# **Supporting Information**

# Extraordinary solution-processability of lignin in phenol-maleic anhydride and dielectric films with controllable properties

Qi Fan, Tao Liu, Chaoqun Zhang, Zhenzhen Liu, Wenxu Zheng, Rongxian Ou\* and Qingwen Wang\*

College of Materials and Energy, South China Agricultural University, Guangzhou,

510642, PR China

\*Corresponding authors. E-mail: rongxian\_ou@scau.edu.cn (Rongxian Ou).

\*Corresponding authors. E-mail: qwwang@scau.edu.cn (Qingwen Wang).

#### Experimental

## Materials

Enzymatic hydrolysis lignin ( $M_w \approx 5056$  Da, denoted as EL) was the fermentation residue from bioethanol process and supplied by Shandong Longlive Bio-Technology Co., Ltd. (China). Its purity and the residual carbohydrates content were 92.5 % and 0.17 %, respectively.<sup>1</sup> The production information of EL has been also briefly described as follows.<sup>2</sup> EL isolation involves the removal of a substantial amount of carbohydrate fraction with the cellulolytic enzyme hydrolysis of corncob; this procedure was followed by extraction using diluted sodium hydroxide solution, and subsequently with diluted sulfuric acid (2 wt.%) hydrolysis that cleaves lignincarbohydrate bonds. According to the test results by the <sup>31</sup>P NMR, the phenolic hydroxyl group content in EL is about 8.0%. Lignin (dealkaline, from North American soft wood) was purchased from Tokyo Chemical Industry (TCI, Shanghai) and denoted as DAL. Milled wood lignin ( $M_w \approx 52000$ , denoted as ML) was isolated from bagasse, the fractional isolation method of ML can be found in a previous report.<sup>3</sup> Phenol, maleic anhydride (MAH), tetrahydrofuran (THF), dioxane (DOX), and ethylene glycol diglycidyl ether (EGDE) were purchased from Sigma Aldrich (St. Louis, MO) and used as received. All other chemicals and reagents were purchased from Sigma Aldrich and TCI Development Co., Ltd. and used as received unless otherwise noted.

# Preparation of Phenol-MAH supramolecule

Supramolecular eutectic liquid, composed of phenol and maleic anhydride (MAH), was produced in sealed glass container by simply mixing and stirring until a homogeneous yellowish liquid was formed within one hour at room temperature.

### Preparation of renewable dielectric film

The lignin-based dielectrics were prepared by a simple three-step procedure, including lignin dissolution in Phenol-MAH solution and cross-linking curing of the lignin + Phenol-MAH + EGDE. The EL was initially dissolved in Phenol-MAH at concentrations of 0, 20, 33, 43, and 50 wt.%. The resulting viscous solution was mechanically stirred in an oil bath at 80 °C under air atmosphere for 1 h. Subsequently, EGDE was added into the lignin + Phenol-MAH system to obtain mixtures with EL concentrations of 0, 10, 20, 27 and 35 wt.%. The resulting prepolymer solution was stirred at 80 °C for another 1 hour. Then, the prepolymer was poured into a Teflon mold for final curing according to the following profile: 50 °C for 2 h, 80 °C for 2 h, 100 °C for 2 h, and 120 °C for 2 h, as determined by differential scanning calorimetry (DSC) analysis.

### **Calculations**

The electrostatic potential (ESP) calculation was performed using density functional theory (DFT) methods in the Gaussian 09 suite. The relevant calculations were carried out with the B3PW91/6-31G(d,p) procedure. The 6-31G(d) and the 6-31G(d,p) basis sets have been demonstrated to yield reliable electrostatic potentials in conjunction with Hartree–Fock and density functional method.<sup>4</sup> The interaction energy values ( $\Delta E$ ) has been evaluated and corrected from the basis set superposition error (BSSE) according to the site–site function (SSFC) scheme.<sup>5, 6</sup>

The relevant calculations of lignin model compound and Phenol-MAH system were performed with the Gaussian 09 program package. The initial geometry optimizations were obtained using the M06-2X exchange–correlation function combined with the 6-31G\* basis set. The samples were subjected to re-optimization at the M06-2X/6-31+G\*\* level. To eliminate the dispersion effect, we added the keyword of empirical dispersion = gd3 in the route section. The calculations were optimized without symmetry restrictions. The frequency analysis at the M06-2X/6-31+G\*\* level was performed for the optimized structures to verify the energy minima and to provide the zero-point energy corrections. The thermochemical characteristics were obtained for single-point energy calculations at the M06-2X/6-311++G\*\* level to test their consistency and reproducibility.

