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Supporting Information to accompany

Facile New Approach to High Sulfur-Content Materials and Preparation of Sulfur-Lignin Copolymers

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Experimental Section

Chemicals and Materials

Alkali lignin was purchased from Sigma-Aldrich. Sulfur powder (99.5%) was purchased from Alfa Aesar. Carbon disulfide, sodium chlorate and hydrochloric acid, sodium hydroxide (99.5%), were purchased from Bean Town Chemical, VWR Analytical, respectively. **Tris**(hydroxymethyl)aminomethane hydrochloride and 5, 5'-Dithio-*bis*-(2-nitrobenzoic acid were purchased from VWR Analytical. These chemicals were used without further purification unless otherwise noted.

General Considerations

Phosphorus-31 NMR spectra wer recorded on a Bruker Avance spectrometer operating at 300 MHz in a 10 s pulse delay and 90° pulse angle. Chromium (III) acetylacetonate was added as a spin relaxation agent following the established procedure.[1] Thermogravimetric analysis (TGA) data were recorded on a Mettler Toledo 2STARe instrument over the range 20 to 800 °C, with a heating rate of 5 °C min^{-1} under a flow of N_2 (100 mL min^{-1}). Mettler Toledo DSC 3 STAR^e System was used to collect the Differential scanning calorimetry (DSC) data over the range of –60 to 140 °C, with a heating rate of 10 °C min^{-1} under a flow of N_2 (200 mL min^{-1}). All the reported data were taken from the third heat/cool cycles. Melting enthalpies and the cold crystallization enthalpies were calculated using DSC data and the following equation[2, 3] was used to calculate the reduction of percent crystallinity of each material with respect to sulfur.

$$\Delta\chi_c = 1 - \left\{\frac{\Delta H_{m(LS_x)} - \Delta H_{cc(LS_x)}}{\Delta H_{m(S)} - \Delta H_{cc(S)}}\right\} * 100\%$$

$\Delta\chi_c$ - Change of percentage crystallinity with respect to sulfur
$\Delta H_{m(LS_x)}$ - Melting enthalpy of composite materials (LS_X)
$\Delta H_{cc(LS_x)}$ - Cold crystallization enthalpy of composite materials (LS_X)
$\Delta H_{m(S)}$ - Melting enthalpy of sulfur
$\Delta H_{cc(S)}$ - Cold crystallization enthalpy of sulfur

Dynamic Mechanical Analysis (DMA) was performed using a Mettler Toledo DMA 1 STAR^e System in single cantilever mode. DMA samples cured for 120 h were cast from silicone resin molds (Smooth-On Oomoo® 30 tin-cure). The sample dimensions were approximately 19×9×2 mm. The clamping force was 1 cN·m and the temperature range was –60 to 80 °C with a heating rate of 5 °C min^{-1}. The results were collected with the measurement mode of displacement control with a displacement amplitude of 5 µm and a frequency of 1 Hz. Each Sample was cured for 120 h prior to stress-strain analysis at room temperature with the DMA instrument operating in single cantilever mode. The force was varied from 0 to 10 N with a ramp rate of 0.1 N·min^{-1}. Fourier transform infrared spectra were obtained using a Shimadzu IR Affinity-1S instrument with ATR attachment, operating over the range of 400-4000 cm^{-1} at ambient temperature. Cary 50-Bio UV-Vis Spectrophotometer was used to obtain the UV-Visible spectra, scanning from 800-200 nm.

Chlorination of Lignin[4]

Excess of 8.5 g of $NaClO_3$ (1.5 equiv with respect to total phenolic groups in lignin) in water (158 mL) was added to a fine powder of alkali lignin (15 g) taken in a 500 ml round-bottom flask equipped with a magnetic stirring bar at room temperature. After that HCl (31.6 mL) was added dropwise for 15 minutes. The precipitate was collected by vacuum filtration followed by four consecutive washes with distilled water. The final product was vacuum dried for 24 hours at 40° C.

General synthesis of CLS_x (*x* = wt.% sulfur in monomer feed)

Elemental sulfur was weighed directly into a pressure tube under inert environment. The tube was heated to 180 °C in an oil bath over which time the sulfur melted. Once the sulfur turned a viscous dark red-orange color (indicative of thermal ring-opening), the appropriate amount of chloro lignin was slowly added to the molten sulfur. Following addition, the temperature was increased to 230°C and heating was continued for 24 h with continuous stirring with a magnetic stir bar. The whole procedure was done under N_2 gas. This general synthesis was used to synthesize **CILS$_{99}$**, **CILS$_{95}$**, **CILS$_{90}$, CILS$_{85}$** and **CILS$_{80}$** Each of the lignin- sulfur combination was subjected to elemental combustion microanalysis.

CAUTION: Heating elemental sulfur with organics can result in the formation of H_2S gas. H_2S is toxic, foul-smelling, and corrosive

Depolymerization with $AlBr_3$
The highest lignin incorporated sample was selected for the below procedure. 30 mg of powdered CLS$_{80}$ sample and 60 mg of $AlBr_3$ were added to a 20 mL scintillation vial. The mixture of solid was dissolved in 6 mL of anhydrous toluene in N_2 environment for 72 h. At the end of the reaction time, the solvent was filtered and 5% (v/v) HCl : ethanol 5 mL was added. The solution was subjected into three consecutive washing and the organic layer was separated out.

