

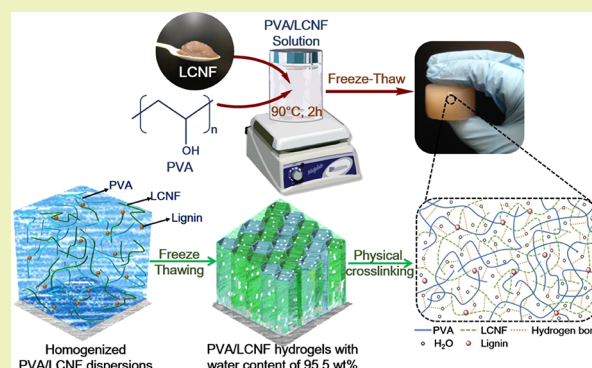
## Lignin-Containing Cellulose Nanofibril-Reinforced Polyvinyl Alcohol Hydrogels

Huiyang Bian,<sup>†,‡</sup> Liqing Wei,<sup>‡</sup> Chunxiang Lin,<sup>‡,§</sup> Qianli Ma,<sup>‡,||</sup> Hongqi Dai,<sup>†</sup> and J.Y. Zhu<sup>\*,‡,§</sup><sup>†</sup>Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing 210037, China<sup>‡</sup>Forest Products Laboratory, U.S. Forest Service, U.S. Department of Agriculture, Madison, Wisconsin 53726, United States<sup>§</sup>College of Environment and Resources, Fuzhou University, Fuzhou 350108, China<sup>||</sup>State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China

## Supporting Information

**ABSTRACT:** Two lignin-containing cellulose nanofibril (LCNF) samples, produced from two unbleached kraft pulps with very different lignin contents, were used to produce reinforced polyvinyl alcohol (PVA) hydrogels. The effects of LCNF loading (0.25–2 wt %) and lignin content on the rheological and mechanical properties of the reinforced hydrogels were investigated. The 2 wt % LCNF-reinforced PVA hydrogels exhibited up to a 17-fold increase in storage modulus and a 4-fold increase in specific Young's modulus over that of pure PVA hydrogel. Both the mechanical and rheological properties of LCNF-reinforced PVA hydrogels can be tuned by varying LCNF loading and LCNF lignin content. During LCNF production, lignin reduced cellulose depolymerization, resulting in LCNF with high aspect ratios that promoted entanglement and physical bridging of the hydrogel network. Free lignin particles generated during LCNF production acted as multifunctional nanospacers that increased porosity of the hydrogels. Because LCNFs were produced from unbleached chemical pulps, which have high yields and do not require bleaching, this study provides a more sustainable approach to utilize lignocelluloses to produce biomass-based hydrogels than by methods using commercial bleached pulps.

**KEYWORDS:** Lignin containing cellulose nanofibrils (LCNFs), Hydrogel, Polyvinyl alcohol (PVA), Rheological and mechanical properties



## INTRODUCTION

Hydrogels are soft and three-dimensional structural materials with very high water content, and when made using lignocelluloses, they are nontoxic, biocompatible, and biodegradable with antibiofouling properties.<sup>1</sup> As a result, hydrogels have been widely applied in many fields, for example, as scaffolds for tissue engineering, as vehicles for drug delivery, and 3D matrices for cell cultures.<sup>2–4</sup> Hydrophilic polyvinyl alcohol (PVA) can form physically and/or chemically cross-linked hydrogels, owing to the hydroxyl groups in each of the repeating molecular units.<sup>5–8</sup> However, PVA hydrogels have poor mechanical properties, which can impede their applications.<sup>9,10</sup>

Incorporating carbon nanotubes, clay, or metallic particles can enhance the mechanical properties of hydrogels.<sup>11–13</sup> Cellulose nanomaterials (CNM), such as cellulose nanocrystals (CNCs) and nanofibrils (CNFs), are advantageous over inorganic nanomaterials owing to their reactive surfaces, high aspect ratios, and excellent mechanical properties.<sup>14–16</sup> The reinforcing effects of CNM on mechanical strength, cross-

linking, and rheological properties of PVA hydrogels have been studied.<sup>17–19</sup> These CNC or CNF reinforced PVA hydrogels were cross-linked through hydrogen bonds after cyclic freezing-thawing with or without cross-linking agents (Table 1).<sup>20</sup> They exhibited higher strength and storage modulus than those prepared by irradiation techniques;<sup>9,21</sup> however, multiple cyclic freezing-thawing is tedious and time-consuming.<sup>18</sup> Surface-oxidized cellulose whiskers have also been used as reinforcing agents to cross-link PVA hydrogels at a high loading of 3.88%.<sup>16</sup> Introducing a reversible cross-linking agent, such as borax, was an efficient pathway to generate network structure between polymer molecule chains.<sup>22,23</sup> Lu et al. found that incorporating microfibrillated cellulose (MFC) from bamboo pulp into the PVA-borax system resulted in reinforced hydrogels with self-healing and pH-responsive abilities.<sup>22</sup> The effects of particle size, aspect ratio, crystal structure, and surface charge of CNM

