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Supporting Information

Novel Composite Hydrogels Containing Fractionated, Purified Lignins for Aqueous-Based Separations

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^{1}H NMR Spectroscopy

As mentioned in the Experimental Section of the manuscript, ^{1}H NMR was performed on the lignins pre- and post-functionalization to confirm the addition of the vinyl-containing acrylate groups. The results from this analysis are shown in Figure S1.

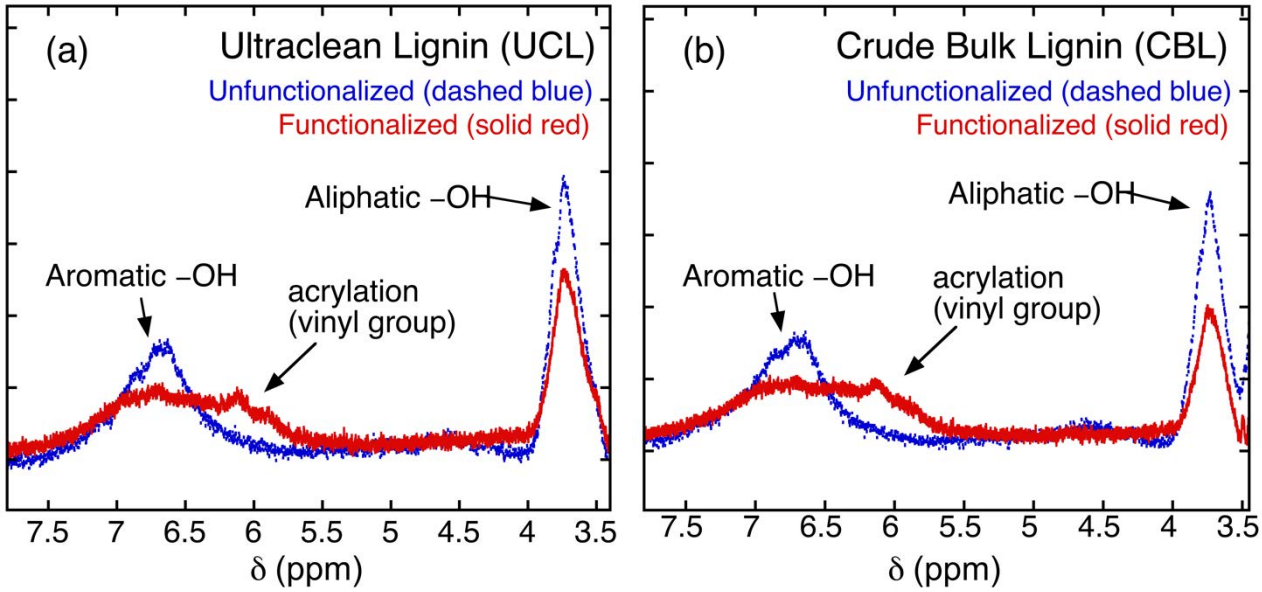

Figure S1. ^{1}H NMR spectra of unfunctionalized (dotted blue line) and functionalized (solid red line) (a) ultraclean lignin (UCL) and (b) crude bulk lignin (CBL).

As seen in Fig. S1, the NMR peaks associated with the aliphatic and aromatic –OH groups decrease after acrylation. This decrease in spectral peaks associated with the –OH groups is accompanied by the emergence of broad peak centered around 6.2 ppm, which is indicative of the hydrogens on the C=C double (i.e., double bond a vinyl group).

Hydroxyl (–OH) Content of Crude Bulk and Ultraclean Lignins

The hydroxyl content of the unfunctionalized and functionalized crude bulk lignins (CBLs) and ultra-clean lignins (UCLs) was determined from the ^{31}P NMR spectrum for each sample (shown in Figures 1b and 1c in the manuscript). A summary of these data is presented in Table S1.