The bond-acceptor–donor interactions were analyzed through 2D (the reduced density gradient S, versus the product of the sign of the second eigenvalue of the Hessian matrix and the electron density, the signal  $(\lambda 2)\rho$ ), the and 3D-NCI (non-covalent interactions) plots with the software Multiwfn and VMD.<sup>7, 8</sup> The 2D-NCI plot showed the weak interactions and allowed comparison to strong interactions. The 3D-NCI plot uses a three-color code to differentiate between attractive interactions (blue), very weak non-covalent interactions (green), and repulsive interactions (red). The darkest shade of blue corresponds to the strongest hydrogen bonds.

#### **Characterization**

Solubilization of lignin: In a typical process, 1 mL Phenol-MAH or another solvent as control was placed into a 1.5 mL plastic tube. The lignin was added in a stepwise fashion into the tube and simply mixed by magnetic stirring (500 rpm) for 5 min. The solubility of lignin in the solvent was confirmed by using a Zeiss Axioplan 2 imaging E Microscope with 20–60× magnification.

Surface tension of experimental solutions: The surface tension of the experimental solutions was measured by platinum ring detachment method with a Drop Shape Analyzer (DSA100, KRŰSS; Germany) at 298.15 K. The precision of measurement was within  $\pm 0.1$  mN m<sup>-1</sup>. To maintain the temperature of the system throughout the

experiment, the solution was placed in a double-walled glass vessel and autothermostated water was continuously circulated.

<sup>1</sup>*H-NMR*: The structures of Phenol-MAH, phenol and MAH were analyzed by proton nuclear magnetic resonance (<sup>1</sup>H NMR, AVANCE III Bruker) in CDCl<sub>3</sub> at 600 MHz.

*FTIR:* The curing process of the prepolymer was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) analysis. FTIR analyses were conducted using a SHIMADZU IRTracer-100 FTIR Spectrometer equipped with an ultra-highperformance, and a versatile attenuated total reflectance (ATR) sampling accessory. The spectra were scanned over a wavenumber range of 400–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

*Curing temperature test:* Curing temperature tests of the samples were performed on a NETZSCH DSC 214 *polyma* instrument (NETZSCH, Germany) under N<sub>2</sub>. The sample of about 5–10 mg) was scanned from 35 °C to 250 °C at heating rates of 5, 10, 15, and 20 °C/min. For each sample, the non-isothermal DSC scan was repeated twice and the average value of the results was calculated.

<sup>31</sup>*P NMR*: The hydroxyl values of PDL and PDL-epoxy monomers were determined using <sup>31</sup>*P* NMR. The <sup>31</sup>*P* NMR spectra were obtained on a Bruker 400 NMR spectrometer. Approximately 25.0 mg of lignin compound and an excessive amount of 2-chloro-4,4,5,5,-tetramethyl-1,2,3-dioxaphospholane (TMDP) were dissolved in a mixture solvent of pyridine/CDCl<sub>3</sub> (1.6:1 v/v). Chromium acetylacetonate was used as a relaxation agent and cyclohexanol as the internal standard (IS). The <sup>31</sup>P NMR spectra were acquired using an inverse gated decoupling pulse sequence, 90° pulse angle, and 25 s pulse delay. Chemical shifts were calibrated by referring to the peak signal at  $\delta$  145.1 ppm for the IS of cyclohexanol.