Received: November 10, 2017

Revised: February 13, 2018

Published: March 13, 2018

Table 1. Comparisons of Production Conditions between This Study and Literature Work for Producing Cellulose Nanofibril-Reinforced PVA Hydrogels

|                              | process                                         | T (°C) | thawing time (h) | PVA molecular weight and loading | nanocellulose loading                 | cross-linking agent | maximum $G'$ with LVR, $G'_{\max}$ (Pa) | energy consumption |
|------------------------------|-------------------------------------------------|--------|------------------|----------------------------------|---------------------------------------|---------------------|-----------------------------------------|--------------------|
| Chang et al. <sup>20</sup>   | freezing-thawing (−20 °C), 12 h, seven cycles   | 60     | 0.5              | DP = 1750 ± 50; 4 wt %           | CNF; 4 wt %                           | none                | approximately 5000                      | high               |
| Abitbol et al. <sup>18</sup> | freezing-thawing, 2–3 cycles                    | 90     | 6                | 25 kDa; 15 wt %                  | CNC; 0–3 wt %                         | none                | not detected                            | high               |
| Mithranyan <sup>17</sup>     | freezing-thawing (−18 °C), overnight, one cycle | 60     | 0.5              | 98000 g/mol; 10 wt %             | TEMPO oxidized MCC; 3.88 wt %         | none                | approximately 10000                     | medium             |
| Han et al. <sup>24,28</sup>  | chemical cross-linking                          | 90     | 2                | 146000–186000 g/mol; 2 wt %      | CNC and CNF; 1 wt %                   | Borax; 0.4 wt %     | 1715                                    | low                |
| Lu et al. <sup>22</sup>      | one-pot, chemical cross-linking                 | 90     | 2                | 75000–80000 g/mol; 4 wt %        | MFC; 0.5–5 wt %                       | Borax; 0.4 wt %     | 11380                                   | Medium             |
| this study                   | freezing-thawing (−20 °C), 4h, one cycle        | 90     | 2                | 89000–98000 g/mol; 4 wt %        | CNF, LCNF-IL and LCNF-hL; 0.25–2 wt % | none                | 7724                                    | low                |

on the rheological properties of the composite hydrogels formed with borax were investigated. A plausible mechanism for complexation between CNM, PVA, and borax was proposed.<sup>24</sup>

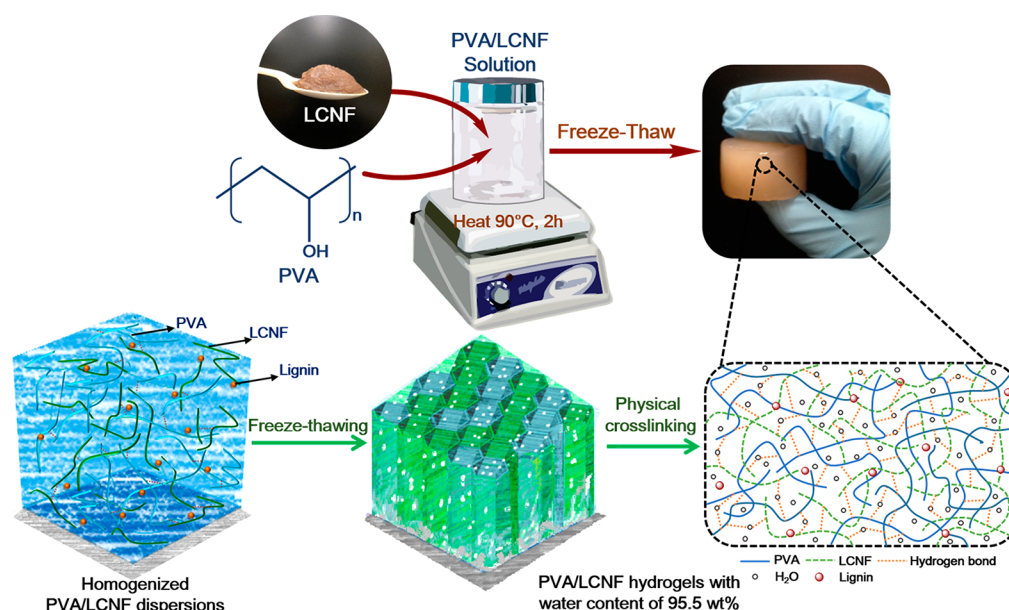
CNC or CNF used in reported studies on PVA hydrogels such as those mentioned above were all produced from fully bleached chemical pulp fibers. We are not aware of publicly available studies on the production of lignin-containing cellulose nanofibril (LCNF) reinforced PVA hydrogels. Producing lignin-containing cellulose nanomaterials such as LCNF is more environmentally sustainable by elimination of bleaching chemicals, which also results in higher yields.<sup>25</sup> Furthermore, LCNF can be directly produced from raw lignocellulosic biomass using low cost and environmentally friendly fractionation without the need for using commercial pulps.<sup>26,27</sup> Moreover, lignin serves as a binder to hold the major biopolymers in lignocelluloses together, therefore, LCNF can be a promising reinforcement polymer for PVA matrix.