Table S1. Aliphatic and aromatic hydroxyl (–OH) content for both unfunctionalized (UF) and functionalized (F) crude bulk lignins (CBLs) and ultraclean lignins (UCLs)

Type of lignin	Aliphatic –OH (mmol OH/g lignin)	Aromatic –OH syringyl (S) (mmol OH/g lignin)	guaiacyl (G) (mmol OH/g lignin)	*p*-hydroxyl phenol (H) (mmol OH/g lignin)
CBLs				
UF	1.88	0.64	2.25	0.38
F	0.23	0.59	1.14	0.40
UCLs				
UF	1.60	0.64	2.40	0.43
F	0.44	0.26	1.06	0.22

Infrared Characterization of UCLs and CBLs

To further confirm successful functionalization of the UCLs and CBLs, the lignins were analyzed using FTIR spectroscopy using a Thermo Scientific Nicolet iS50R FT-IR equipped with Specac Golden Gate attenuated total reflectance (ATR) attachment. All spectra were collected using a liquid nitrogen-cooled mercury-cadmium-telluride detector with 64 scans per spectrum at a resolution of 4 cm^{-1}. FTIR spectra of pre- and post-functionalized UCLs and CBLs are presented in Figures 2a and 2b, respectively.

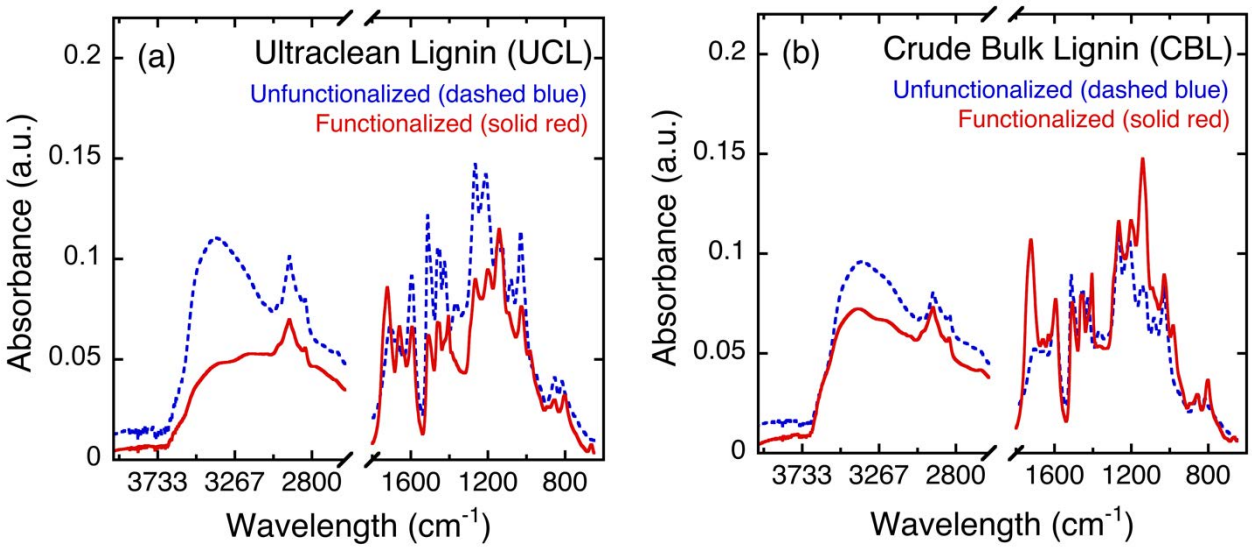

Figure S2. FTIR spectra of unfunctionalized (dashed blue line) and functionalized (solid red line) for (a) ultraclean lignin and (b) crude bulk lignin.

Thermal Stability of Composite Hydrogels

To confirm the stability of the fabricated hydrogels at lower temperatures, the hydrogels were cut and soaked in DI water, at room temperature (~20 °C) for at >120 days. Following this initial soaking, the membranes were exposed to increasing temperatures to visually detect the thermal stability of the composite membranes when compared to the thermally-crosslinked PVA hydrogel. A summary of the images for each membrane, at each temperature, is provided in Table S2.

Table S2. The following table contains images of the two series PVA–lignin hydrogel composite membranes under hydration at temperatures ranging from room temperature (~25 °C) to 80 °C. Note, the first column shows the membranes that have been under hydration for >120 days.

	20 °C, >120 days	40 °C, 4 h	60 °C, 4 h	80 °C, 4 h	80 °C, 24 h
Neat PVA					

PVA–UCL–10UF					
PVA–UCL–20UF					
PVA–UCL–10F					
PVA–UCL–20F					
PVA–UCL–50UF					
PVA–CBL–10UF					
PVA–CBL–20UF					
PVA–CBL–10F					

PVA–CBL–20F					
PVA–CBL–50UF					

As seen in Table S2, all of the PVA–lignin composite hydrogels are stable in room temperature water for >120 days.