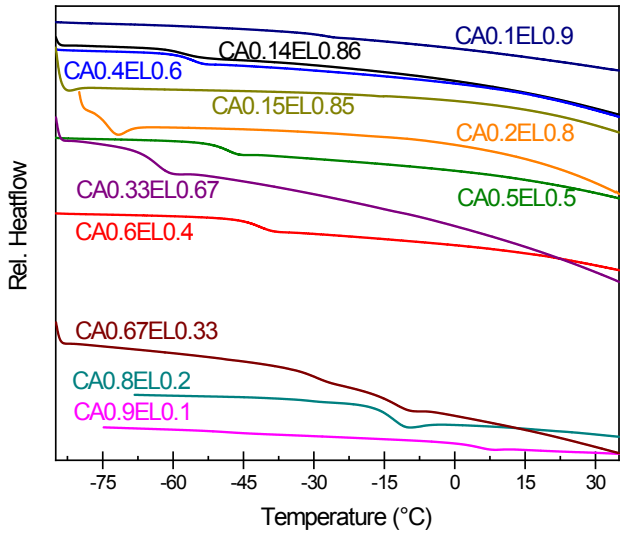

Figure S3. Combined DSC traces of the varying CA-EL mixtures.

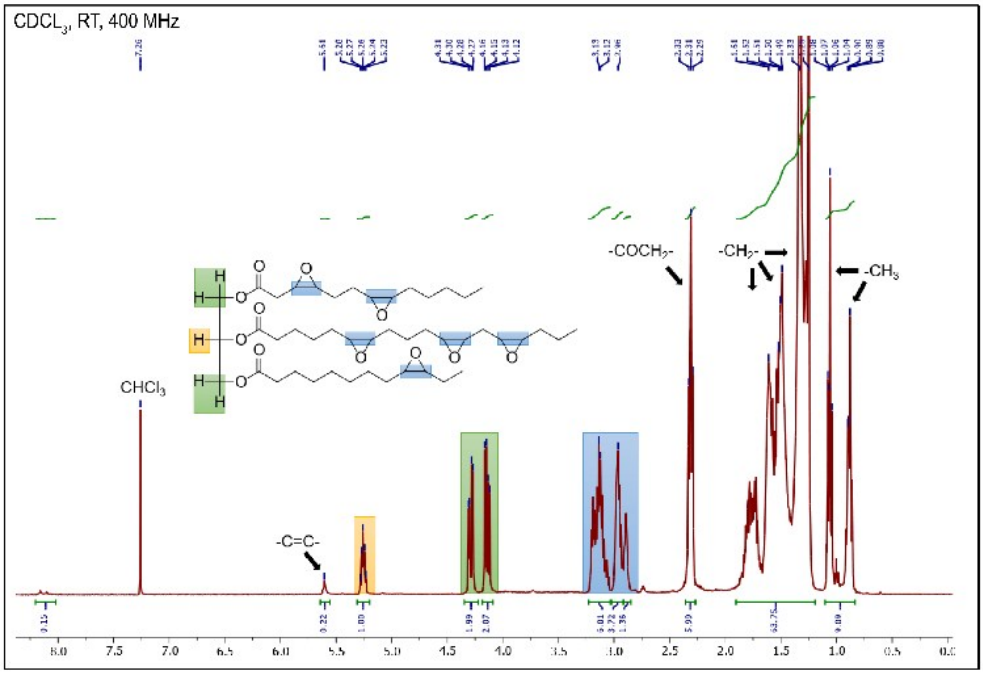

Figure S4. NMR spectrum of Epoxidized Linseed oil (ELO) in deuterated Chloroform.