 ${}^{1}H^{-13}C$  2-dimensional-heteronuclear single quantum correlation (2D-HSQC) NMR spectroscopy: The two dimensional  ${}^{1}H^{-13}C$  heteronuclear single-quantum coherence (HSQC) spectra was obtained on a Bruker Avance II 600 MHz spectrometer equipped with a 5 mm CPTCI  ${}^{1}H^{-13}C/{}^{15}N/{}^{2}H$  cryogenic probe with z-gradients at 25 °C, using the Q-CAHSQC pulse program. Matrices of 2048 data points for the  ${}^{1}H$ -dimension and 128 data points for the  ${}^{13}C$ -dimension were collected with a relaxation delay of 6 s and spectral widths that ranged from 13 ppm to -1 ppm and from 160 ppm to 0 ppm for the  ${}^{1}H$  and  ${}^{13}C$  dimensions, respectively. Prior to Fourier transform analysis, the data matrices were zero-filled to 1024 points in the  ${}^{13}C$  dimension. A 90 mg lignin sample was dissolved in 0.5 mL deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) and chemical shifts were referenced to the solvent signals (2.50/39.5 ppm). The spectra were processed using MestReNova software. Prior to Fourier transformation, free induction decays were apodised with a  $\pi/2$  sine square bell function in both dimensions and then zero-filled up to 512 points in the  ${}^{13}C$ -dimension and 4096 points in the <sup>1</sup>H-dimension. A semi-quantitative analysis of the intensities of the HSQC cross-signal was performed according to the method given in a previous article.<sup>9</sup>

*Dielectric properties:* Dielectric spectroscopy was performed using an Alpha L (Novocontrol Technologies, Germany) dielectric impedance analyzer. Thin disc samples 20 mm in diameter and with a thickness of 1 mm were clamped between two gold-coated electrodes in a shielded sample chamber. The impedance and the phase information of the samples were measured with a signal amplitude of 1 V (rms) and frequencies of  $10^{-1} - 10^5$  Hz. The sample's real and imaginary permittivity and conductivity were obtained by modeling the material as an equivalent parallel RC circuit whose impedance, *Z*\*, is defined as:

$$Z^* = \frac{1}{\frac{1}{R(\omega)} + i\omega C(\omega)}$$
(1)

where  $R(\omega)$  and  $C(\omega)$  are the sample's resistance and capacitance. Based on Equation (1), the complex permittivity, the  $\varepsilon^*$ , and conductivity, and the  $\sigma^*$  of the sample can be described by:

$$\varepsilon^*(\omega) = \frac{d(C^*(\omega) - C_0(\omega))}{\varepsilon_0 A} = \frac{\sigma^*}{i\omega\varepsilon_0}$$
(2)

where, *d* is the sample thickness, *A* is the sample area,  $\varepsilon_0$  is the permittivity of free space, and *C*<sub>0</sub> is the capacitance of the empty cell.

*Mechanical and thermal physics:* Dynamic mechanical analysis (DMA) of thin films with dimensions  $0.5 \times 5 \times 20$  mm was performed on an TA Q800 Instrument under

tensile mode at 0.1 % strain rate, a frequency of 1 Hz, and a heating rate of 3 °C min<sup>-1</sup> over a temperature range of -40 to 180 °C. Dumbbell specimens with a thickness of 2 mm were prepared by curing crosslinking in a teflon mold (ASTM D638-5-1MP) mounted on an MTS Alliance RT/5 equipped with a 2000 N load cell. These specimens were tested at a strain rate of 10 mm min<sup>-1</sup>. Five specimens of each sample type were tested, and average values are reported. Thermal stability studies were carried out on a TG 209F3 (NETZSCH Instruments) under a nitrogen flow of 40 mL/min. Samples (15–20 mg) were placed in a platinum pan and scanned from 30–800 °C at a ramp rate of 10 °C/min.