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The Procedure for the reaction of aryl thiols with Ellman's reagent
The procedure was carried out according to a known method[5][8]. The stock solution of DTNB (5, 5'-Dithio-*bis*-(2-nitrobenzoic acid) was prepared by dissolving 40 mg of DTNB in 10 mL of DMSO. The solution was100-fold diluted into 0.1 mM DTNB solution using 0.1 MTris HCl (**Tris**(hydroxymethyl)aminomethane hydrochloride) buffer solution at pH 7.4. 1mL of the solution containing depolymerized products and 19 mL of 0.1 mM DTNB were mixed together and let it to sit for 2 minutes at room temperature. The samples were then analyzed through UV-vis spectrophotometer by using 10% (v/v) Tris HCl: DTNB solution as the blank. In order to confirm that the initial CLS$_{80}$ sample does not carry the thiol groups, the same procedure was carried out without adding $AlBr_3$ and obtained the spectroscopy.

Note; DTNB solution was freshly prepared for the experiment and wrapped with aluminum foils throughout the experiment in order to minimize the formation of yellow degradation products.

Elemental Analysis

Table S1. Elemental Analysis of CLS$_x$ Materials

Materials	C wt%	H wt%	S wt%	Cl wt%
CLS$_{80}$	11.8	0.6	81.4	1.0
CLS$_{85}$	8.6	1.1	88.4	0.6
CLS$_{90}$	5.8	0.7	91.1	0.5
CLS$_{95}$	3.3	0.3	95.4	0.6
CLS$_{99}$	0.8	0.0	98.6	0.4

Table S2. Elemental Analysis of CS_2 insoluble Fraction

Materials	C wt%	H wt%	S wt%	Cl wt%
CLS_{80}	44.9	2.5	33.4	2.4
CLS_{85}	35.8	1.8	49.8	1.4
CLS_{90}	25.7	1.3	63.3	1.3

Incorporation of Lignin into Composites for Various Monomer Feeds

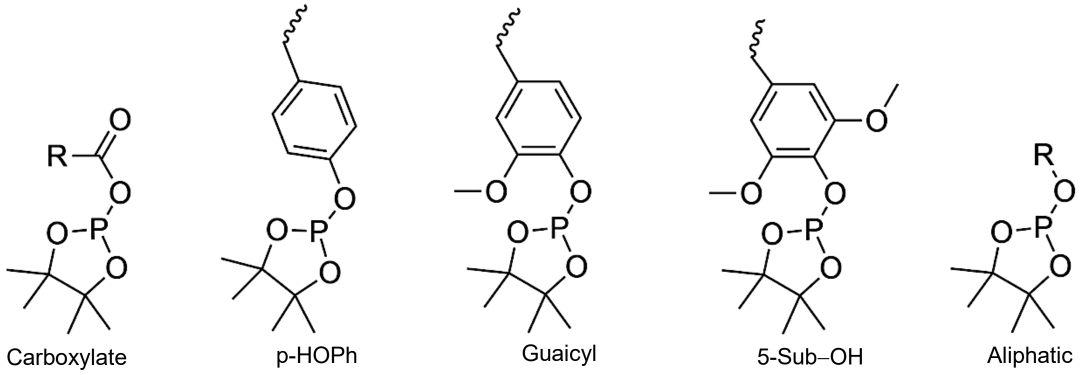
Table S3. Composition data

Materials	Chloro Lignin in monomer feed wt%	Chloro Lignin incorporated wt%	CS_2 Insoluble wt%	Removal of Cl wt%	Average Sulfur crosslink chain length
SAL_{80}	20	5	92	NA	48
CLS_{80}	20	19	31	58	12
CLS_{85}	15	13	24	66	19
CLS_{90}	10	9	22	64	31
CLS_{95}	5	5	21	NA	NA
CLS_{99}	1	1.0	19	NA	NA

Composition Analysis of Lignin

Table S4. Phosphorus-31 NMR quantification of subunit composition of lignin used in this work.

Functionality	Chemical shift (ppm)	Lignin (mmol/g)
Carboxylate	134-135.5	0.36
p-HOPh	137-138.5	0.25
Guaicyl	138.5-140	1.69
5-Sub–OH	140.2-145	1.61



Scheme S1. Phosphitylated subunits of lignin[2]

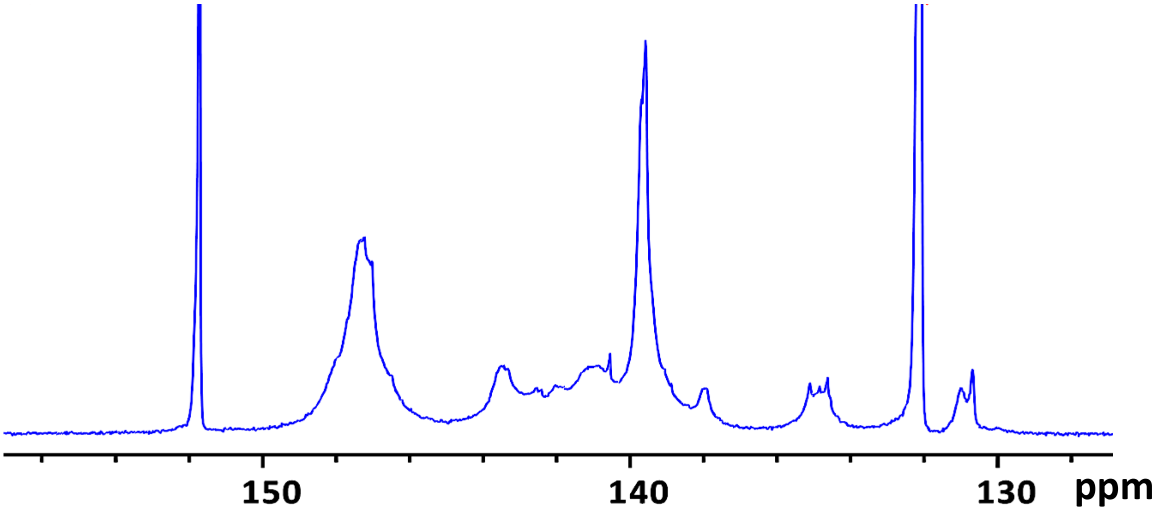


Figure S1. ^{31}P NMR of the phosphitylated lignin.