The objective of the present study is to demonstrate the utility of lignin containing carboxylated LCNF as a polymer reinforcement for producing PVA hydrogels through an efficient and facile one freeze–thawing cycle, rather than multiple cycles in the literature. The small amount of free lignin separated from starting wood fibers through mechanical fibrillation during LCNF production could play a positive role, acting as nanospacers to increase the porosity of 3D-hydrogel networks. The effects of aspect ratio and the loadings of LCNF on the density, water content, viscoelastic, and compression properties of hydrogels were investigated. The development of physically cross-linked PVA structure reinforced by carboxylated LCNF may extend this technology to polymer chemistry and open new application potentials for valorization of lignocelluloses.

## MATERIALS AND METHODS

**Materials.** Lignin-free and lignin-containing cellulose nanofibrils were produced from bleached dry lap eucalyptus kraft pulp (Aracruz Cellulose, Brazil) and unbleached virgin mixed hardwood pulp fibers (complementarily provided by International Paper Company, USA), respectively. The CNF and LCNF production process included maleic acid hydrolysis at 60 wt % acid concentration and 120 °C for 120 min followed by 5 passes through a microfluidizer (M-110EH, Microfluidics Corp., Westwood, MA), as described previously.<sup>25</sup> These cellulose nanofibril samples were labeled as CNF (lignin-free), LCNF-IL (low lignin content of 4.6%), and LCNF-hL (high lignin content of 17.2%). The basic properties of these (L)CNF samples were presented in a previous study,<sup>25</sup> and their morphologies are shown in Figure S1. The CNF and LCNF suspensions were sealed in plastic containers and stored at 5 °C in a refrigerator until they were used. Polyvinyl alcohol (PVA, Mw = 89000–98000 g/mol, 99% hydrolyzed) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Deionized (DI) water was used in the preparation of all solutions.

**Preparation of Hybrid PVA-CNF and PVA-LCNF Hydrogels.** Hybrid hydrogels of PVA with varied contents of CNF or LCNF were prepared via a one-pot reaction system as schematically shown in Figure 1. CNF or LCNF aqueous suspension (0.25–2 wt %) were added into a 25 mL conical flask with continuous stirring at room temperature for 30 min. PVA powder was gently added into the stirred suspension. The final PVA loading was 4 wt % in the (L)CNF suspension for all hydrogels. The mixtures were stirred for another 30 min to avoid the formation of PVA lumps. After complete swelling of the PVA powder, the solution was heated at 90 °C in an oil bath with magnetic stirring for 2 h. A hermetically sealed flask was used for heating to prevent water evaporation. The PVA powder was gradually dissolved, and the solution became homogeneous with increasing time. Finally, the solution was cooled to ambient temperature to form a



**Figure 1.** Schematic illustration of the preparation and synthesis process of the PVA-CNF (or LCNF) hydrogels via the freezing-thawing method.