According to the theory of rubber elasticity, the cross-linking density ( $\rho$ ) of a cured epoxy network is proportional to its storage modulus in the rubbery region, and the cross-linking density can be calculated using the equation:

$$\rho = \frac{E'}{3RT} \tag{3}$$

where E' is the storage modulus at Tg + 30 °C, R is the gas constant, and T is the absolute temperature at Tg + 30 °C.<sup>10</sup>

*Morphology:* To characterize the morphology of the material, thin sections were obtained by performing cryo-microtome at -70 °C using a Leica ultra-microtome equipped with a cryo-chamber and a diamond knife. The thin sections were picked up with lacey carbon copper grids (obtained from Electron Microscopy Science) and analyzed via transmission electron microscopy (TEM, FEI Talos F200) at an operating voltage of 120 kV. The cryo-fractured surfaces of specimens were observed by FE-SEM Hitachi S4800 at 5 kV after sputter coating with a thin layer of gold.



Figure S1. Photos of (a) the freshly prepared Phenol-MAH and (b) the Phenol-MAH stored

for about one year under room temperature away from light.



Figure S2. Differential scanning calorimetry (DSC) thermograms of Phenol-MAH.



Figure S3. The <sup>1</sup>H NMR spectra of Phenol-MAH, phenol and MAH.



**Figure S4.** Solubilities comparison of EL in the different solvent systems at room temperature, after ultrasound treatment of 40 kHz for 30 min. Photos of the Phenol-MAH (above), the DOX (middle), and the THF (below) contained various quantities of EL.



**Figure S5.** Schematic illustration of lignin concentration versus the surface tension of the solution.



**Figure S6.** (a-c) Optimized configurations for the dimeric lignin model/Phenol-MAH calculated at the M06-2X/6-31+G\*\* level. The corresponding H-bonds are marked. (d) The structure of the dimeric lignin model (guaiacylglycerol-beta-guaiacyl ether, GG).



Figure S7. Diagram of solvent uptake mechanism for lignin dissolution in Phenol-MAH.

The changes started at the interface between the amorphous lignin macromolecule aggregates and Phenol-MAH. The border quickly broke and the sharp interface began to soften. During swelling, the Phenol-MAH molecules slowly diffused into the lignin aggregates, and the lignin macromolecules slowly diffused outwards. Once the Phenol-MAH molecules reached the center of lignin aggregates, the lignin macromolecules accelerated transfer. The lignin completely dissolved when the lignin macromolecule was coated with a layer of Phenol-MAH molecules.



Figure S8. Rapid solubilization and regeneration of EL: (a) the solution of EL/Phenol-MAH,(b) Precipitation of lignin.



Figure S9. 2D HSQC NMR spectra of EL in DMSO– $d_6$  revealing the structure changes of

lignin unit compositions after treatment with Phenol-MAH. (a, b) original EL; (c, d) the

regenerated EL from EL/Phenol-MAH solution stirred at room temperature for 2 h; (e, f) the regenerated EL from EL/Phenol-MAH solution stirred at 60 °C for 2 h. Lignin aromatic units are colored and labeled to match the structures below.



**Figure S10.** The original EL and the regenerated EL from the solution of Phenol-MAH dissolving lignin at different temperatures (25 °C, 40 °C, 60 °C, 80 °C, and 100 °C) for two hours. The different regenerated EL samples were denoted as EL-25, EL-40, EL-60, EL-80 and EL-100, respectively.



**Figure S11.** <sup>31</sup>P NMR spectra for (a) the original EL and (b-f) the regenerated lignin from the solution of EL/Phenol-MAH after phosphitylation.



**Figure S12.** DSC test curves for the curing temperatures of pre-polymers with an EL content of 27 wt.%: (a) pre-polymers based on Phenol-MAH and (b) control samples with same EL content.



**Figure S13.** (a, b) The TEM images of lignin-based films containing 10 wt.% and 35 wt.% of EL using Phenol-MAH as solvent, respectively. (c) The TEM images of control sample containing 10 wt.% of EL. (d, e) The SEM images of cryo-fractured surfaces of lignin-based films containing 10 wt.% and 35 wt.% of EL using Phenol-MAH as solvent, respectively. (f) The SEM images of cryo-fractured surfaces of control sample containing 10 wt.% of EL.