2-chloro-4,4,5,5,-tetramethyl-1,3,2-dioxaphospholane was used as the phosphitylation agent and for the accurate quantification *endo*-*N*-hydroxy-5-norbornene-2,3-dicarboximide was used as the internal standard.[6]

IR Spectroscopy analysis

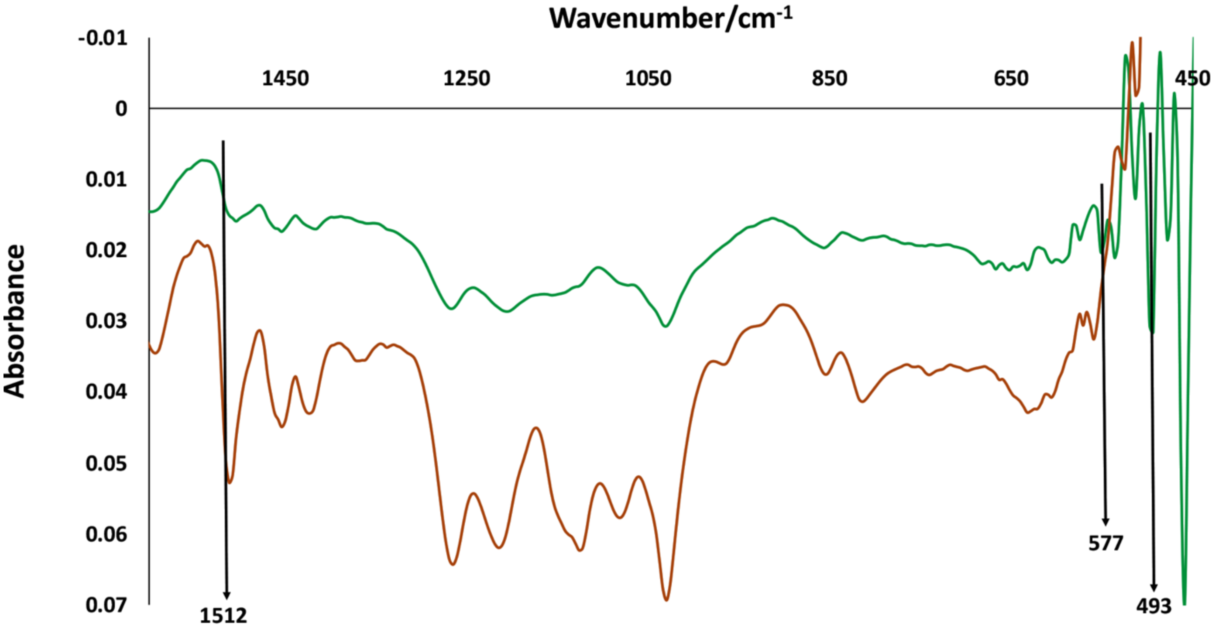


Figure S2. Inset of the IR spectra for lignin (brown solid line) and chloro lignin (green solid line). The highlighted peaks at the chloro lignin IR spectra are the distinguished peaks to differentiate chlorinated lignin over the initial, unchlorinated lignin sample**.**