**Table 2.** Physical, Rheological and Mechanical Properties of CNF or LCNF Reinforced PVA Hydrogels at Different CNF or LCNF Loadings

| material        | water content (wt %) | maximum $G'$ with LVR at $\omega = 10$ rad/s, $G'_{\max}$ (Pa) | $G''$ with LVR at $\omega = 10$ rad/s (Pa) | compression stiffness $E$ at $\varepsilon = 20\%$ (kPa) | energy absorption at $\varepsilon = 50\%$ (kJ/m <sup>3</sup> ) |
|-----------------|----------------------|----------------------------------------------------------------|--------------------------------------------|---------------------------------------------------------|----------------------------------------------------------------|
| PVA             | 94.7                 | 237.2                                                          | 26.0                                       | 2.081                                                   | 0.46                                                           |
| PVA-CNF         |                      |                                                                |                                            |                                                         |                                                                |
| PVA-0.25CNF     | 95.3                 | 456.6                                                          | 58.8                                       | 2.629                                                   | 0.55                                                           |
| PVA-0.5CNF      | 95.2                 | 645.7                                                          | 83.3                                       | 3.000                                                   | 0.57                                                           |
| PVA-1CNF        | 94.8                 | 840.3                                                          | 120.2                                      | 4.591                                                   | 0.78                                                           |
| PVA-2CNF        | 93.6                 | 4513.8                                                         | 841.0                                      | 19.06                                                   | 1.26                                                           |
| PVA-LCNF-IL     |                      |                                                                |                                            |                                                         |                                                                |
| PVA-0.25LCNF-IL | 95.5                 | 547.5                                                          | 72.2                                       | 4.200                                                   | 0.60                                                           |
| PVA-0.5LCNF-IL  | 95.2                 | 874.2                                                          | 107.7                                      | 3.888                                                   | 0.64                                                           |
| PVA-1LCNF-IL    | 94.7                 | 1468.5                                                         | 244.8                                      | 10.89                                                   | 0.84                                                           |
| PVA-2LCNF-IL    | 93.6                 | 4403.3                                                         | 901.3                                      | 15.08                                                   | 1.47                                                           |
| PVA-LCNF-hL     |                      |                                                                |                                            |                                                         |                                                                |
| PVA-0.25LCNF-hL | 95.3                 | 492.3                                                          | 66.4                                       | 3.180                                                   | 0.57                                                           |
| PVA-0.5LCNF-hL  | 95.1                 | 1287.3                                                         | 203.4                                      | 3.520                                                   | 0.66                                                           |
| PVA-1LCNF-hL    | 94.4                 | 2701.6                                                         | 500.0                                      | 3.829                                                   | 0.86                                                           |
| PVA-2LCNF-hL    | 93.0                 | 7724.8                                                         | 1426.7                                     | 9.976                                                   | 1.62                                                           |

stable PVA-(L)CNF aqueous solution. No additional reinforcement agents were added throughout the entire process. The solution was then placed in an ultrasonic water bath for 5 min to remove air bubbles. The resultant uniform solution was poured into a cylindrical plastic beaker and stored in a freezer at  $-18^{\circ}\text{C}$  overnight to freeze the sample. Only one freeze–thawing cycle was applied, which can substantially increase productivity and therefore overall production cost.

