Supplementary Information (SI) for RSC Sustainability.

Biobased Epoxy Resins from Itaconic Anhydride Functionalized Lignin: Insights and Comparison with Succinic Analogues

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Summary

Materials

Organosolv beech wood lignin was kindly donated by the Fraunhofer Center for Chemical-Biotechnological Processes CBP (Leuna, Germany) and dried at 60 °C under vacuum (10 mbar) for 24 hours before use. Pripol™ 1009 (Acid value provided from manufacturer: 196 mg KOH /g) was kindly provided by Cargill Company. ESBO (Vikoflex® 7170, Cargill), itaconic anhydride (97%, Fisher Scientific), succinic anhydride (>95.0%, TCI), potassium carbonate (K_2CO_3, >99%, anhydrous, Fisher Scientific), 2-chlor-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (TMDP, 95%, Sigma-Aldrich), *N*-hydroxy-5-norbornene-2,3-dicarboxylic acid imide (NHND, 97%, Alfa Aesar), chromium(III) acetylacetonate (99.99% trace metal basis, Sigma Aldrich) (anhydrous, >99%, Sigma-Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, >98%, Fluorochem), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, >98%, TCI Chemicals), 1,1,3,3-tetramethylguanidine (TMG, >99%, TCI), 3,4,5-trichloropyridine (97%, Chempur), acetone (dried and stored over molecular sieves, ≥99.5%, Sigma-Aldrich), dimethyl sulfoxide (DMSO, dried and stored over molecular sieves, >99.7%, Acros Organics), pyridine (≥99%, Sigma Aldrich) were used without further purification. Deionized water (DI) was used in all experiments. Deuterated solvents (DMSO-d_6 and chloroform-d_1) were purchased from Eurisotop.

Instruments Specifications and Methods

Infrared (IR) Spectroscopy

Infrared spectra were recorded using a Bruker ALPHA attenuated total reflection (ATR) IR spectrometer or PerkinElmer Spectrum 100 instrument with an attenuated total reflection (ATR) unit on a diamond crystal and a temperature-controlled stage (Specac, High Temperature ATR Golden Gate accessory). 16 scans in the range of ν = 4000 – 400 cm^{-1} or ν = 4000 – 600 cm^{-1} at ambient temperature were recorded at a resolution of 4 cm^{-1}. Real-time FTIR measurements were conducted at 140 °C, with spectra collected at 6 min intervals. All spectra were baseline-corrected and normalized to the aromatic C=C stretching vibration at 1509 cm^{-1} using Spectrum software.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H–NMR spectra were recorded using a Bruker Ascend 400 MHz or a Bruker Avance DRX 500 MHz spectrometer, with 16 to 128 scans, a delay time d_1 ranging from 1 to 5 s, at 298 K. The chemical shift was reported in parts per million (ppm) and referenced to characteristic signals of deuterated solvents, *e.g.* DMSO-d_6 at 2.50 ppm or chloroform-d_1 at 7.26 ppm. ^{13}C–NMR spectra were recorded using a Bruker Avance DRX spectrometer at 126 MHz with 1024 to 32768 scans, with delay time d_1 of 1 to 4 s at 298 K. The chemical shift was reported in parts per million (ppm) and referenced to characteristic signals of deuterated solvents, e.g. DMSO-d_6 at 39.52 ppm or chloroform-d_1 at 77.16 ppm. Peak deconvolution was performed applying the GSD (Global Spectrum Deconvolution) method with refinement level 3 (10 fitting cycles) and 10 improvement cycles.

Quantitative ^{31}P–NMR

For quantitative determination of hydroxyl values, an exact amount of 28 – 32 mg of lignin sample (previously dried under vacuum at 70 °C) was weighed. Subsequently, 100 µL of a solution of chromium(III) acetylacetonate (5 mg/mL) as relaxation agent and the internal standard (IS) endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (NHND, 18 mg/mL) in $CDCl_3$:pyridine (1 : 1.6 v/v) are added to the lignin sample, and 450 µL of solvent mixture $CDCl_3$:pyridine (1 : 1.6 v/v) are added to aid solubilization. After a homogeneous solution was obtained, 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (TMDP, 70 µL) was added and the solution was stirred for an additional 15 minutes. Afterwards, it was transferred into a NMR tube for subsequent measurement using a Bruker Ascend instrument at 162 MHz with 512 scans and a delay time d_1 of 10 seconds at 298 K and a spectral width of 100 ppm (190 – 90 ppm).[1,2]

The chemical shifts are reported relative to the reaction product of 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane with water, at 132.2 ppm. Integrals are assigned to the functional groups as followed: δ = 152.5 – 151.7 (NHND), 149.5 – 145 (aliphatic hydroxyl groups), 145 – 141.2 (syringyl hydroxyl groups), 140.8 – 137.7 (guaiacyl hydroxyl groups), 135.7 – 134 (carboxylic acids).

Calculations were performed by first determining the mole quantity of IS in the IS solution:

$$NHND\ in\ IS\ solution\ (mmol) = \frac{mass\ of\ NHND\ added\ to\ the\ IS\ solution\ (g)}{M_w\ of\ NHND\ (179.17\frac{g}{mol})} * purity\ of\ NHND\ (\%) * 1000 \qquad \text{Eq. S1}$$

Afterwards, the mole quantity of IS (NHND) in the NMR sample was calculated:

$$NHND\ in\ NMR\ sample\ (mmol) = \frac{NHND\ in\ IS\ solution\ (mmol)}{total\ mass\ of\ IS\ solution\ (g)} * mass\ of\ 0.1\ mL\ of\ IS\ solution\ (g) \qquad \text{Eq. S2}$$

I_{ratio} between the spectral region of interest (I_{OH}) over the IS integration peak (I_{NHND}) is determined:

$$I_{ratio} = \frac{integral\ of\ the\ region\ of\ interest}{integral\ of\ IS\ peak} = \frac{I_{OH}}{I_{NHND}} \qquad \text{Eq. S3}$$

Finally, to calculate the amount of different hydroxyl groups in lignin, *i.e.* OH / g lignin:

$$mmol\ of\ \ OH\ groups\ per\ g\ of\ lignin = \frac{I_{ratio} * mmol\ of\ NHND\ in\ NMR\ sample}{dry\ weight\ of\ lignin} \qquad \text{Eq. S4}$$

Size Exclusion Chromatography

SEC measurements were performed on an Agilent Technologies 1260 Infinity II system equipped with a Mixed-C and Mixed-E Agilent column and a differential refractive index detector. The used eluent was DMAc containing 0.034wt% LiBr. The number average molar mass (M_n), the weight average molar mass (M_w), and the dispersity ($Đ = M_w/M_n$) of the samples were determined using a calibration of polystyrene (PS) standards with M_p ranging from 370 to 2.52×10^6 Da. The samples were dissolved in the eluent at a concentration of 2 mg / mL and filtered over a 0.2 µL filter.

TGA

TGA was performed using a TGA/DSC-1 instrument (Mettler Toledo). Approximately 10 mg of sample was placed in a 70 µL alumina crucible and heated from 25 °C (10 min isothermal) to 600 °C at 10 °C min^{-1} under nitrogen (50 mL min^{-1}). The temperatures corresponding to 5% (T_5%) and 50% (T_{50}%) weight loss were determined as well as the residues. Thermogravimetric measurements were performed using a TGA Q5500 instrument from TA Instruments. The samples were dried under vacuum (10 mbar) at 70 °C overnight before measurement. The samples (5 – 6 mg) were heated in a Pt crucible from 25 to 600 °C under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. $T_{d,5\%}$ is defined as the temperature at which 5% weight loss of the sample occurred, while $T_{d,50\%}$ is defined as the temperature at which 50% of the weight loss of the sample occurred. Residue (%) is defined as the weight percentage of residual mass at the end of the analysis.

DMA and Tensile strength measurements

Thermomechanical properties were measured using a DMA Q800 instrument equipped with an ACS-3 cooling accessory (TA Instruments) in tension film mode. Samples were tested under a 0.1 % oscillatory strain at a frequency of 1 Hz, with a pre-load force of 0.01 N. Samples were cooled to -50 °C, equilibrated for 5 min, and subsequently heated to 100°C at 3 °C min^{-1}. Three replicates were tested for every sample. The crosslinking densities (ν_e) of the thermosets were calculated from the storage modulus in the rubbery state, according to the theory of rubber elasticity, with the following equation:

$$\nu_e = \frac{E_e^{'}}{3RT} \qquad \text{Eq. S5}$$

where:

$E_e^{'}$ is the storage modulus in the rubbery plateau region (Pa); R is the universal gas constant (J mol^{-1} K^{-1}); T is the absolute temperature (K) at which $E_e^{'}$ was measured, corresponding to T_g + 20

Tensile measurements were performed on the same instrument in tension film mode, with a strain ramp. An initial strain of 0.01 % was applied, then increased to 100 % with an increase of 10 % strain min^{-1} at a temperature of 25 °C, with a pre-load force of 0.001 N.

DSC

DSC thermograms were obtained using a DSC-1 instrument (Mettler Toledo). Approximately 5 mg of sample was sealed in a 40 µL aluminum crucible with a pierced lid. The samples were measured in two heating cycles to remove any thermal history. For lignin samples: from 25 to 170, 170 to -50, and -50 to 170 °C. For thermoset samples: from 25 to 180, 180 to −90, and −90 to 180 °C. DSC curves presented are relative to the second heating cycle. A heating or cooling rate of 10 °C min^{-1} was applied. Glass transition temperatures (T_g) were determined as the midpoint of the second heating cycle.

Rheometer

Rheological analyses were conducted using a Discovery Hybrid Rheometer 2 (DHR-2, TA Instruments) equipped with a peltier plate temperature-control system. Responses were evaluated in a 20 mm stainless steel plate–plate geometry. Amplitude-sweep experiments were performed at a constant frequency (ω) of 1 Hz and temperature of 25 °C, strain (γ) was increased until deviation from linear range were detected. Frequency-sweep experiments were performed at the maximum strain detected in the LVER at a constant temperature of 25 °C and frequency range between 10 and 0.01 Hz.

Gel content determination

Weighed bar samples of the cured thermosets were immersed in THF for 24 hours. Afterwards, the swollen samples were dried gently between paper sheets and weighed again. Then, the samples were dried at 60 °C for 24 h, and their final weight was recorded.

The gel content of the samples is defined as:

$$Gel\ content\ (\%) = \frac{m_d}{m_i} \times 100\% \qquad \text{Eq. S6}$$

where:

m_d is the final weight of the sample after drying at 60 °C for 24 hours

m_i is the initial weight of the sample

Calculations yield and conversions for lignin

A simplified theoretical yield was calculated, with the assumption of quantitative conversion for the reactive sites towards the main reaction, following Eq. S7:

$$m_f = m_i \left(1 + \Delta M_{graft} \left(reactive\ sites\ in \frac{mol}{g}\right)\right) \qquad \text{Eq. S7}$$

where:

m_f = final mass of the modified lignin (g)

m_i = initial mass of starting lignin (g)

ΔM_{graft}= increase in the molecular weight caused by the modification (g/mol)

Reactive sites = number of moieties participating in the reaction (depending on the reaction type) in mol/g.