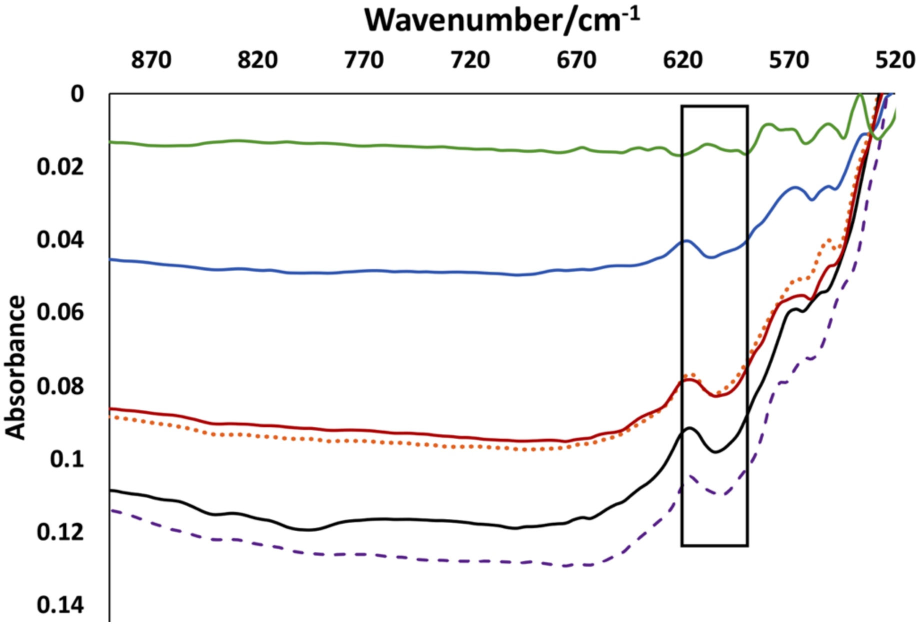


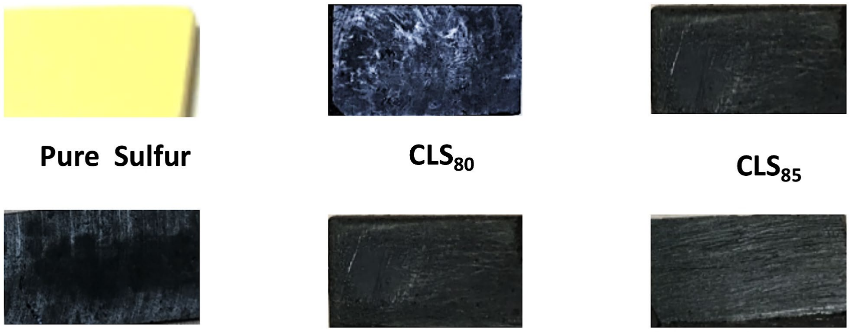
Figure S3. C–S stretching IR absorbance peak of composite materials **CLS$_{80}$** (blue solid line), **CLS$_{85}$** (purple dashed line), **CLS$_{90}$** (orange dotted line), **CLS$_{95}$** (black solid line), **CLS$_{99}$** (red dashed line) and the absence of the peak in Chloro lignin (green solid line**)** spectrum. The box highlights the emergence of the C–S stretching band.[7]

Physical Properties analysis

Table S5. Water uptake test results and the densities of **CLS$_x$** materials.

Materials	Change in the wt% upon water uptaking^a	Density g/cm^3
CLS$_{80}$	0.49	1.54
CLS$_{85}$	0.46	1.61
CLS$_{90}$	0	1.77
CLS$_{95}$	0	1.73
CLS$_{99}$	0	1.77

[a] Samples were soaked in water for 24 h and calculated the change in the weight percentage



Pure Sulfur **CLS$_{80}$** **CLS$_{85}$**

CLS$_{90}$ **CLS$_{95}$** **CLS$_{99}$**

Figure S4. Photos of **CLS$_x$** materials and sulfur.

The **CLS$_x$** materials are brown to black solids and took on a progressively glassier appearance as the percentage of chlorolignin in the monomer feed increased. The black color of the CLS$_x$ materials retained with the aging while the pure sulfur sample heated in the same temperature and time period, turned into yellow color from the initial black-brown color

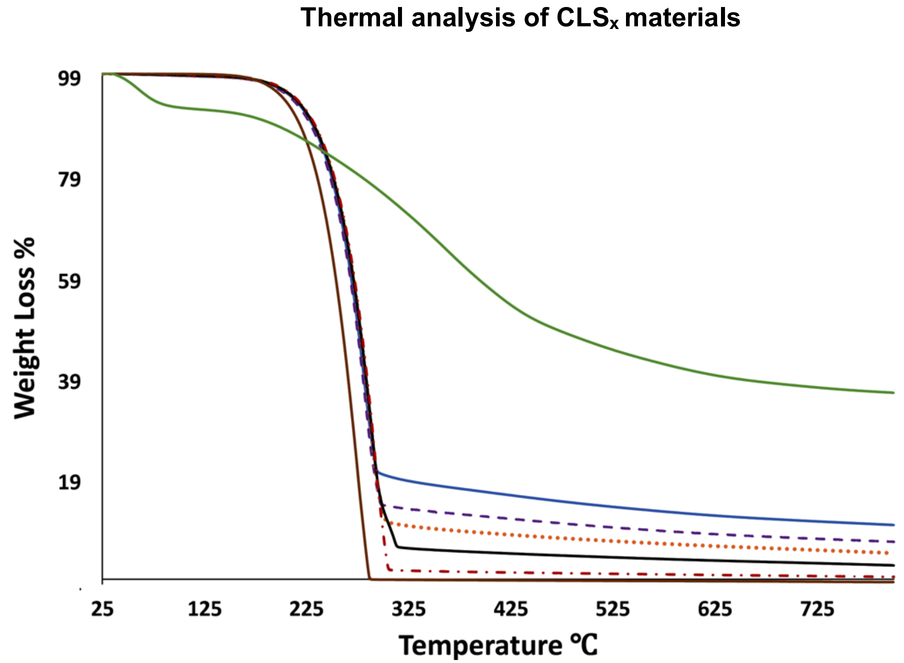


Figure S5. TGA curves of CLS$_x$ materials. **CLS$_{80}$** (blue solid line), **CLS$_{85}$** (purple dashed line), **CLS$_{90}$** (orange dotted line), **CLS$_{95}$** (black solid line), **CLS$_{99}$** (red dashed line) and the Chlorinated lignin (green solid line)