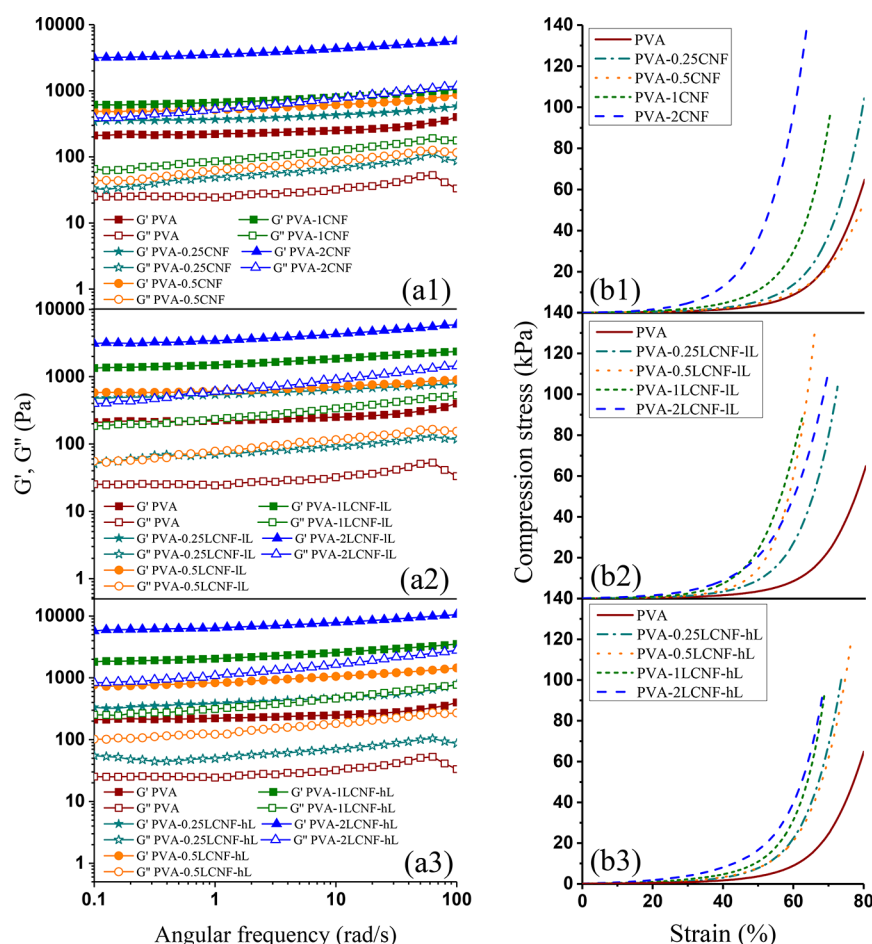
**Water Content of Hydrogels.** Each hydrogel specimen was first taken out of the sealed vials and weighed after removing excess water using a tissue paper. The water content ( $W_c$ ) of the hydrogel was calculated using eq 1:

$$W_c = \frac{W_i - W_d}{W_i} \times 100\% \quad (1)$$

Where  $W_i$  is the initial weight of hydrogel and  $W_d$  is the weight of hydrogel after oven drying at  $105^{\circ}\text{C}$  overnight.

**Dynamic Viscoelastic Analyses.** The rheological behavior of pure PVA and PVA-CNF (or LCNF) hydrogels was analyzed using an Anton Paar MCR302 Rheometer (Anton Paar, Ashland, VA, USA) with a parallel plate geometry 25 mm in diameter. Samples were prepared in the form of disks with a diameter of approximately 20 mm and a thickness of 1 mm. The dynamic strain sweep from 0.01 to 100% at an angular frequency  $\omega = 10$  rad/s was first performed at  $25^{\circ}\text{C}$ . The storage modulus ( $G'$ ) was recorded to define the linear viscoelastic region (LVR) within which the storage modulus is independent of strain. Oscillatory frequency sweeps were measured over the  $\omega$  range of 0.1–100 rad/s at  $25^{\circ}\text{C}$ .

**Compression Tests of Hydrogels.** Uniaxial compression stress–strain measurements were performed using an Instron 5544 mechanical tester (Instron Canton, MA, USA) equipped with a 1000 N load cell. Due to the slightly uneven top surface of the



**Figure 2.** (left) Angular frequency dependence of shear storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of PVA hydrogels reinforced by CNF or LCNF at various loadings: (a1) PVA-CNF, (a2) PVA-LCNF-IL, and (a3) PVA-LCNF-hL, measured at shear strain  $\gamma = 0.1\%$ . (right) Compression stress–strain curves of the same hydrogels in the left panel: (b1) PVA-CNF, (b2) PVA-LCNF-IL, and (b3) PVA-LCNF-hL.

hydrogels, a preload of 0.1 N was used to stabilize the cylindrical hydrogel samples (approximately 34 mm in diameter based on the vial internal diameter and cut with a knife into 8 mm in height). Each specimen was compressed vertically at a rate of 0.2 mm/s at 25 °C in air.<sup>28</sup> Compression stress, strain, and energy absorption values were calculated from measured forces and sample displacements based on the initial dimensions of the hydrogels.

**FE-SEM.** To observe the pore distribution and microstructure of pure PVA and PVA-CNF (or LCNF) hydrogels, the cross section was exposed by fracturing the hydrogel in liquid nitrogen. The morphologies were obtained by field-emission scanning electron microscopy (FE-SEM, Nova NanoSEM 230, FEI, USA). The liquid nitrogen fractured hydrogels were freeze-dried, then cut with a razor blade, and coated with gold before imaging.