For the determination of the consumed aliphatic and aromatic hydroxyl groups – and consequently the calculation of conversion percentages – it is essential to account for the molecular weight increase resulting from the modification with the cyclic anhydride, relative to the starting material (Organosolv lignin, acetone-fractionated). The consumption of aliphatic and phenolic hydroxyl groups was quantified using Eq. S8 and S9, while the corresponding percentage conversions were calculated according to Eq. S10 and S11.

$$OH_{aliph,\ consumed} = \frac{OH_{aliph,\ starting\ lignin} - OH_{aliph,\ modified\ lignin}}{\left(1 + \left(\frac{Mw_{Itaconic\ anhydride}}{1000} \times OH_{aliph,\ modified\ lignin}\right)\right)} \qquad \text{Eq. S8}$$

$$OH_{arom,\ consumed} = \frac{OH_{arom,\ starting\ lignin} - OH_{arom,\ modified\ lignin}}{\left(1 + \left(\frac{Mw_{Itaconic\ anhydride}}{1000} \times OH_{arom,\ modified\ lignin}\right)\right)} \qquad \text{Eq. S9}$$

$$XOH_{aliph} = \frac{OH_{aliphatic,\ consumed}}{OH_{aliph,\ starting\ lignin}} \qquad \text{Eq. S10}$$

$$XOH_{arom} = \frac{OH_{arom,\ consumed}}{OH_{arom,\ starting\ lignin}} \qquad \text{Eq. S11}$$

Characterization of Epoxidized Soybean Oil (ESBO)

For quantifying the epoxide groups of ESBO, a quantitative ^{1}H–NMR spectrum was conducted with 3,4,5- trichloropyridine as internal standard (IS). The resulting spectrum is reported in **Figure S1**.

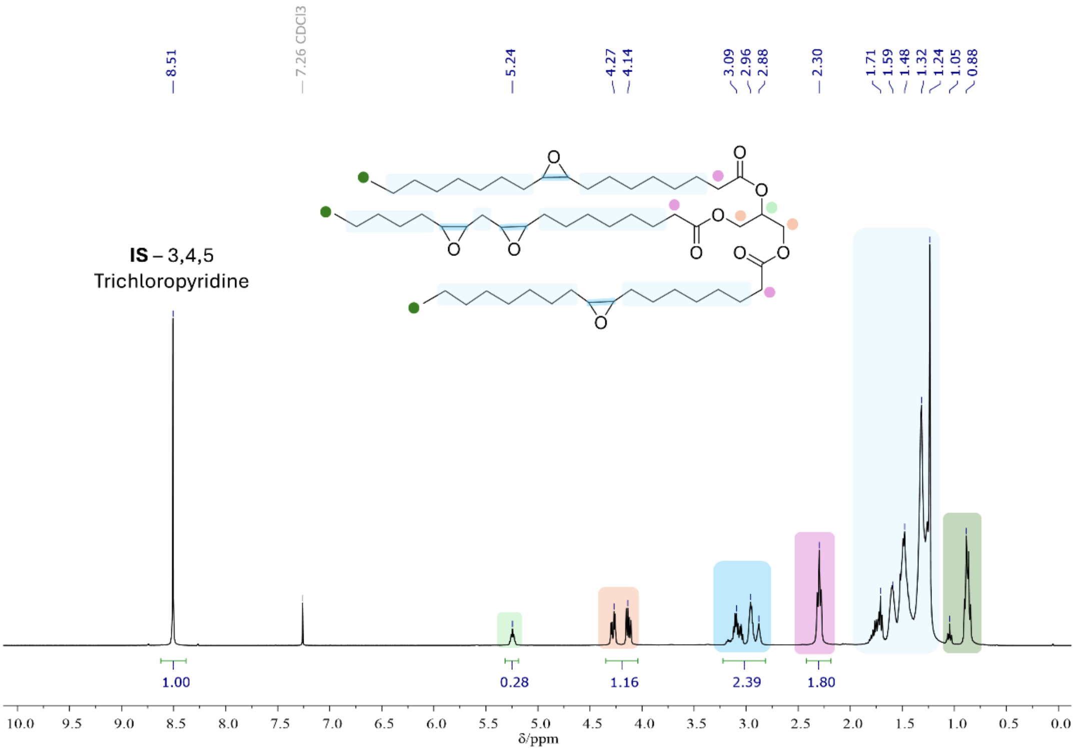

Figure S1 – ^{1}H–NMR of ESBO in $CDCl_3$ with the IS 3,4,5-trichloropyridine and peak assignement.

The following calculations (Eq. S12) were followed to calculate the value of epoxy groups in mmol/g:

$$mmol\,/g\ of\ epoxy\ groups\ in\ ESBO = \frac{\dfrac{\int epoxy\ region * H_{IS}}{\int IS *\ H_{epoxy}} * mmol\ of\ IS}{mass\ of\ ESBO\ (g)} \qquad \text{Eq. S12}$$

Where:

- *Integral of epoxy region* corresponds to the integral of the area between 3.25 – 2.75 ppm;
- *Integral of IS* is the integral value of the internal standard
- H_{IS} equals to 2;
- H_{epoxy} equals to 2;
- *Mass of ESBO* is the mass of the unknown sample to analyze in grams

For the calculation of the mmol of IS added to the sample the Eq. S13 was used:

$$mmol\ of\ IS\ added\ to\ the\ sample = \frac{mass\ of\ IS\ (mg)}{M_w\ of\ IS\ \left(\frac{mg}{mmol}\right)} * Purity\ of\ IS \qquad \text{Eq. S13}$$

Where:

- *Purity of IS* is 97 %;
- *Mass of IS* is the mass of internal standard used in the test in mg;
- M_w *of IS* is the molecular weight of the internal standard.

Internal standard: 3,4,5-Trichloropyridine (Purity: 97%)

Table S1 – Values of the masses of ESBO and IS taken for the triplicate tests, as well as the calculated values of mmol/g of epoxides.

Test #	**ESBO (mg)**	**IS (mg)**	**Epoxides (mmol/g)**
1	33.8	12.6	4.74
2	33.0	12.6	4.75
3	34.1	12.6	4.77

The test was performed in triplicate giving an average value of (**4.753 ± 0.015**) mmol epoxy/g.

Lignin Functionalization

General procedure for the fractionation of lignin with acetone

Organosolv beechwood lignin (previously dried at 70 °C under 10 mbar vacuum) was suspended in acetone with a concentration of 100 g/L. The suspension was stirred at r.t. for 3 hours, afterwards it was filtrated on a Buchner filter equipped with grade 5 filter paper. The filtrates were collected, and the solvent was evaporated under reduced pressure. The residue was collected with a minimal amount of clean acetone and precipitated in a tenfold amount of acidic water (pH<2). The solids were filtrated on a fritted filter (porosity P-4), washed with cleaned deionized water, and dried under vacuum (10 mbar, 70 °C) for at least 48 hours prior to analysis.

Fractionation was performed in a 15 g scale and a 50 g scale, with yields of 62 and 67 %, respectively (gravimetric yield of fractionation, based on starting weight). The 15 g scale acetone lignin fractionation will be indicated hereon with OL Acetone (1), while the 50 g scale acetone lignin fractionation will be indicated with OL Acetone (2). Characterization of both lignin is reported in **Table S2**.

OL Acetone (3) was performed on a 60 g scale with a 67% yield and used as starting material to synthesize succynilated (SAn-BB-TMG) and itaconated lignin (IAn-BB-TMG) with TMG as catalyst.

Table S2 – Characterization of pristine lignin (OL) and both batches after acetone fractionation.

Entry	Total [mmol/g][a]	Aliphatic [mmol/g][a]	Aromatic [mmol/g][a]	–COOH [mmol/g][a]	M_n [Da]	M_w [Da]	$Đ$
OL	4.35 ± 0.08	2.42 ± 0.05	1.83 ± 0.04	0.1 ± 0.004	3000	11000	3.7
OL Acetone (1)	5.01 ± 0.07	2.52 ± 0.03	2.42 ± 0.04	0.06 ± 0.005	2900	7800	2.7
OL Acetone (2)	4.34 ± 0.05	2.24 ± 0.03	2.03 ± 0.02	0.07 ± 0.004	2800	7400	2.6
OL Acetone (3)	4.42 ± 0.05	2.26 ± 0.02	2.12 ± 0.07	0.08 ± 0.002	2500	6200	2.5

[a]: Determined via ^{31}P–NMR. Measurements were performed in triplicate.

For the optimization of the reaction conditions between fractionated lignin and IAn, the first fractionation in a 15 g batch (**OL Acetone (1)**) was utilized. For the upscaling of the functionalization reaction of lignin with itaconic anhydride with DBU as catalyst (IAn-BB-DBU), the 50 g fractionation batch (**OL Acetone (2)**) was utilized. **OL Acetone (3)** was used in the final part of the project to synthesize two upscaled batches of succinylated and itaconated lignin with TMG.

OL Acetone (2): T_g = 125 °C; $T_{d,5\%}$ = 252 °C.

OL Acetone (3): T_g = 127 °C; $T_{d,5\%}$ = 252 °C

General procedure for the functionalization of lignin with itaconic anhydride (0.5 g batch scale)

0.5 g of **OL Acetone (1)** were dissolved in 5 mL of dry acetone. Afterwards, the desired amount of itaconic anhydride (IAn) was added to the reaction mixture, as well as the catalyst. The reaction vessel was flushed with argon and heated to the desired temperature.

At the end of the reaction time, the vessel was allowed to cool down, and the reaction mixture was precipitated in a tenfold amount of acidic water (pH<2). Afterwards, solids were recovered *via* filtration on a P4 fritted filter, washed with cleaned deionized water, and dried under vacuum (10 mbar, 70 °C) for at least 24 hours prior to analysis. If needed, the process of redissolution in acetone and reprecipitation in acidic water (pH<2) was repeated to remove impurities. For specific parameters tested, please refer to main text in the manuscript.

General procedure for the functionalization of lignin with itaconic anhydride (15 g batch – DBU)

15 g of OL Acetone (2) were dissolved in dry acetone (150 mL) in a 500 mL round bottom flask. Afterwards, IAn (4.2 equiv. related to the total of OH groups) and the catalyst DBU (6 mol% related to the total of OH groups) were added. The flask was equipped with an air condenser. The system was flushed with argon for a few minutes. After reaching the desired temperature, the reaction was stirred for 24 h at 45°C.

At the end of the reaction time, the vessel was allowed to cool down, and the reaction mixture was precipitated in a tenfold amount of acidic water (pH<2) and stirred for one hour. Afterwards, solids were recovered *via* filtration on a P4 fritted filter, washed with cleaned deionized water until filtrates were neutral, and dried under vacuum (10 mbar, 70 °C) for 72 hours prior to analysis. The procedure of dissolution in minimal amount of acetone and precipitation in acidic water was repeated three times to eliminate impurities.