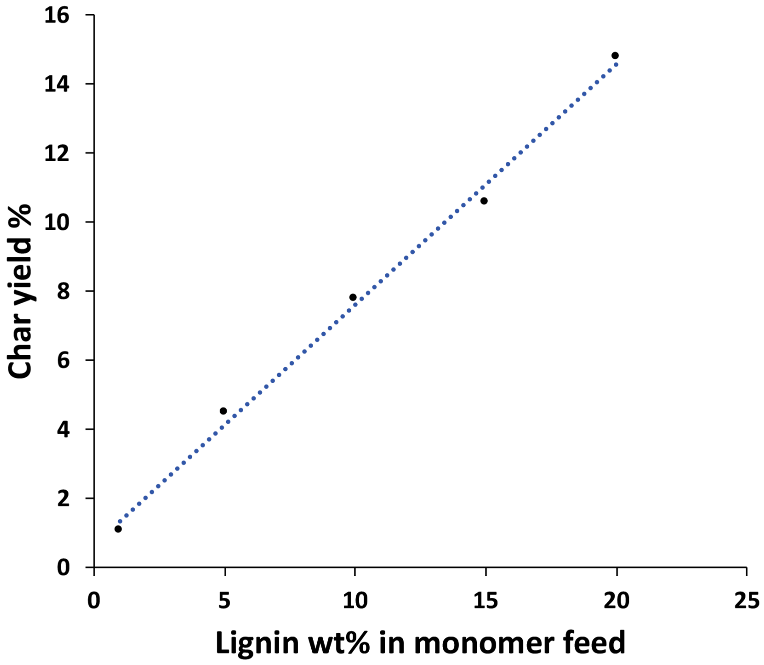


Figure S6. The graph of char yield percentage vs the lignin wt%in monomer feed

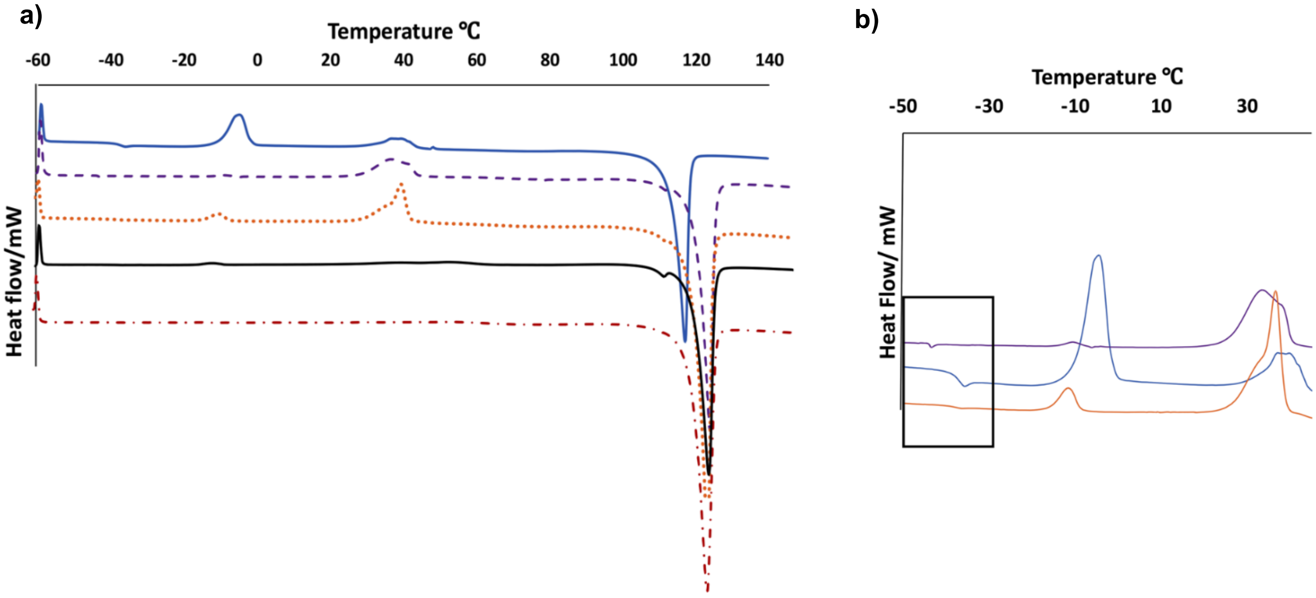


Figure S7. a) DSC curves of **CLS$_{80}$** (blue solid line), **CLS$_{85}$** (purple dashed line), **CLS$_{90}$** (orange dotted line), **CLS$_{95}$** (black solid line), **CLS$_{99}$** (red dashed line), sulfur (brown solid line**. b)** Enlarged view of DSC curves, showing T_g (highlighted area) and cold crystallization peaks of **CLS$_{80}$, CLS$_{85}$**, and **CLS$_{90}$**.