Figure S14. Thermogravimetric analysis of the lignin-based films containing different amounts of EL. Inset exhibits  $T_{5\%}$  (temperature at 5% weight loss) of the lignin-based films as a function of EL content.

Table S1. Assignments of the lignin <sup>13</sup>C<sup>-1</sup>H correlation peaks in the 2D HSQC spectra of EL

Label	$\delta_C / \delta_H (ppm)$	Assignment		
$C_{\beta}$	53.1/3.43	$C_{\beta}$ -H <sub><math>\beta</math></sub> in phenylcoumaran substructures (B)		
-OMe	55.6/3.73	C–H in methoxyls		
$\mathbf{A}_{\gamma}$	59.4/3.40 and 3.72	$C_{\gamma}$ -H <sub><math>\gamma</math></sub> in $\gamma$ -hydroxylated $\beta$ -O-4' substructures (A)		
$F_{meta}$	59.5/2.75	$C_{\beta}$ -H <sub><math>\beta</math></sub> in spirodienone substructures (F)		
$\mathbf{C}_{\gamma}$	62.6/3.67	$C_{\gamma}$ -H <sub><math>\gamma</math></sub> in phenylcoumaran substructures (B)		
$(\mathbf{A},\mathbf{A}')_{\alpha}$	70.9/4.71,	$C_{\alpha}$ -H <sub><math>\alpha</math></sub> in $\beta$ -O-4' substructures (A) linked to a G-unit		
	71.8/4.83	and S-unit, respectively		
$A_{\beta}(G/H)$	80.11/4.41	$C_{\beta}$ -H <sub><math>\beta</math></sub> in $\beta$ -O-4' substructures linked to G and H		

and the EL regenerated from Phenol-MAH solution<sup>a</sup>

			units (A)		
Eα	79.5/5.50		$C_{\alpha}$ -H <sub><math>\alpha</math></sub> in $\alpha$ -O-4' substructures (E)		
$A'_{\beta}(S)$	83.09/4.45		$C_{\beta}$ -H <sub><math>\beta</math></sub> in $\gamma$ -acylated $\beta$ -O-4' substructures linked to S		
			units (A')		
$A_{\beta}(S)$	86.60/4.11		$C_{\beta}$ -H <sub><math>\beta</math></sub> in $\beta$ -O-4' substructures linked to S units (A)		
$A_{ox\beta}$	82.7/5.12		$C_{\beta}$ -H <sub><math>\beta</math></sub> in $\alpha$ -oxidized $\beta$ -O-4' substructures (A <sub>ox</sub> )		
F <sub>a</sub> '	84.6/4.75		$C_{\alpha}$ - $H_{\alpha'}$ in spirodienone substructures (F)		
$C_{\alpha}$	86.8/5.43		$C_{\alpha}$ -H <sub><math>\alpha</math></sub> in phenylcoumaran substructures (B)		
S <sub>2,6</sub>	103.8/6.69		$C_2$ -H <sub>2</sub> and $C_6$ -H <sub>6</sub> in etherified syringyl units (S)		
S´ <sub>2,6</sub>	106.21/7.23 an	nd	C <sub>2,6</sub> -H <sub>2,6</sub> in oxidized (C $\alpha$ =O) syringyl units (S')		
	7.05				
S* <sub>2,6</sub>	106.10/6.50 an	nd	C <sub>2,6</sub> -H <sub>2,6</sub> in oxidized (C <sub><math>\beta</math></sub> =O) syringyl units (Hibbert's		
	7.05		ketone) (S*)		
FA <sub>2</sub>	111.0/7.32		$C_2$ - $H_2$ in ferulate (FA)		
$PCA_{\beta}$	113.5/6.27		$C_{\beta}$ -H <sub><math>\beta</math></sub> in p-coumarate (PCA)		
$FA_{\beta}$	116.5/6.40		$C_{\beta}$ -H <sub><math>\beta</math></sub> in ferulate (FA)		
G <sub>6</sub>	118.7/6.77		$C_6$ -H <sub>6</sub> in guaiacyl units (G)		
G/G*	114.9/6.72 at	nd	C-H in guaiacyl units (G) and their derivative units		
	6.94		(G*)		
PCA <sub>3,5</sub>	115.5/6.77		$C_3$ - $H_3$ and $C_5$ - $H_5$ in <i>p</i> -coumarate (PCA)		
FA <sub>6</sub>	123.2/7.15		C <sub>6</sub> -H <sub>6</sub> in ferulate (FA)		
H <sub>2,6</sub>	127.8/7.22		C <sub>2,6</sub> -H <sub>2,6</sub> in <i>p</i> -hydroxyphenyl units (H)		