Yield: 93 %; DSC: T_g = 140 °C; TGA: $T_{d,5\%}$ = 212 °C

Table S3 – Characterization data of the synthesized upscale batch of Lignin Itaconate.

Entry	Total [mmol/g][a]	Aliphatic [mmol/g][a]	Aromatic [mmol/g][a]	–COOH [mmol/g][a]	M_n [Da]	M_w [Da]	$Đ$
Lignin Itaconate (DBU)	3.55 ± 0.02	0.90 ± 0.004	1.26 ± 0.02	1.39 ± 0.02	5200	37600	7.2

[a]: Determined via ^{31}P–NMR. Measurements performed in triplicate.

General procedure for the functionalization of lignin with itaconic anhydride (15 g batch – TMG)

15 g of OL Acetone (3) were dissolved in dry acetone (150 mL) in a 500 mL round bottom flask. Afterwards, itaconic anhydride (4.2 equiv. related to the total of OH groups) and the catalyst TMG (6 mol% related to the total of OH groups) were added the flask, equipped with an air condenser. The system was flushed with argon for a few minutes. After reaching the desired temperature, the reaction was stirred for 24 h at 45°C.

At the end of the reaction time, the vessel was allowed to cool down, and the reaction mixture was precipitated in a tenfold amount of acidic water (pH<2) and stirred for one hour. Afterwards, solids were recovered *via* filtration on a P4 frit, washed with cleaned deionized water until filtrates were neutral, and dried under vacuum (10 mbar, 70 °C) for 72 hours prior to analysis. The procedure of dissolution in minimal amount of acetone and precipitation in acidic water was repeated three times to eliminate impurities.

Yield: 92 %; DSC: T_g = 149 °C; TGA: $T_{d,5\%}$ = 209 °C

Table S4 – Characterization of the synthesized upscale batch of lignin itaconate.

Entry	Total [mmol/g][a]	Aliphatic [mmol/g][a]	Aromatic [mmol/g][a]	−COOH [mmol/g][a]	M_n [Da]	M_w [Da]	*Đ*
Lignin Itaconate (TMG)	3.50 ± 0.06	0.68 ± 0.02	1.20 ± 0.02	1.62 ± 0.02	5100	57000	11.2

[a]: Determined via ^{31}P−NMR. Measurements performed in triplicate.

General procedure for the functionalization of lignin with succinic anhydride (0.5 g batch)

0.5 g of OL Acetone (2) were dissolved in 5 mL of dry acetone. Afterwards, the desired amount of succinic anhydride (4.2 equiv.) was added to the reaction mixture, as well as the catalyst TMG (6 mol%). The reaction vessel was flushed with argon and heated to the desired temperature (45 °C, 24 h).

At the end of the reaction time, the vessel was allowed to cool down, and the reaction mixture was precipitated in a tenfold amount of acidic water (pH<2). Afterwards, solids were recovered *via* filtration on a P4 fritted filter, washed with cleaned deionized water, and dried under vacuum (10 mbar, 70 °C) for at least 24 hours prior to analysis. If needed, the process of redissolution in acetone and reprecipitation in acidic water (pH<2) was repeated to remove impurities.

General procedure for the functionalization of lignin with succinic anhydride (15 g batch – TMG)

15 g of OL Acetone (3) were dissolved in dry acetone (150 mL) in a 500 mL round bottom flask. Afterwards, succinic anhydride (4.2 equiv. related to the total of OH groups) and the catalyst TMG (6 mol% related to the total of OH groups) were added the flask, equipped with an air condenser. The system was flushed with argon for a few minutes. After reaching the desired temperature, the reaction was stirred for 24 h at 45°C.

At the end of the reaction time, the vessel was allowed to cool down, and the reaction mixture was precipitated in a tenfold amount of acidic water (pH<2) and stirred for one hour. Afterwards, solids were recovered *via* filtration on a P4 fritted filter, washed with cleaned deionized water until filtrates were neutral, and dried under vacuum (10 mbar, 70 °C) for 72 hours prior to analysis. The procedure of dissolution in minimal amount of acetone and precipitation in acidic water was repeated twice times to eliminate impurities.

Yield: 71 %; DSC: T_g = 104 °C; TGA: $T_{d,5\%}$ = 229 °C

Table S5 – Characterization data of the synthesized upscale batch of lignin succinate.

Entry	**Total [mmol/g]**[a]	**Aliphatic [mmol/g]**[a]	**Aromatic [mmol/g]**[a]	**−COOH [mmol/g]**[a]	**M_n [Da]**	**M_w [Da]**	**$Đ$**
Lignin Succinate (TMG)	3.72 ± 0.05	0.46 ± 0.01	1.47 ± 0.04	1.79 ± 0.02	3700	10100	2.7

[a]: Determined via ^{31}P−NMR. Measurements performed in triplicate.

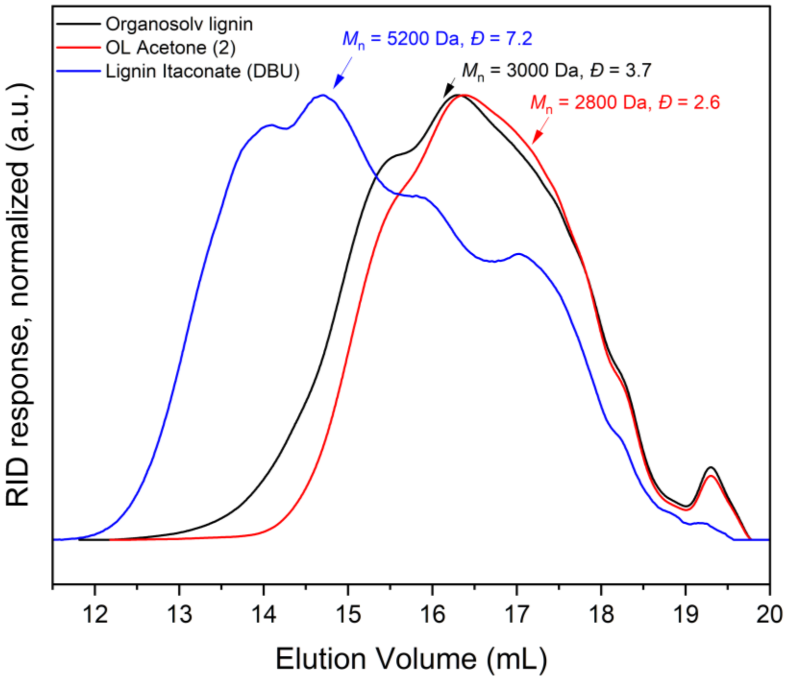

Figure S2 — GPC traces of pristine organosolv lignin (black), fractionated in acetone (OL Acetone 2, red), and modified lignin itaconate (15 g scale, DBU as catalyst, blue trace) in DMAc−LiBr.

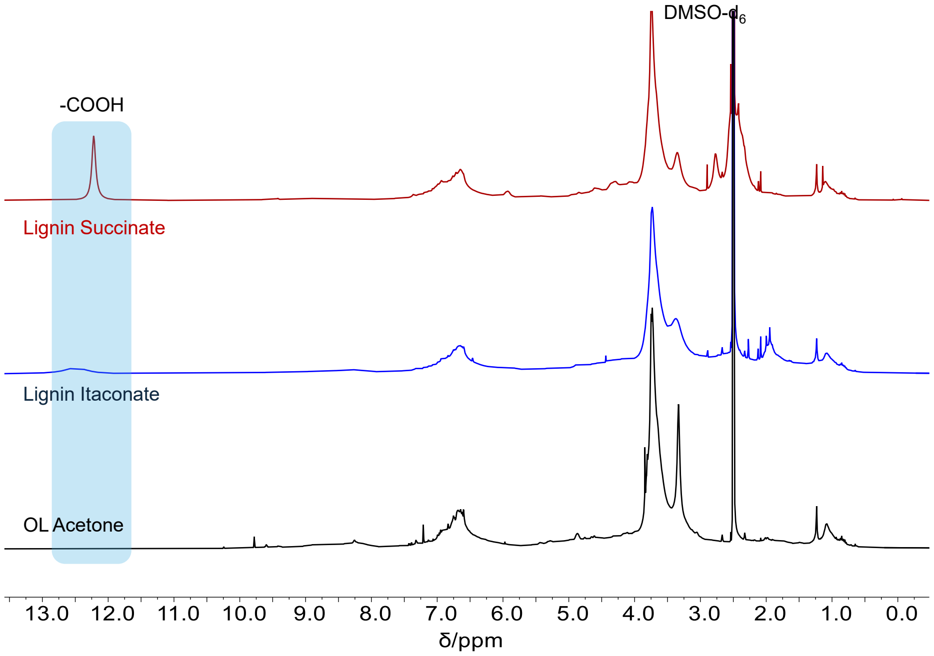

Figure S3 – Exemplary ^{1}H–NMR spectra in DMSO-d_6 of lignin fractionated in acetone (OL acetone, black), lignin itaconate (blue) and lignin succinate (red). Highlighted in blue the region where the signal ascribed to the carboxylic acid is visible.

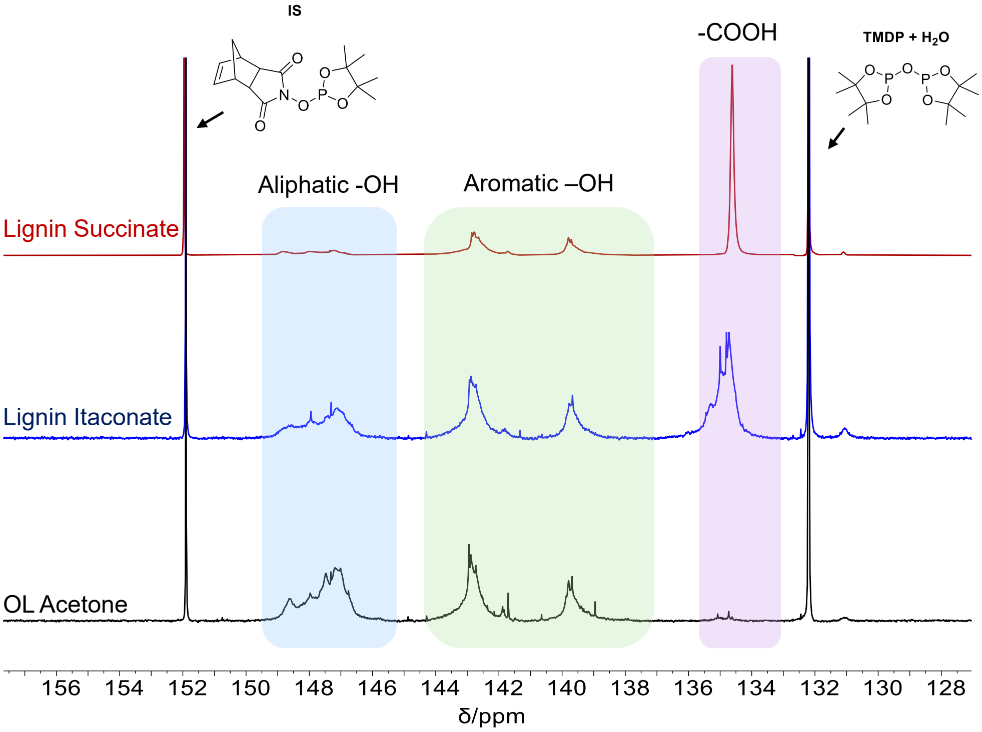

Figure S4 – Exemplary ^{31}P–NMR spectra of lignin fractionated in acetone (OL Acetone, black), lignin itaconate (blue) and lignin succinate (red). Highlighted in blue the region of aliphatic hydroxyl groups, in green the region where aromatic hydroxyl groups are visible and in pink the region associated with the signal of carboxylic acids. The chemical structures of the phosphitylated internal standard (NHND) and the reaction product of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) and water are shown as well.