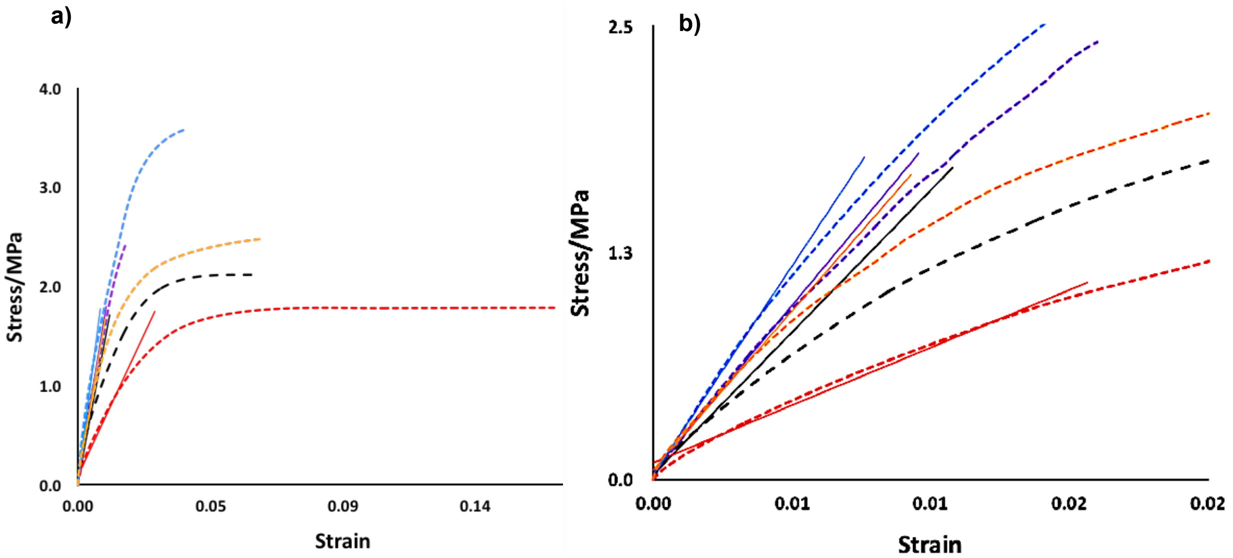


Figure S8. a) Stress strain curves of **CLS$_x$** materials of **CLS$_{80}$** (blue dashed line), **CLS$_{85}$** (purple dashed line), **CLS$_{90}$** (orange dashed line), **CLS$_{95}$** (black dashed line), **CLS$_{99}$** (red dashed line). All the trend lines are depicted in solid lines. b) Enlarged view of the linear region of stress strain curves with the trend lines.

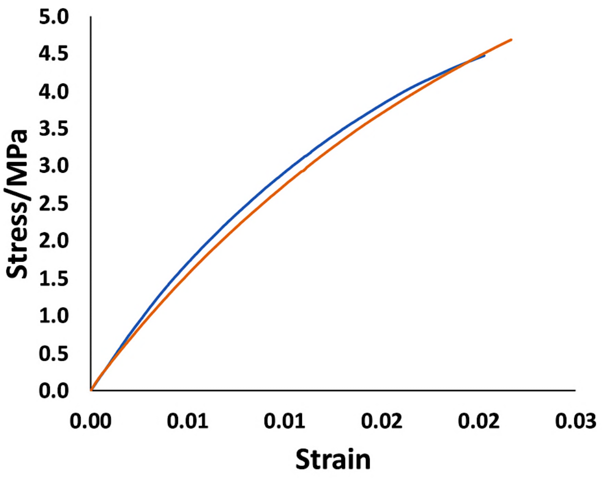


Figure S9. Stress strain curves comparison upon 24 h, 0.5 *M* H_2SO_4 soaking. Blue line indicates before soaking and the orange line after soaking.

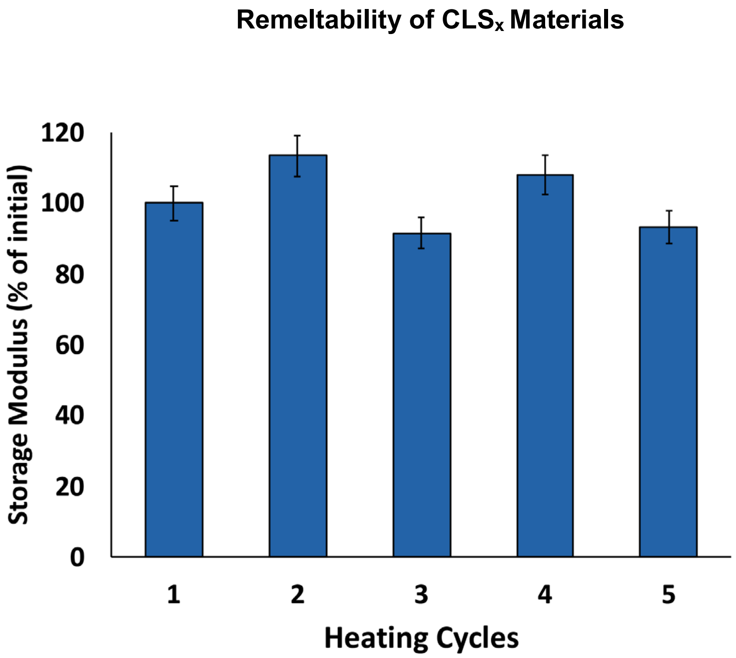


Figure S10. Storage moduli of **CLS$_{85}$** as the percentage of initial over five pulverizing-melt-recast cycles.