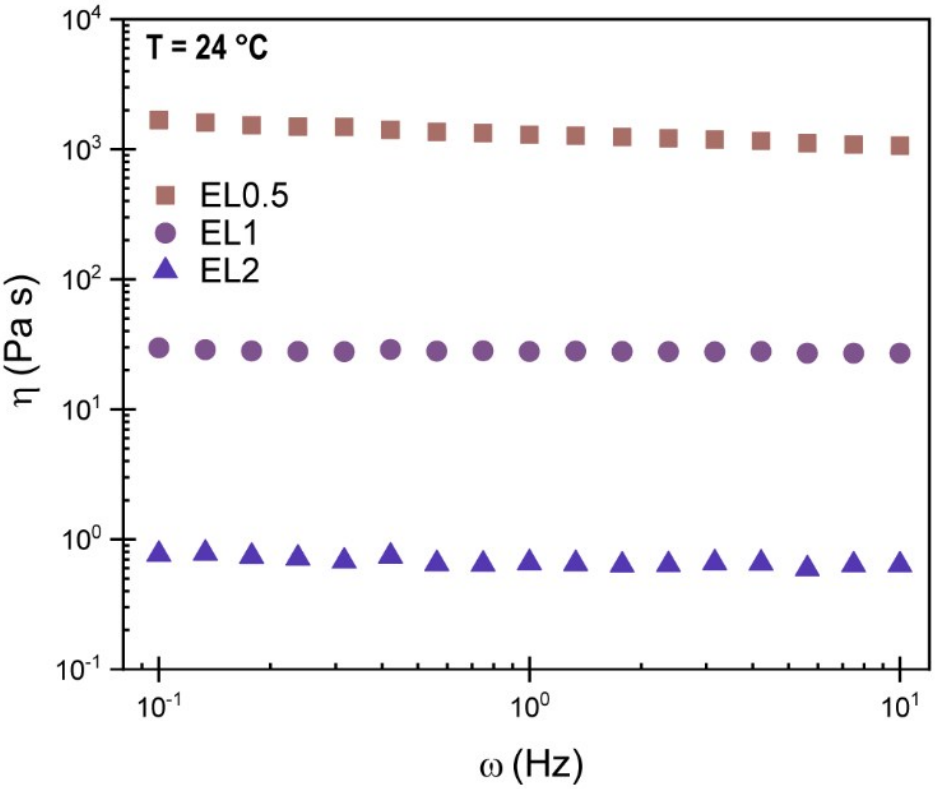

Figure S5. Viscosity η as a function of Frequency ω of Eutectic CA-EL mixtures with $R_{Eutecic} = \left(\frac{n(EL)}{n(CA)}\right) = 0.5;1;2$ at 24 °C and γ_0 = 1 %.