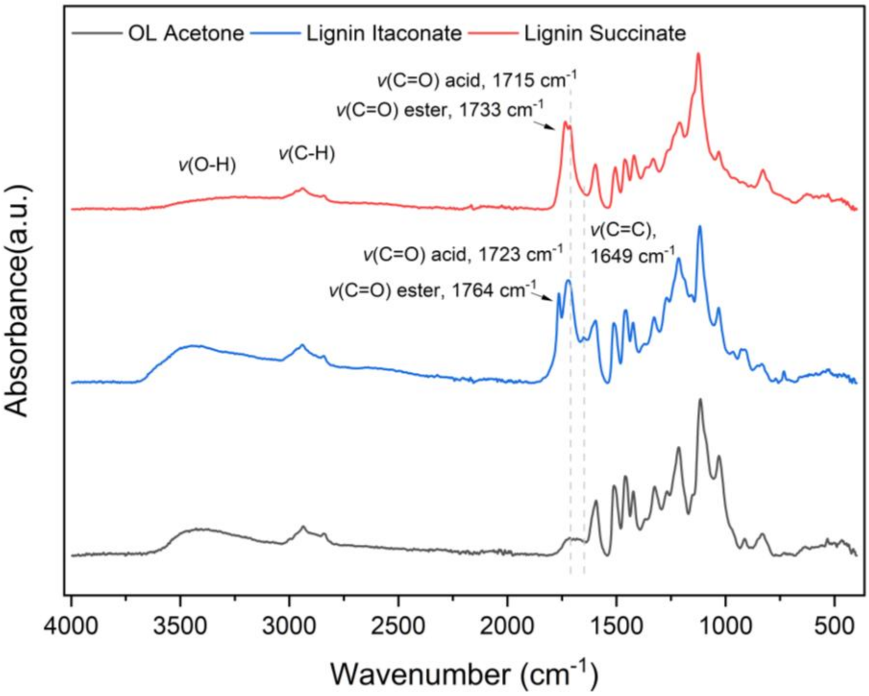

Figure S5 – Overlay of IR spectra for both the starting material (OL acetone, black) and the lignin derivative modified with itaconic anhydride, lignin itaconate (blue), as well as the derivative modified with succinic anhydride, lignin succinate (red). Typical signal associated with the functionalization are shown.

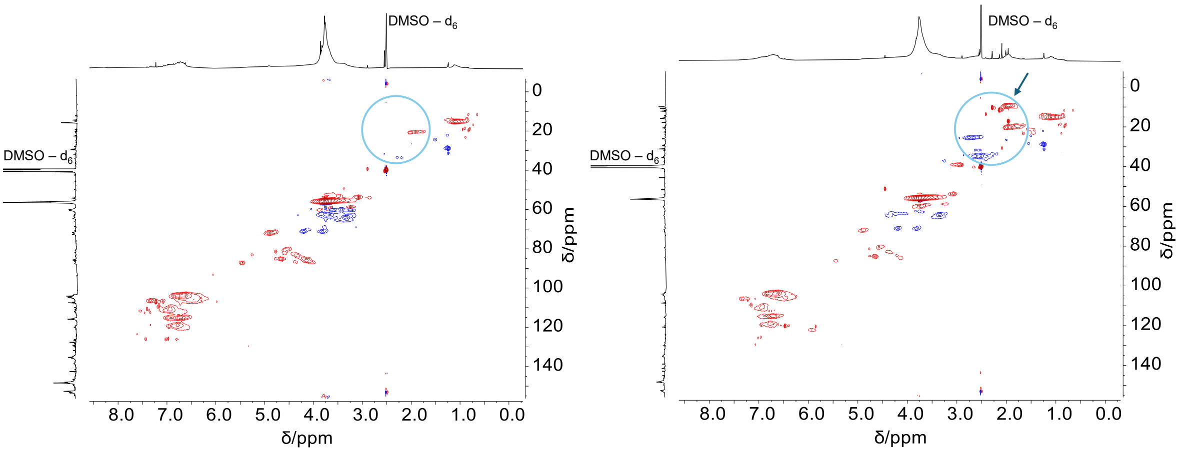

Figure S6 – Complete HSQC traces for OL acetone (left) and lignin itaconate (right) in DMSO-d_6. In the circled area, new signals appear after the modification. In particular, a new methyl signal (indicated with the arrow) could be associated with the methyl group of the citraconate moieties.

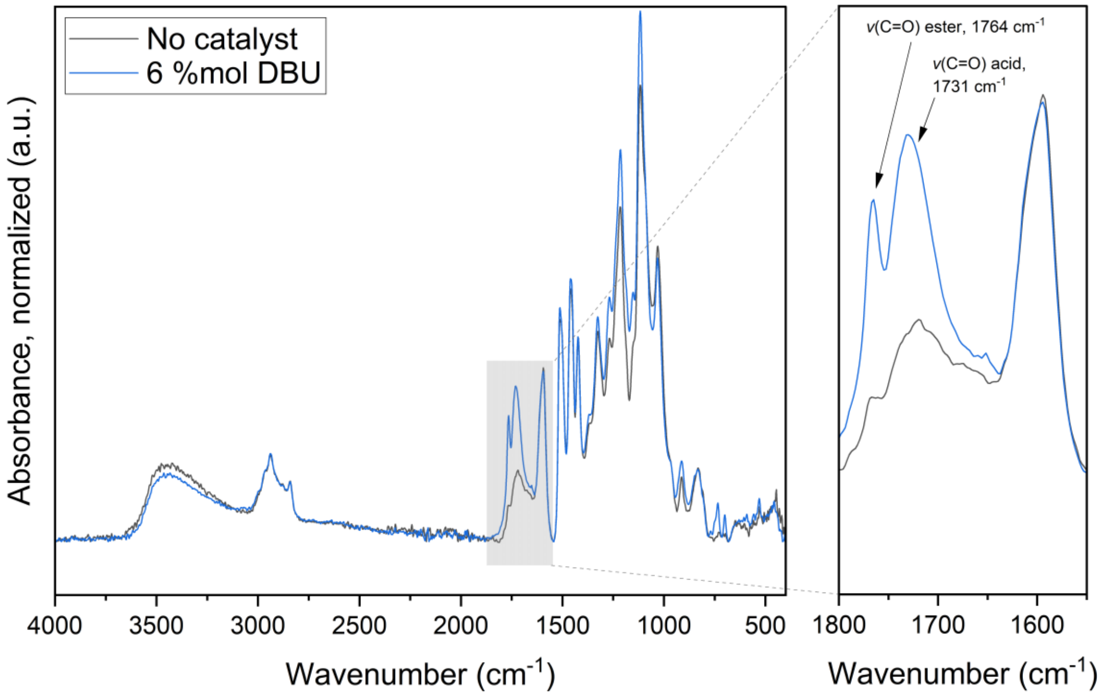

Figure S7 – IR overlay showing the beneficial catalyst effect on the conversion of the reaction, comparing a reaction without any catalyst (black) and a reaction with 6 mol% DBU (blue), under otherwise same reaction conditions. On the right, a zoom in the region 1800 – 1550 cm^{-1} shows the characteristic signals ascribed to the functionalization. All IR spectra are normalized to the signal at 1504 cm^{-1} for the lignin C_{ar}=C_{ar} stretching vibrations.

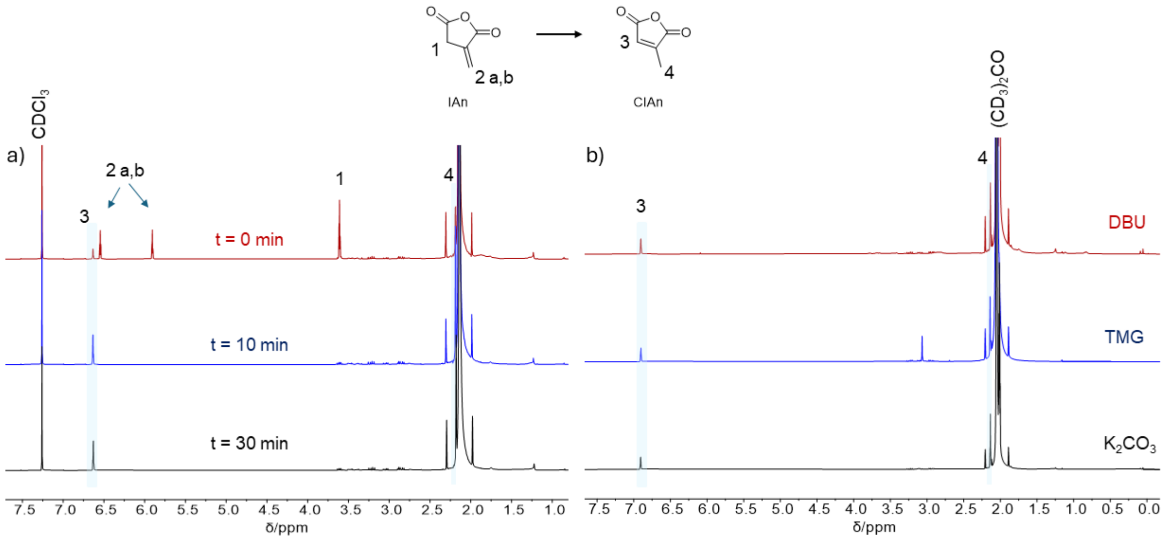

Figure S8 – a) ^{1}H−NMR ($CDCl_3$) of the screening for isomerization of itaconic anhydride (conditions: 0.4 g of IAn, 5 mL dry acetone, 22.2 µL DBU, 45 °C); b) ^{1}H−NMR (acetone-d_6) of the screening for isomerization of itaconic anhydride after 30 minutes with different bases.