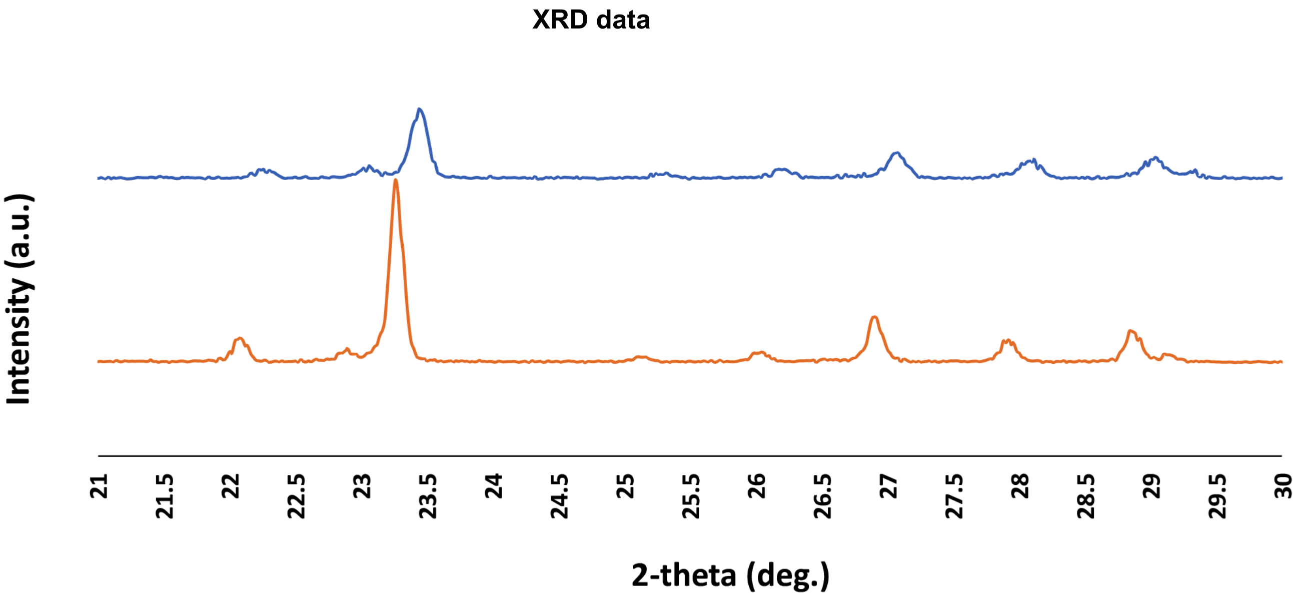
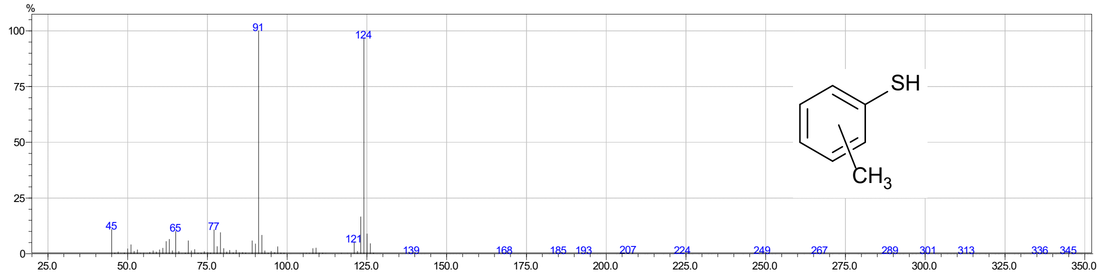


Figure S11. XRD Data of CLS$_{80}$ (blue solid line) and Pure sulfur sample (orange solid line)
All the peaks present in the CLS80 sample are broader and less intense compared to pure sulfur sample, exhibiting the less crystallinity of CLSx samples



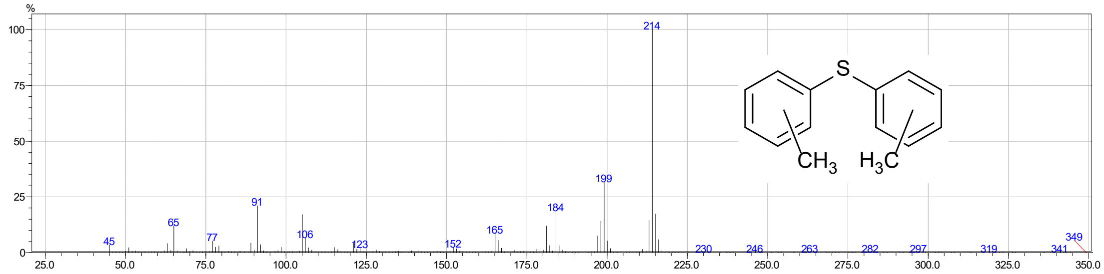


Figure S12. The GC-MS analysis of depolymerization products from **CLS$_{80}$** sample revealed aryl thiols such as those whose structures and mass spectra are shown above.