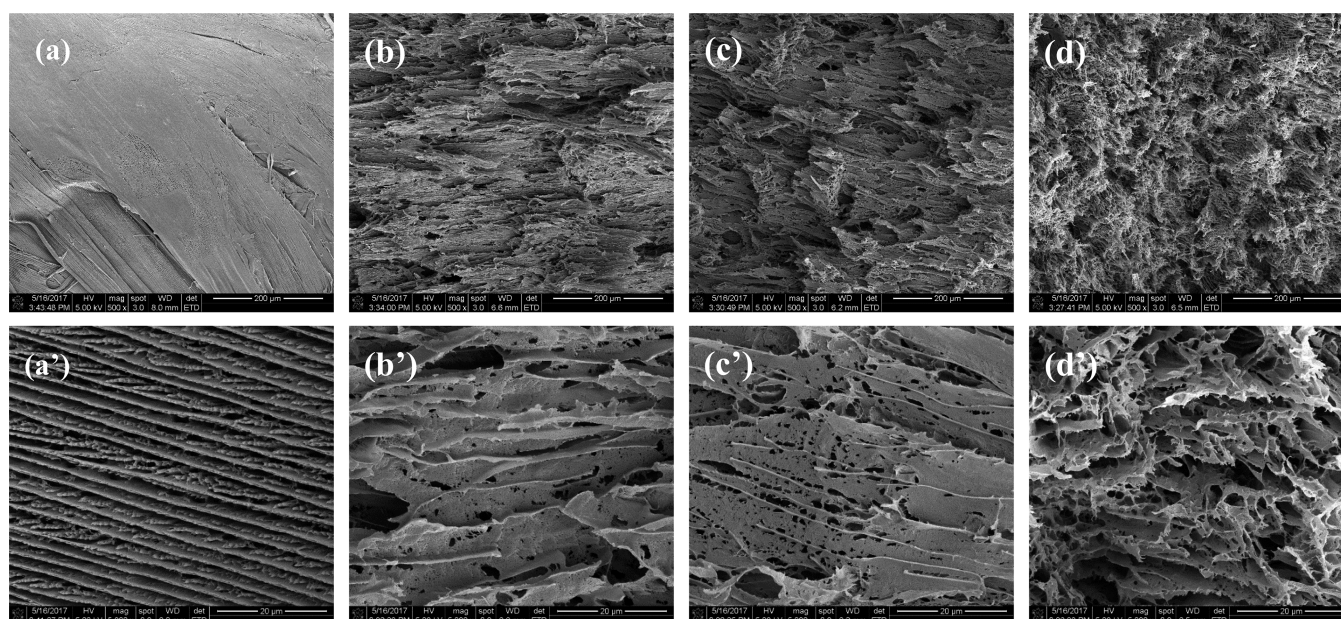
**FTIR.** FTIR spectra of the hydrogels were obtained on a commercial Fourier-transform infrared spectrometer (Spectrum Two, PerkinElmer, UK) using a universal attenuated-total-reflection (ATR) probe over the wavenumber range of 4000–400  $\text{cm}^{-1}$ . All samples were freeze-dried prior to analyses.

**X-ray Diffraction (XRD).** X-ray diffraction patterns of the pure PVA and PVA-CNF (or LCNF) hydrogels were obtained using an X-ray diffractometer (Bruker D8 Discover, Bruker Co., Billerica, MA) equipped with Cu  $K\alpha$  radiation in the range of 10–38° in steps of 0.02°. All freeze-dried samples were pressed at 180 MPa to make pellets and were dried again in a vacuum oven at 40 °C for 24 h to remove moisture before measurements.

## RESULTS AND DISCUSSION

**Water Content and Dynamic Viscoelasticity of Hydrogels.** As listed in Table 2, the water content of the hydrogels decreased with increasing solid content of CNF or LCNF; however, they remained at a high level of roughly 94% due to the strong hydrogen bonds and sufficient interaction between the hydroxyl groups of adjacent polymer strands. It was also noted that the PVA-LCNF hydrogels were translucent or opaque due to the presence of lignin, while the pure PVA and PVA-CNF hydrogels have good transparencies.