Recyclability of the solvent and E-factor calculations

After lignin functionalization in a 15 g scale with itaconic anhydride, the same workup procedure as described above was applied. After precipitation and filtration of the desired product, the acetone was then recovered from the remaining mixture *via* vacuum distillation. However, efficient separation proved challenging, due to the low acetone concentration in the mixture (~0.1 mL acetone per mL precipitation medium) and the elevated volume of the mixture to distill. Nevertheless, a total of 75 % of the initial acetone was recovered and dried over 3 Å molecular sieves for 72 hours. Spectroscopic analysis reveal that the recovered solvent is clean, however water impurities remain present (19 %, as calculated form ^{1}H–NMR).

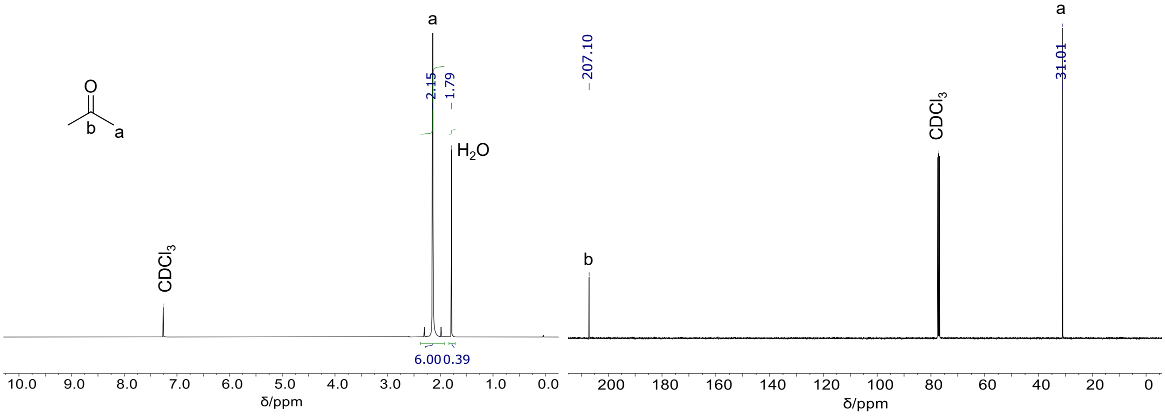

Figure S9 – ^{1}H–NMR and ^{13}C–NMR of the recovered solvent in $CDCl_3$.

General Information concerning E-factor calculations

The E-factor values reported in this work are intended as a simplified metric to illustrate the solvent contribution and its impact on the synthetic procedures. These calculations do not account for the lignin pretreatment (fractionation) or for the aqueous medium used during the work-up. This choice was made to remain consistent with Sheldon's original work on the E-factor, in which water is excluded to avoid misleading or non-comparable results.[3] Furthermore, we aimed to ensure comparability with our previous work, where synthetic E-factors for lignin modifications were also calculated without including the water used in precipitation or purification steps.[4] Despite this simplification, we consider the presented E-factor values to be a useful comparative parameter for assessing solvent influence and comparing with literature data. For the E-factor calculations the following general formula was used:

$$E - factor = \frac{Mass\ of\ raw\ material - Mass\ of\ desired\ product}{Mass\ of\ derided\ product} \qquad \text{Eq. S13}$$

For the E-factor calculations and definition of the solvent contribution, two cases are defined:

No recycling of solvent

Weight of raw materials: Organosolv Lignin (acetone fractionated): 15.00 g; DBU: 0.63 g; IAn: 30.65 g; Acetone: 116.87 g; Total: 163.15 g

Weight of desired product: 20.7 g

$$E - factor = \frac{163.15 - 20.7}{20.7} = 6.9$$

With recycling of solvent

Weight of raw materials: Organosolv lignin (acetone fractionated): 15.00 g; DBU: 0.63 g; IAn: 30.65 g; Acetone: 116.87 g; Total: 163.15 g

Weight of desired product: 20.7 g

Weight of recovered solvent: 87.23 g

$$E - factor = \frac{163.15 - 20.7 - 87.23}{20.7} = 2.7$$

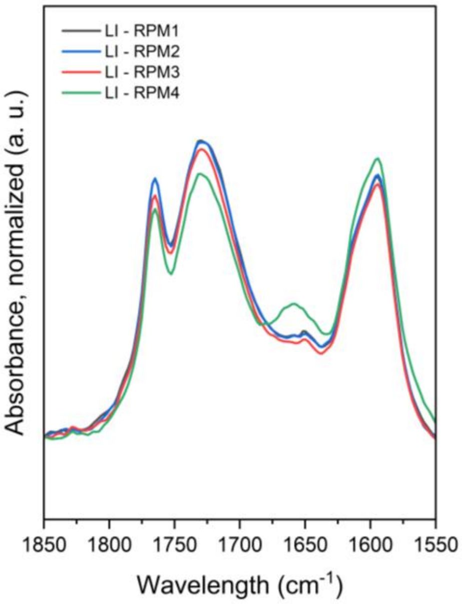

Figure S10 – Zoom in the region 1850 – 1550 cm^{-1} of the IR spectrum of lignin itaconates obtained reutilizing several times the same precipitation medium. The nomenclature corresponds to LI and the number of Reutilizations of Precipitation Medium (RPM#).

Epoxy Resin Formulation

For the preparation and curing of the epoxy resins, 125 mg of lignin derivative (itaconate or succinate, previously dried under vacuum at 10 mbar for 24 h) were weighed into a 10 mL scintillation vial together with predetermined amounts of Pripol™ and ESBO. The total stoichiometric ratio of COOH to epoxy groups was maintained at 1:1.2. A minimal amount of anhydrous DMSO (as much as needed to solubilize the mixture, typically 1.5 mL for lignin contents ≥ 15 mol% to 2 mL for lignin contents ≤ 10 mol%) was added to ensure homogeneity, and the mixture was vortexed at room temperature for 5 min. The samples were then sonicated for 30 min, after which 0.5 wt% of DBU catalyst (relative to the total weight of the components, excluding the solvent) was added. The mixture was vortexed again for 5 min and subsequently transferred with a pipette into circular Teflon molds.

Curing was carried out in two stages: initially, the samples were equilibrated overnight at 80 °C under a Petri dish cover, followed by a gradual temperature increase (20 °C/h) to 140 °C. Afterwards, the Petri dish was removed and the curing was then continued at 140 °C for 2 days, and subsequently under vacuum (10 mbar) at 140 °C for an additional day.

Table S6 – Overview of the molar composition for the synthesized epoxy thermosets, with varying lignin contents.

Lignin content (mol%)[a]	**Carboxylic Acid component (equiv.)**			**Epoxy component**
	Pripol™ 1009	**Lignin Itaconate or Succinate**	**Total –COOH (equiv.)**	**ESBO (equiv.)**
0	**1**	**0**	**1**	**1.2**
5	**0.95**	**0.05**	**1**	**1.2**
10	**0.9**	**0.1**	**1**	**1.2**
15	**0.85**	**0.15**	**1**	**1.2**
25	**0.75**	**0.25**	**1**	**1.2**
35	**0.65**	**0.35**	**1**	**1.2**

[a]: molar content of Lignin LI or LS (in percent) with respect to the total moles of carboxylic acid component.

Figure S11 – Left: thermoset with 15 mol% of lignin, cured with acetone as solvent. Phase separation is clearly visible in the final material. Right: thermoset with 15 mol% of lignin cured in DMSO. No sign of phase separation is observed.

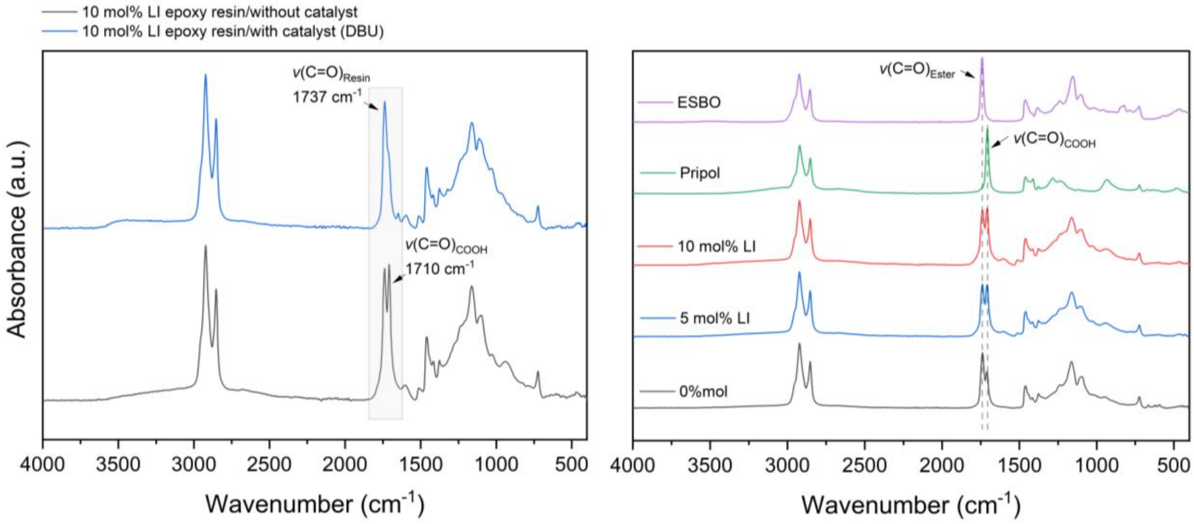

Figure S12 – Left: IR overlay of the resins with 10 mol% LI without catalyst (black) and with – DBU (blue), under the same curing conditions. Right: Overlay of the starting materials (ESBO and Pripol) and three formulations of the resins with different mol percentages of LI without DBU as catalyst. All the presented data are related to LI as lignin component.

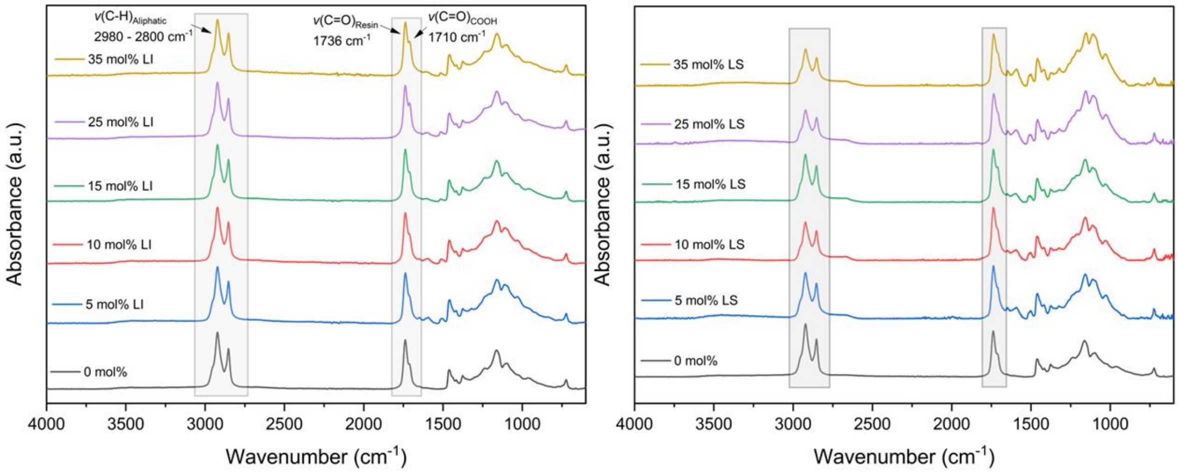

Figure S13 – Left: overlay of IR spectra with different lignin contents (ranging from 0 to 35 mol%) for the epoxy resins obtained with LI as lignin component. Right: overlay of IR spectra with different lignin contents (ranging from 0 to 35 mol%) for the epoxy resins obtained with LS as lignin component.