$PCA_{\alpha}$ and	144.7/7.41	$C_{\alpha}$ -H <sub><math>\alpha</math></sub> in p-coumarate (PCA) and ferulate (FA)
$PCA_{\alpha}$ and	144.7/7.41	$C_{\alpha}$ -H <sub><math>\alpha</math></sub> in p-coumarate (PCA) and ferulate (FA)
PCA <sub>2,6</sub>	130.1/7.45	$C_2$ - $H_2$ and $C_6$ - $H_6$ in <i>p</i> -coumarate (PCA)

<sup>a</sup>Signals were assigned by comparison with the literature.<sup>11-13</sup>

 Table S2 Structural characteristics from integration of <sup>1</sup>H–<sup>13</sup>C correlation signals in the 2D 

Samples –	Inter-unit linkages (/100Arc)			Lignin aromatic units (%)			
	β-O-4′	$\beta - \beta'$	$\beta$ –5'	S	G	Н	
EL	27.51	0.32	4.01	39.8	24.3	35.9	
EL-25	27.33	0.20	3.99	35	22.9	42.1	
EL-60	26.98	0.14	3.87	22.9	17	60.1	

HSQC spectra of EL and regenerated lignin.

# References

- C. Cai, Y. Bao, X. Zhan, X. Lin, H. Lou, Y. Pang, Y. Qian and X. Qiu, *Green Chem.*, 2019, 21, 1141-1151.
- B. Yan, K. Li, L. Wei, Y. Ma, G. Shao, D. Zhao, W. Wan and L. Song, *Bioresour. Technol.*, 2015, 196, 509-517.
- 3. Z. Ai-Ping, L. Chuan-Fu, S. Run-Cang and X. Jun, *BIORESOURCES*, 2013, 8, 1604-1614.
- 4. J. S. Murray and P. Politzer, *WIREs Comput. Mol. Sci.*, 2017, 7, e1326.
- M. I. Cabaco, M. Besnard, Y. Danten and J. A. Coutinho, J. Phys. Chem. A., 2012, 116, 1605-1620.
- M. I. Cabaco, M. Besnard, Y. Danten and J. A. Coutinho, J. Phys. Chem. B., 2011, 115, 3538-3550.
- 7. T. Lu and F. Chen, J. Comput. Chem., 2012, **33**, 580-592.
- 8. E. R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garcia, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 6498-6506.
- 9. J. L. Wen, S. L. Sun, B. L. Xue and R. C. Sun, *Materials*, 2013, 6, 359-391.
- 10. W. Liu, R. Zhou, H. L. Goh, S. Huang and X. Lu, ACS Appl. Mater. Interfaces, 2014, 6, 5810-5817.

- 11. J. S. Luterbacher, A. Azarpira, A. H. Motagamwala, F. Lu, J. Ralph and J. A. Dumesic, *Energ. Environ. Sci.*, 2015, **8**, 2657-2663.
- S. Constant, H. L. J. Wienk, A. E. Frissen, P. d. Peinder, R. Boelens, D. S. van Es, R. J. H. Grisel, B. M. Weckhuysen, W. J. J. Huijgen, R. J. A. Gosselink and P. C. A. Bruijnincx, *Green Chem.*, 2016, 18, 2651-2665.
- 13. S. D. Mansfield, H. Kim, F. Lu and J. Ralph, Nat. Protoc., 2012, 7, 1579-1589.