To understand the influence of the types of cellulose nanofibrils on the viscoelastic properties of hydrogels, a shear strain ( $\gamma$ ) of 0.1% was chosen in the dynamic strain sweep tests to ensure that the dynamic oscillatory deformation of each sample was within the linear viscoelastic region (Figure S2). Both shear storage modulus  $G'$  and loss storage modulus  $G''$  values decreased with the increase in shear strain ( $\gamma$ ) (Table 2.) As expected, owing to the entanglement and cross-linking performance of CNF (or LCNF) in PVA hydrogels, CNF (or LCNF) reinforced hydrogels exhibited significantly higher  $G'$  and  $G''$  values, especially when the CNF or LCNF loading was increased to 2 wt % (Figure S2). For instance, the  $G'_{\text{max}}$  of PVA hydrogel with 2 wt % LCNF-hL was 7725 Pa, or 15 times greater than 492 Pa with 0.25 wt % LCNF-hL loading. Compared with hydrogels reinforced by CNF and LCNF-IL under the same CNF or LCNF contents, PVA-LCNF-hL



**Figure 3.** Field-emission scanning electron microscopy (FE-SEM) images of the fractured cross sections of pure PVA hydrogel (a, a') and PVA hydrogel reinforced by 2 wt % CNF (b, b'), LCNF-IL (c, c'), and LCNF-hL (d, d'). Scale bar = 200  $\mu\text{m}$  (top panel, a–d) and 20  $\mu\text{m}$  (bottom panel, a'–d').

hydrogel has a higher  $G'_{\text{max}}$ . At a higher lignin content, lignin molecules restrict the motion of PVA chains which results in a significant increase in  $G'$ . The nanofibrils act as physical cross-linkers by embedding themselves within the PVA chains, and above a specific CNF or LCNF loading, known as the rheological percolation threshold, all PVA chains become connected. This could hinder the mobility of individual polymer chains under shear force.

The changes in the  $G'$  (elasticity) and  $G''$  (viscosity) of the hydrogels in the angular frequency range of 0.1–100 rad/s were depicted in Figure 2a1–a3. No crossover of  $G'$  and  $G''$  occurred in the examined full frequency range, exhibiting typical solid-like characteristics. Before the incorporation of CNF or LCNF,  $G'$  and  $G''$  values of pure PVA (4 wt %) hydrogels were significantly lower throughout the entire frequency range. With the increase in the concentration of CNF, the  $G'$  and  $G''$  values of the CNF reinforced hydrogels measured at  $\omega = 10$  rad/s were 17 and 24 times greater than those of the pure PVA hydrogel, respectively (Table 2). Furthermore, PVA-LCNF-hL hydrogels showed the highest  $G'$  and  $G''$  values among all reinforced hydrogels with the same CNF or LCNF loading. Apparently, the entanglements of the cellulose nanofibrils, the physical restriction of polymer mobility by lignin, and the interactions between nanofibrils and lignin in the PVA matrix system are responsible for the observed viscoelastic properties of hydrogels.<sup>24</sup>

#### Compression Stress–Strain Behavior of Hydrogels.

The hydrogel compressive strength is an important property for many applications. All hydrogels exhibited an exponential relationship between compression stress and strain without an obvious plateau (Figure 2b1–b3), which caused difficulties in determining the maximal stress. The compressive stress and strain data can be well fitted by an exponential growth function  $y = A[\exp(Bx) - 1]$  (Figure S3, fitting parameters are listed in Table S1). The compressive stress at 20% strain and the energy absorption at 50% strain (Table 2) were used for comparing hydrogel mechanical properties. Within 20% strain, stress and