Peak Deconvolution Methods

Peak deconvolution of single spectra

For the calculation of the percentage ratio between free carboxylic acid and ester groups in the resins, the overlapping signals were deconvoluted to ensure reliable quantification. These deconvolutional calculations were performed using the software OriginPro 2023, applying a Gauss-amplitude function. For the fitting procedure, the peak centers (xc) were fixed at 1711 cm^{-1} (Fit 1) and 1738 cm^{-1} (Fit 2), corresponding to the free −COOH and ester carbonyl groups, respectively. The peak widths (w), defined as w = FWHM/√ln4, were not fixed during the fitting process. The final ranges obtained for w from the fitting output were 11.48–13.13 for w_1 and 10.57–12.00 for w_2.

Peak deconvolution over time

To quantify the evolution of the signal at 1715 cm^{-1} over time, a peak-fitting procedure was applied to resolve the overlapping bands corresponding to the ester groups (1738 cm^{-1}) and the free −COOH groups (1715 cm^{-1}). A Gaussian amplitude function was employed for the deconvolution. For the fitting of the two peaks, the following constraints were applied: $1700 < x\mathrm{c}_1 < 1720$ and $1730 < x\mathrm{c}_2 < 1745$, where xc represents the peak center; and $8 < (w_1, w_2) < 15$, where w denotes the peak width (w = FWHM/√ln4). These parameters were previously determined through single-spectrum deconvolution. The area of the absorbance peak attributed to free −COOH groups was normalized to its initial value and plotted as a function of time. The deconvolution was performed starting from time values greater than 400 s, as initially the presence of solvent hindered the visibility of the resin peaks.

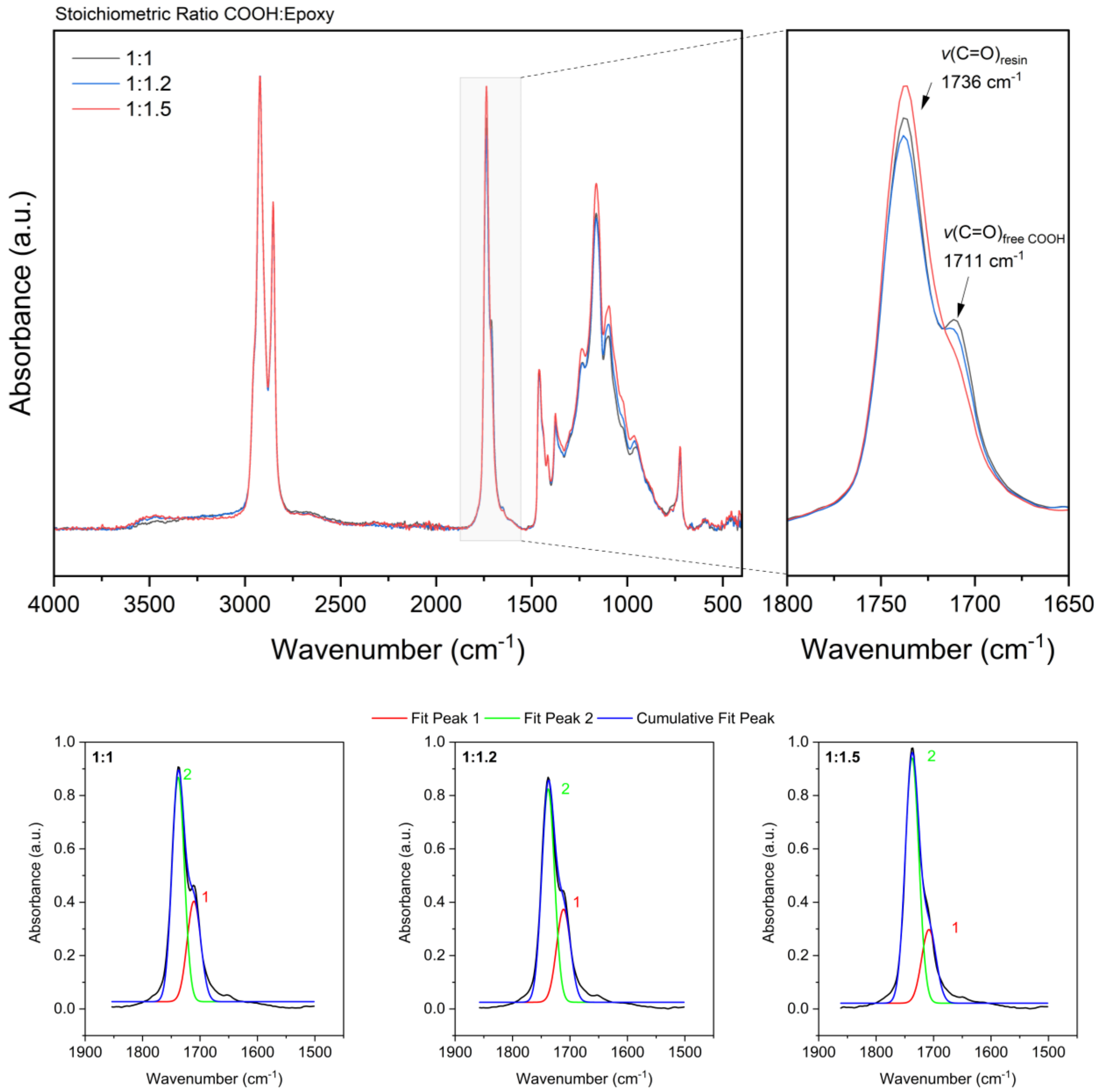

Figure S14 – Above: Overlay of IR spectra for three different stoichiometric ratios (1:1, 1:1.2, 1:1.5 COOH:Epoxy), normalized at the C-H stretching signal (v(C-H), 2920 cm^{-1}). Below, the fitting of the deconvoluted peaks ascribed to the free carboxylic acid carbonyl stretching vibration (1) and ester carbonyl stretching vibration (2).

Table S7 – Results of the peak deconvolution method giving the area of the two peaks (1 = free carboxylic acids and 2 = ester groups), as well as their percentage ratios and R-square.

Ratio COOH:Epoxy	Area (a.u.)		Free carboxylic acid (%)	Ester (%)	R-square
	Peak 1	***Peak 2***			
1:1	11.19	22.58	33%	67%	0.9888
1:1.2	10.59	22.20	32%	68%	0.9879
1:1.5	8.78	27.35	24%	76%	0.9938

Real-Time (RT) FTIR Measurements

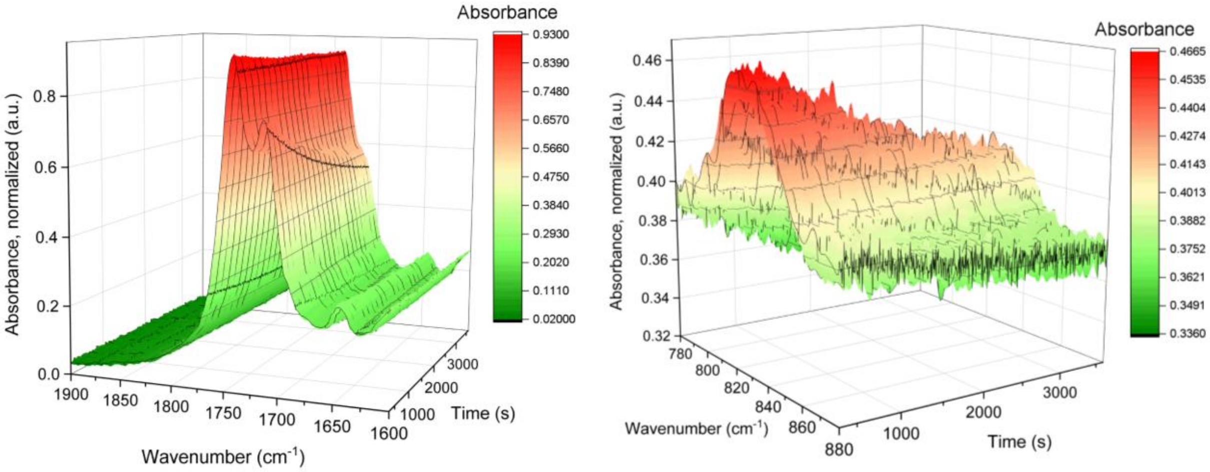

Figure S15 – Real-time curing followed *via* RT- FTIR of a 5 mol% LS epoxy resin in the presence of catalyst.

Thermal Properties

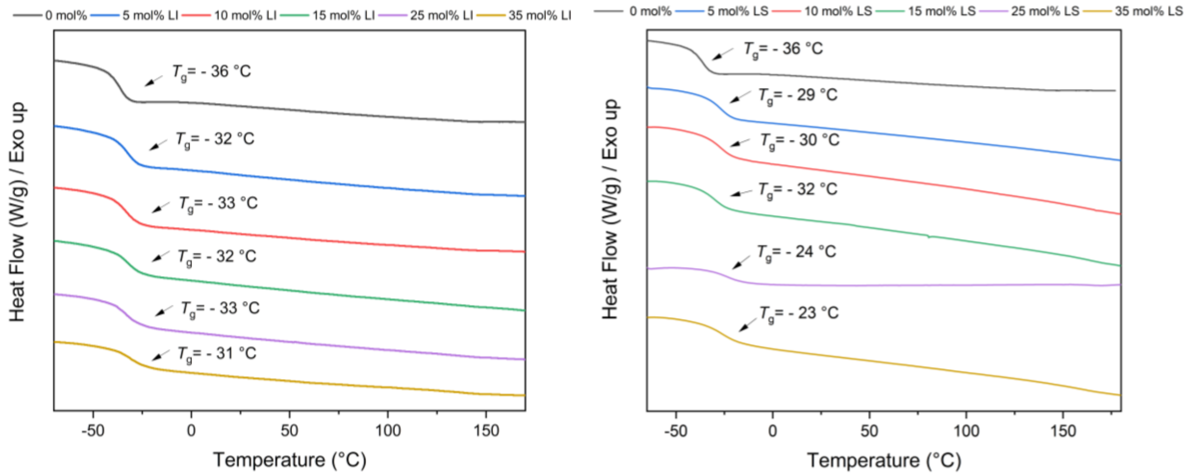

Figure S16 – DSC Traces of the resin formulation with LI and LS, with different lignin contents