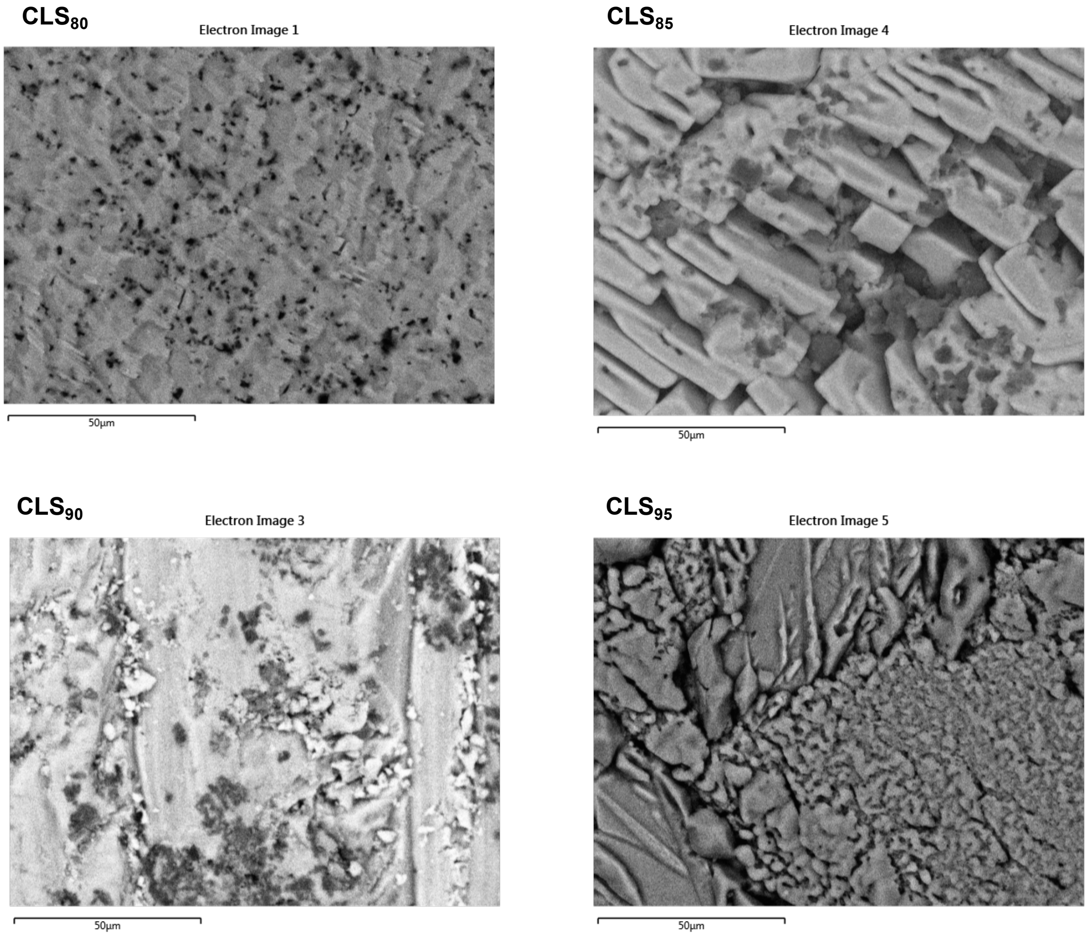


Figure S13. Surface analysis of **CLS$_x$** materials by scanning electron microscopy revealed sample-dependent sulfur crystal morphology consistent with the high orthorhombic sulfur content in the composites.

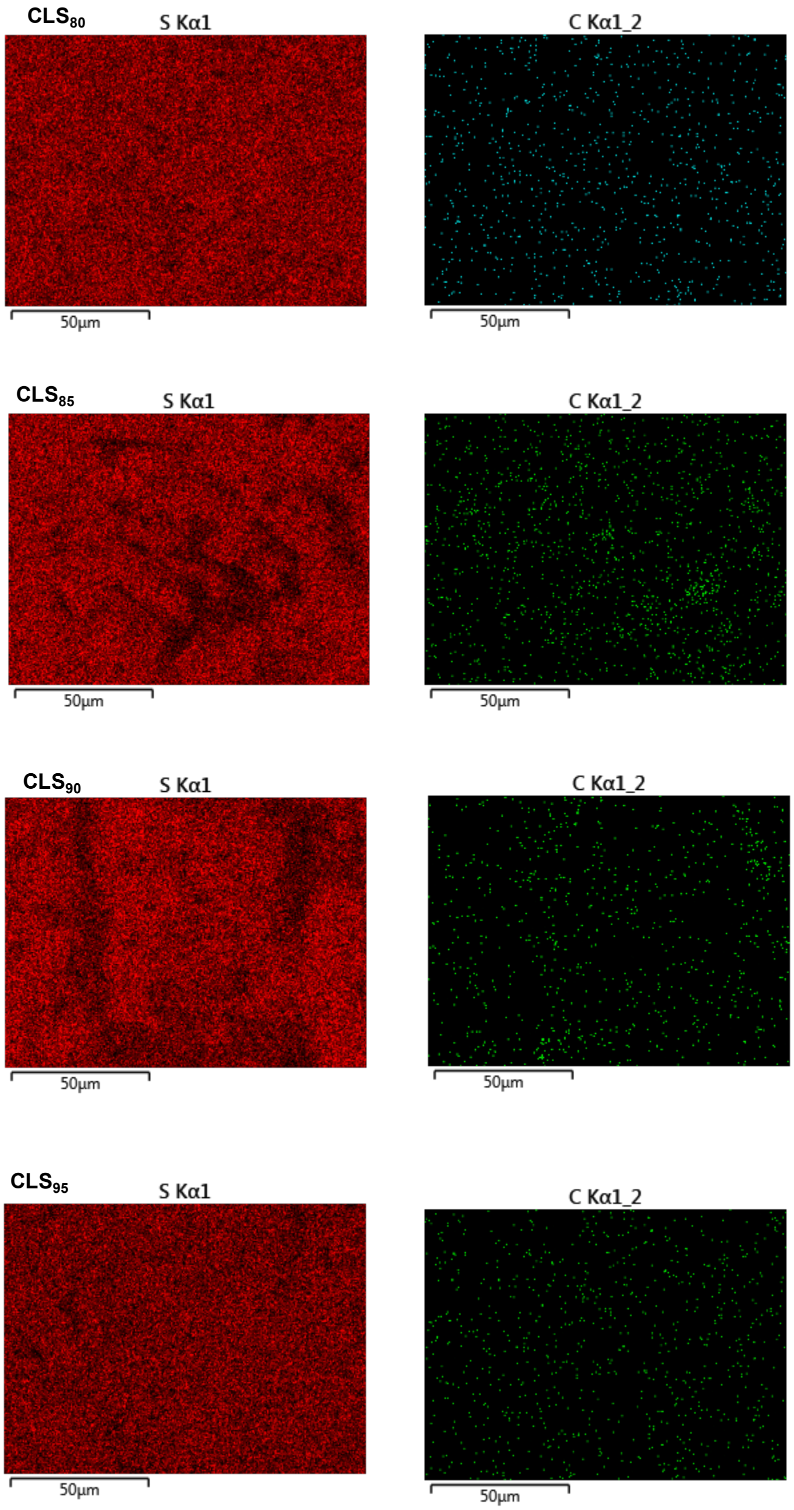


Figure S14. Surface analysis of **CLS$_x$** materials by EPS revealed distribution of carbon and sulfur content on the polymer surface, consistent with the varying amount of chlorolignin in the monomer feed.

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