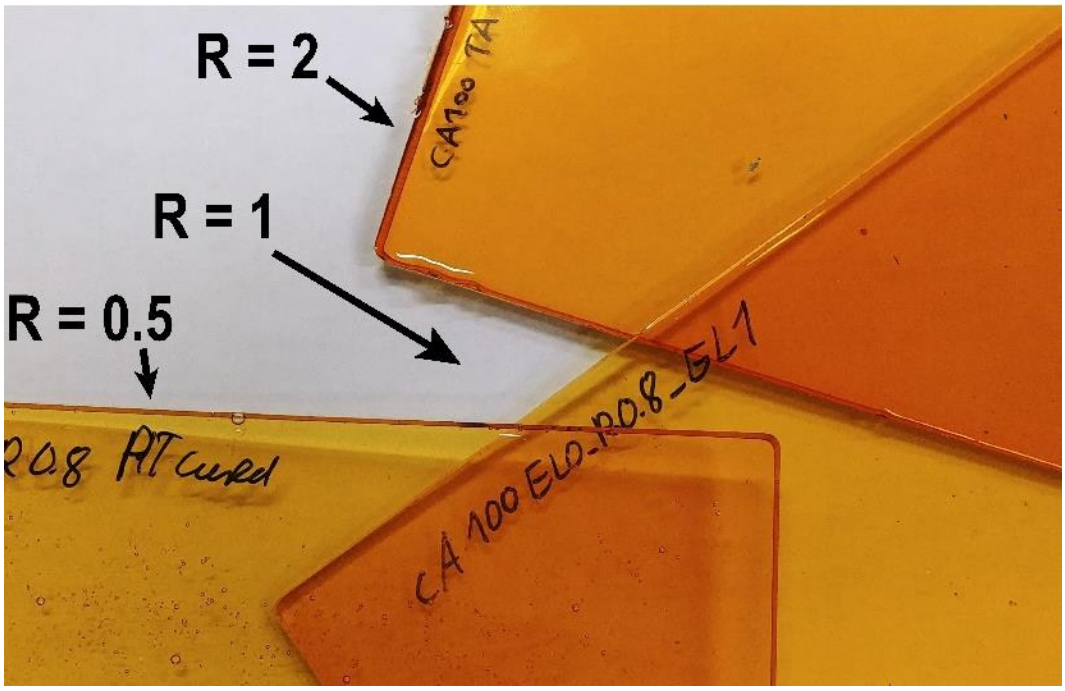

Figure S6. Picture of HTP cured rectangular slabs with $R_{Eutectic}$ = 0.5, 1, and. 2.

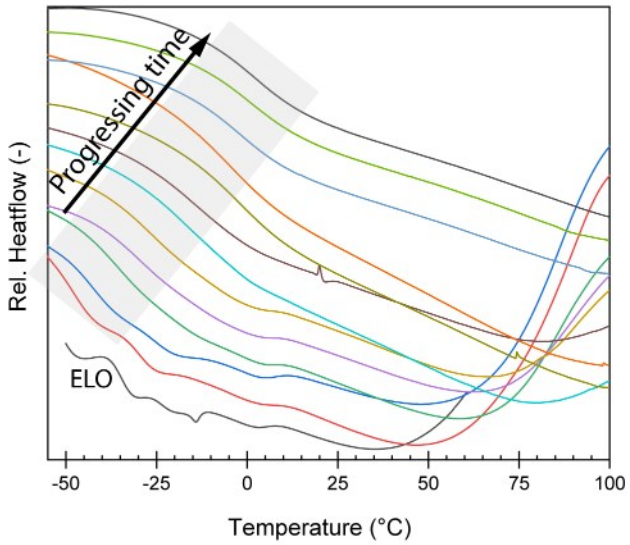

Figure S7. Periodic DSC scans of CA/EL hardener mixture ($R_{Eutectic}$ = 1) and ELO (R_{ELO} = 0.8) cured at room temperature for 8 days. The first Scan on the bottom is a DSC scan of 100% ELO, showcasing the temperature interval of ELO crystallization.

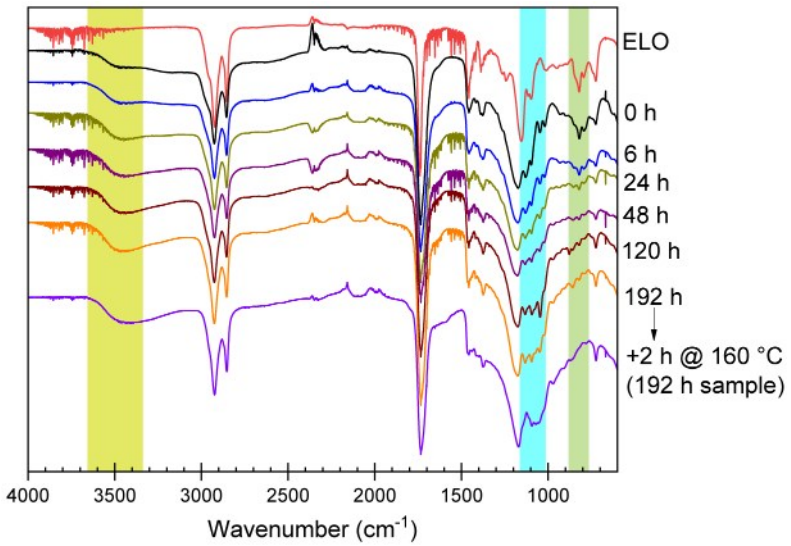

Figure S8. IR spectra of sample cured at 24 °C taken over the course of 8 days. Last spectrum is taken of a sample cured for 192 h (8 days) and then post-cured in an oven for 2 h at 160 °C. The very first spectrum (ELO) is an IR spectrum of pristine ELO without any additive.