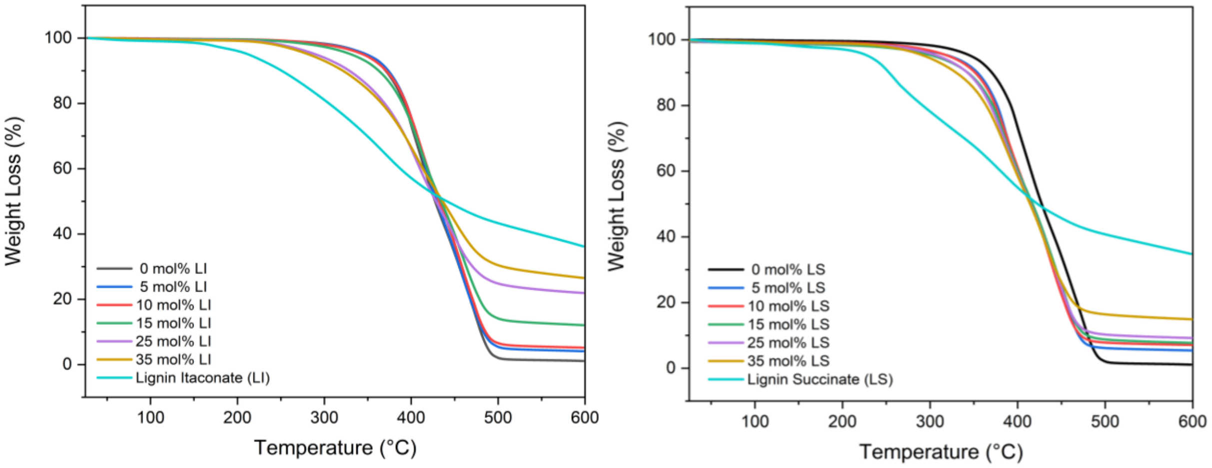

Figure S17 – TGA curves of LI and LS epoxy resins with different lignin contents and LI and LS for comarison.

Rheology and DMA Analyses

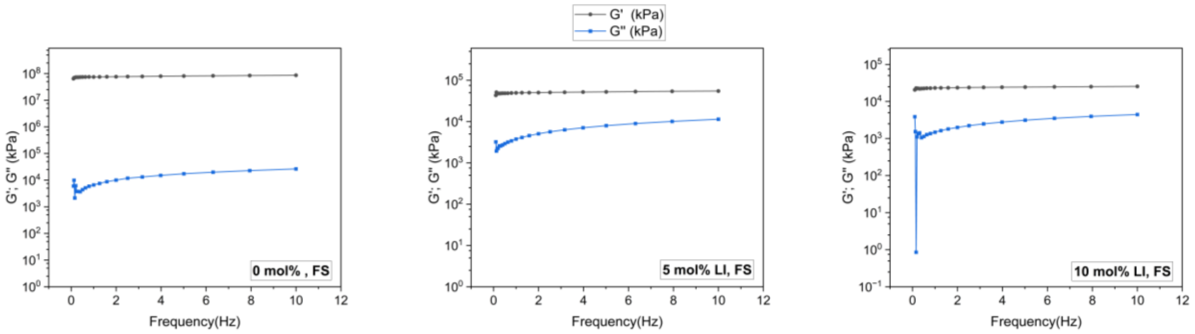

Figure S18 – Frequency sweep experiments for LI epoxy resins with lignin contents of 0, 5, and 10 mol%.

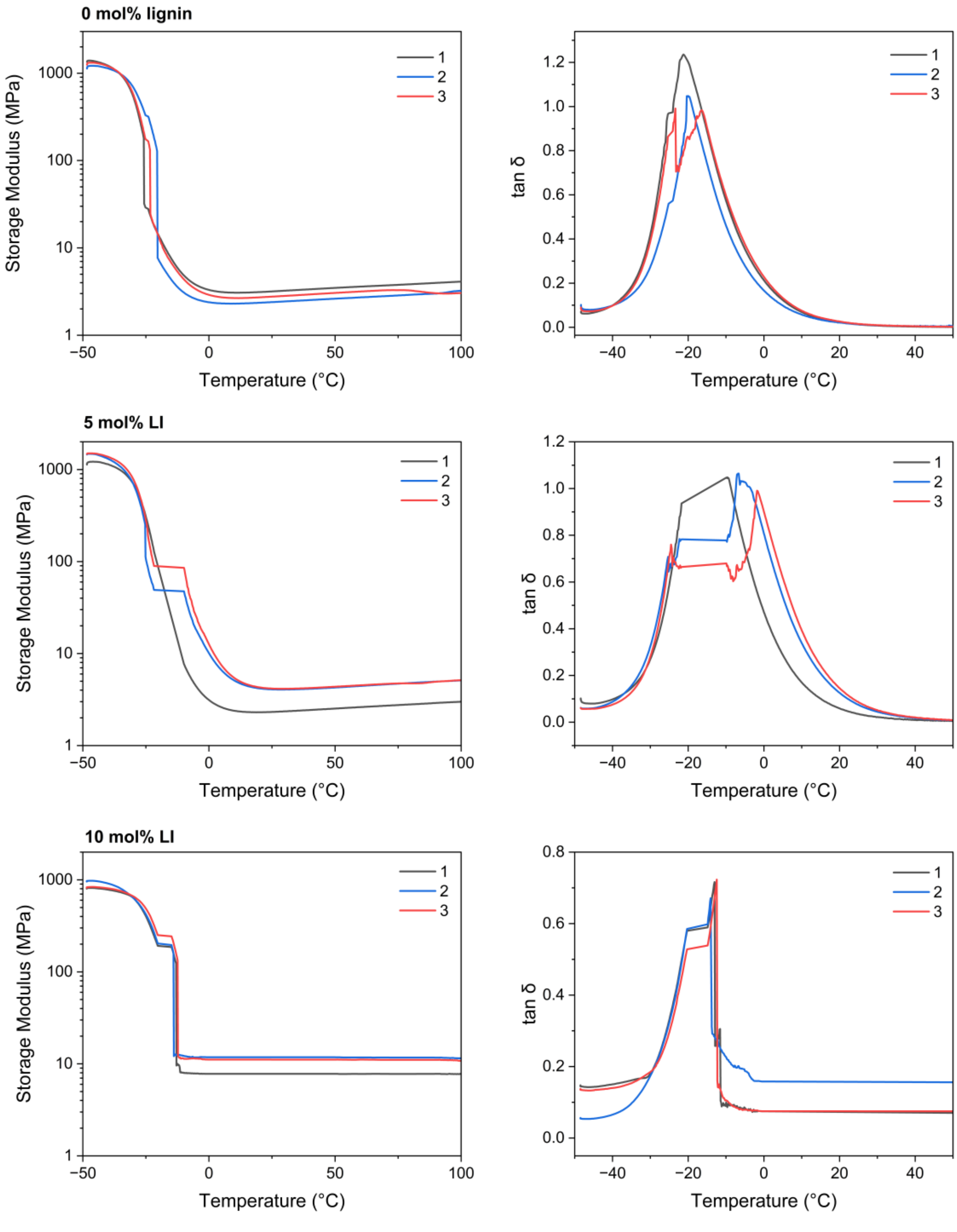

Figure S19 – Triplicate measurements of the DMA analyses for the sample with 0 mol% lignin and LI epoxy resins. For the sample with 10 mol% LI, only the onset could be determined.

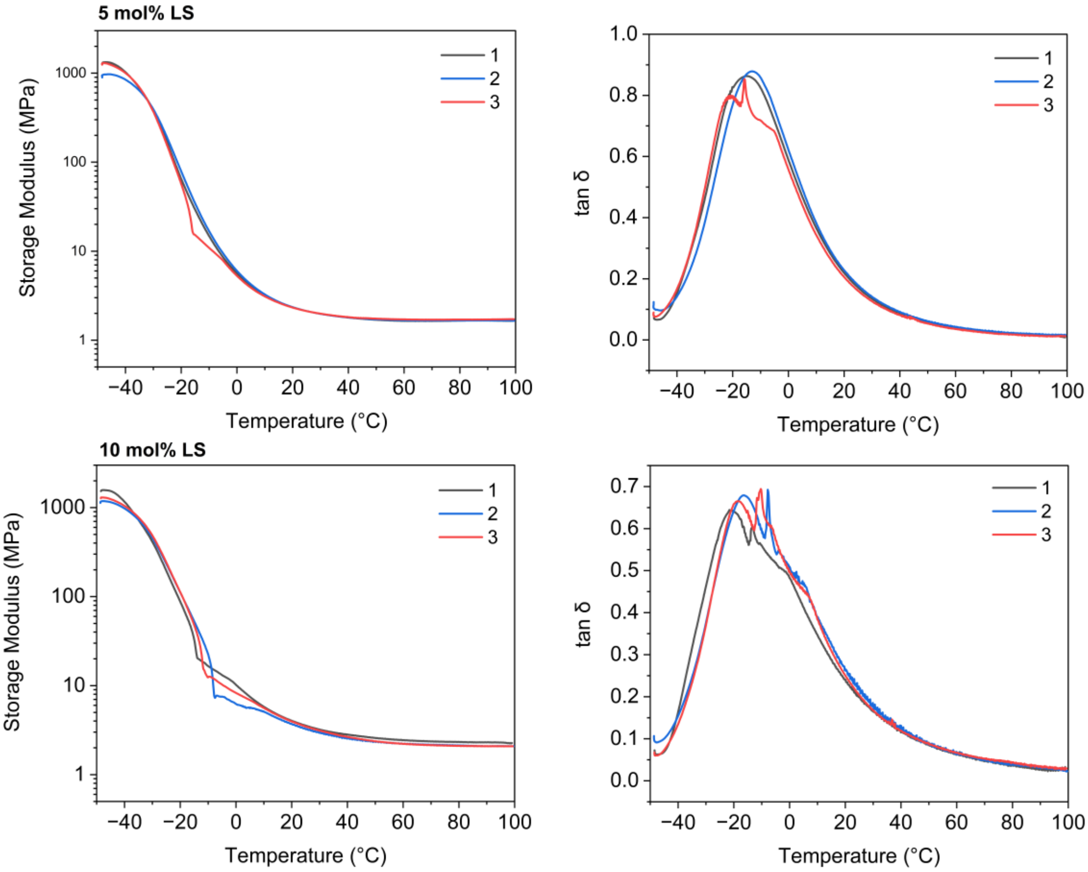

Figure S20 – Triplicate measurements of the DMA analyses for the LS epoxy resins. It can be seen how in some cases the rapid drop in the storage modulus very close to the resolution of the transducer of the instrument, leading to experimental difficulties.

Tensile Strength Measurements

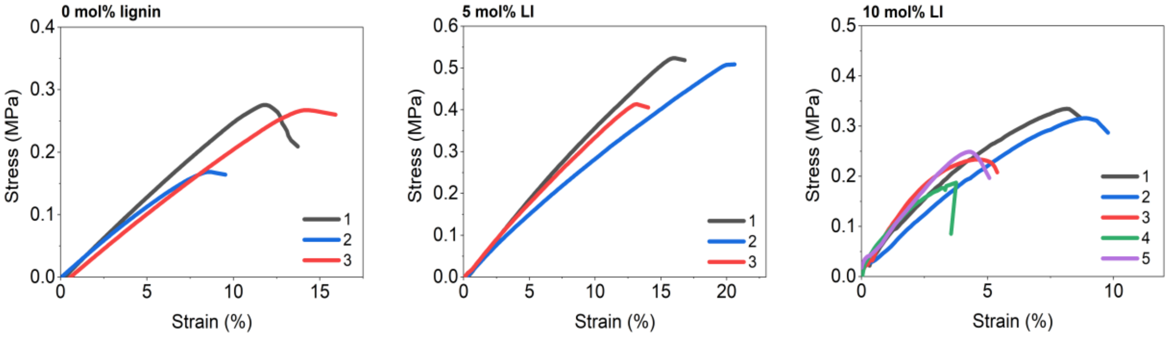

Figure S21 – Overview of the tensile strength measurements for the sample with 0 mol% lignin and LI epoxy resins. In the case of sample containing 10 mol% LI, the measurements were repeated five times because of its lower reproducibility.

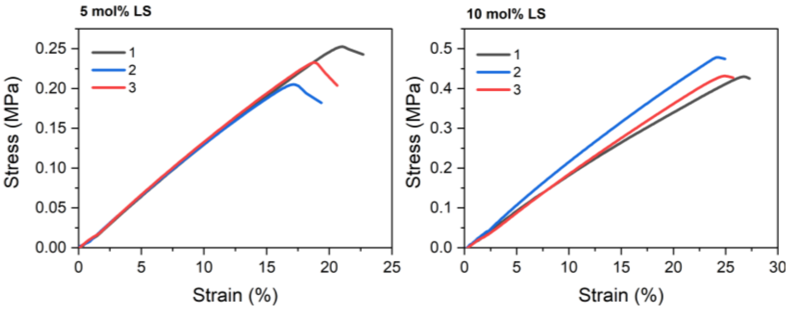

Figure S22 – Overview of the triplicates of the tensile strength measurements for LS epoxy resins.

Epoxy Resins Degradability Tests

For the degradation tests, ca. 500 mg of thermoset were cut into pieces and their exact weight was recorded. Afterwards, they were transferred into a crimp vial and suspended in either a solution of 0.6 M sodium hydroxide (NaOH), 1 M hydrochloric acid (HCl), or 1 M citric acid (CA). The solutions were heated to 80 °C for 4 days. For the alkaline hydrolysis, the resulting solution was acidified with HCl to a pH of 2 and the precipitate was collected *via* filtration and washed with distilled water. For further purification, the filtrates were again dissolved in acetone, reprecipitated in acidic aqueous medium (pH =2) and recollected *via* filtration. For the acidic hydrolysis, some thermoset pieces did not degrade after 4 days of stirring at 80 °C. Therefore, the collected solids after acidic hydrolysis were suspended in acetone, leading to an undissolved fraction (likely the undegraded thermosets, separated *via* hot filtration) and a dissolved fraction, that was collected *via* precipitation in acidic aqueous medium (pH =2) and subsequent filtration.

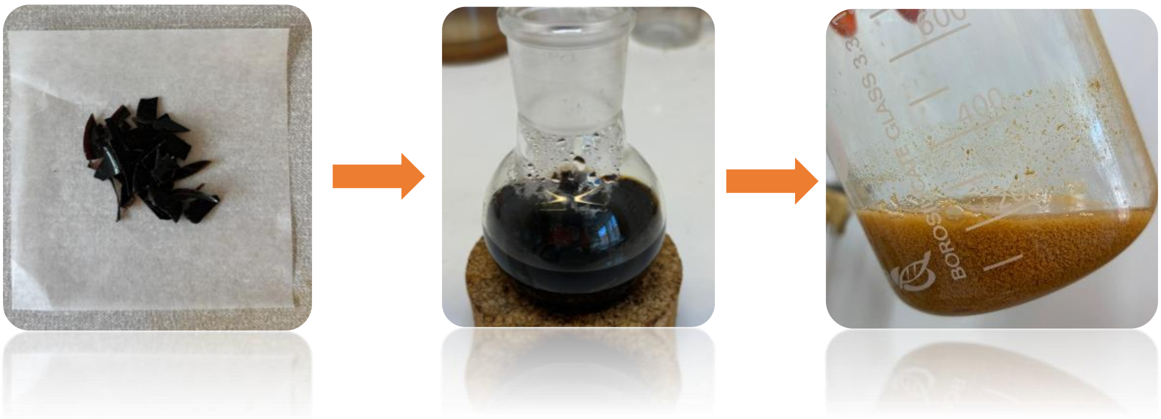

Figure S23 – Left: thermoset containing 10 mol% LI, cut into pieces. Middle: homogeneous brown solution obtained after alkaline hydrolysis. Right: solution after acidification to pH 2, with visible precipitate formation.

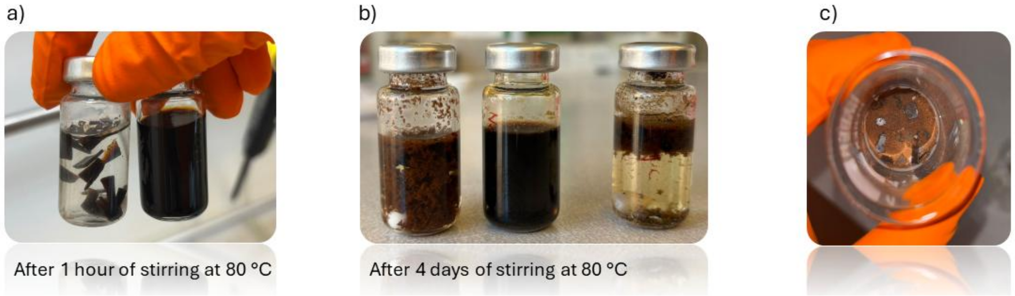

Figure S24 – a) comparison between acidic hydrolysis in HCl (left) and alkaline (right) after 1 hour of stirring at 80 °C. The thermoset under alkaline conditions completely dissolved forming a homogeneous solution. b) left: hydrolysis with HCl solution, middle: hydrolysis with NaOH solution, right: hydrolysis with citric acid solution. the picture was taken 4 days after stirring at 80 °C. c) Recovered solids after hydrolysis with citric acid. The bigger pieces are undegraded thermoset.

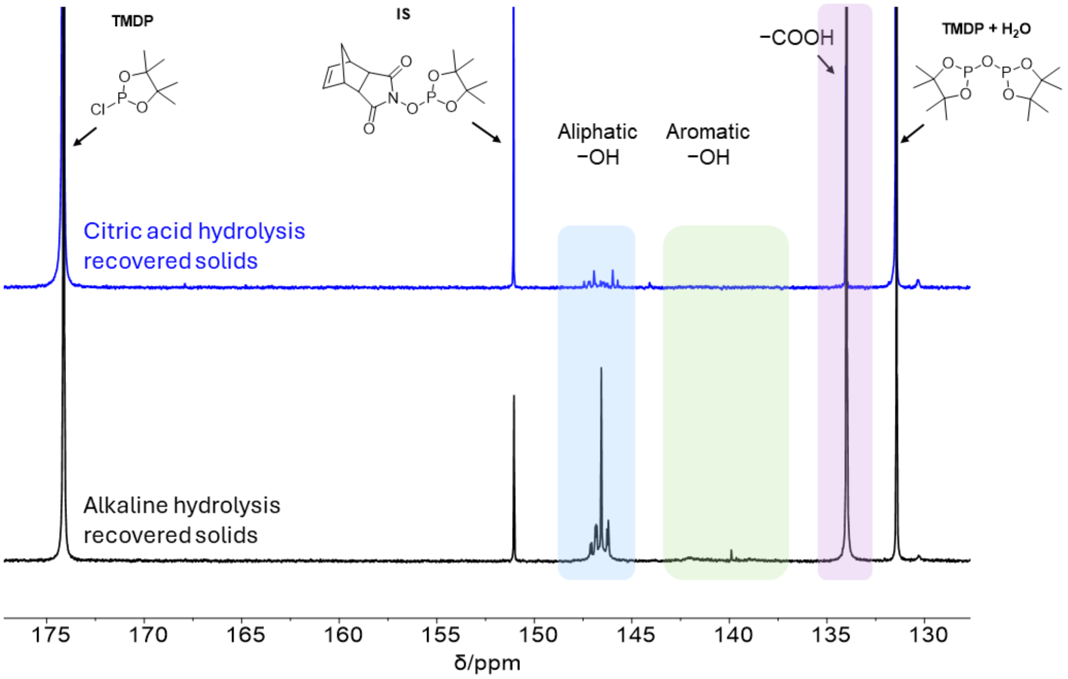

Figure S25 – ^{31}P – NMR of the recovered solids after alkaline hydrolysis (black) and after acid hydrolysis with citric acid (blue). In both cases, aromatic hydroxyl groups are not present (or in very low quantity), while there are strong signals in the aliphatic and carboxylic acid regions, as would be expected after hydrolysis of the aliphatic thermoset matrix.

Table S8 – Overview of the collected weights of the fractions after hydrolysis both under alkaline and acidic conditions. In the parentheses are indicated the percentages in respect of their starting weight.

Hydrolysis Solution	Starting Weight (mg)	Total recovered weight (not purified)	Dissolved Fraction	Undissolved Fraction
NaOH	503	454 (90%)	263 (52%)	n.a.
HCl	503	483 (96%)	28 (6%)	388 (77%)
CA	503	496 (98%)	44 (9%)	399 (79%)

n.a. : non applicable because the entirety of the sample was soluble in acetone.

As shown in **Table S8**, the total unpurified recovered weight correlates very well with the starting weight. For the alkaline conditions, in order to recover the solids and neutralize the mixture, a precipitation step in acidic water was necessary, and this would explain the slightly lower value of the recovered weight (90 %) compared to the other conditions, where this step was not necessary. Afterwards, all the recovered solids were subjected to a first round of dissolution in acetone and reprecipitation in acidic water, as this could help with purification. As can be seen, after this purification step for the alkaline conditions the entire sample dissolved in acetone, with no undissolved fraction visually detected. However, only 52% of the initial sample weight was recovered after reprecipitation (58% compared to the previous step), indicating that some small molecules generated during degradation were soluble in both acetone and water and were therefore lost during filtration. In contrast, under acidic hydrolysis conditions, a large fraction remained insoluble in acetone (77% and 79% for HCl and citric acid, respectively), indicating that degradation was only partial. The dissolved solids recovered via subsequent precipitation were also minimal, and in the case of the HCl-treated sample, the amount was insufficient for further characterization.