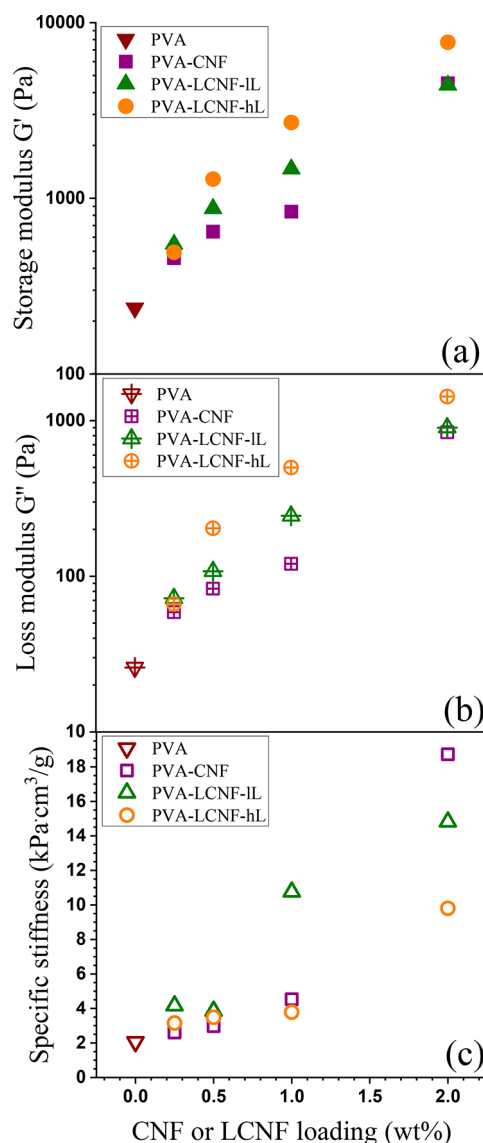
strain showed a linear relationship. It can be clearly seen that increasing the (L)CNF loading resulted in higher compression stress of hydrogel. Similar improvement in compression strength and energy absorption was also reported by Abitbol et al. using CNC at 1.5 wt % loading.<sup>17</sup> It was worth noting that the composites deformed greatly at low load of below 20 kPa; however, further increase in load resulted in much less deformation. The deformation at a low load range was mostly contributed by the compacting of cellulose fibrils with PVA in the matrix and the lost of free water that are not completely entrapped in the hydrogel matrix. Once this compacting caused deformation reaches its limit, further deformation becomes difficult because the hydrogel is made of mostly water, an incompressible liquid. It is well-known that lignin in plant cell wall protects cellulose degradation or depolymerization. This can be seen from the AFM images (Figure S1) of the two LCNF samples that have longer fibrils than the CNF sample. Furthermore, the LCNF-hL sample with a higher lignin content than LCNF-IL has even longer fibrils. The AFM topographic measurements of number-averaged heights were 13.4, 9.6, and 7.1 for CNF, LCNF-IL, and LCNF-hL, respectively.<sup>25</sup> The longer but thinner fibrils (based on AFM mean heights) of LCNF, especially LCNF-hL, certainly promote fibril entanglement (Figure S1). Therefore, incorporating LCNF into PVA hydrogels can improve rheological and mechanical properties.

The entangled cellulose nanofibrils act as physical cross-linker to maintain mechanical integrity of the hydrogels.<sup>23</sup> Visual observations during experiments indicated that CNF or LCNF were well-dispersed in the aqueous PVA systems under continuous stirring without forming visible aggregates; this dispersion facilitated the transfer of compressive stress from PVA polymer chains to CNF or LCNF and inhibited the growth of microcracks.<sup>29</sup> The microstructures of the fractured cross sections of the PVA hydrogel and its composites containing 2.0 wt % CNF or LCNF with different lignin contents were observed by field-emission scanning electron microscopy (FE-SEM) as shown in Figure 3. The fracture

surfaced of a pure PVA hydrogel was rather flat and smooth with regular layered structure in the cross sectional direction (Figure 3a, 3a'), while the addition of CNF or LCNF to the PVA hydrogel resulted in a fine, micron porous network structure (Figure 3b–d). The layered structure was still visible from the hydrogels with CNF (Figure 3b') or LCNF-IL (Figure 3c'). When CNF or LCNF were added into the PVA matrix, flocculation occurred during ice crystal growth. It is worth noting that PVA with LCNF showed less layered structure and appeared more porous; this is especially apparent by comparing the pure PVA hydrogel with LCNF-hL reinforced PVA hydrogel (Figure 3d and d'). It is plausible that free lignin particles (Figure S1), separated from LCNF during fibrillation, behaved as spacers to avoid self-aggregation of cellulose nanofibrils as shown in Figure S4. The improved porous structure and the enhanced interactions between CNF and the PVA matrix lead to superior compressive performance for LCNF reinforced PVA hydrogels. It should be pointed out that quantification of free lignin in a LCNF sample is very difficult. The free lignin and the lignin in LCNFs are chemically identical. The diameters of free lignin particles are in the same range of those LCNFs. Moreover, the amount of free lignin is much lower than LCNFs, i.e., only a couple of percent of LCNF based on the highest lignin content in LCNF of 17% and the amount of free lignin of around 10% or lower of the LCNF lignin. Therefore, good separation free lignin from LCNF for quantifying free lignin using chemical or physical methods is very challenge. Future study is needed to examine the effect of free lignin particles on PVA-CNF hydrogels by purposely spiking various levels of free lignin in the hydrogels.

The specific stiffness values determined from derivatives of the fitted exponential stress–strain relation at different strains (Table S2) were used to further characterize hydrogel mechanical properties.<sup>30</sup> At a constant PVA loading of 4 wt %, increasing the CNF or LCNF loading also increased hydrogel specific shear storage and loss modulus as well as the specific compression stiffness as shown in Figure 4. A plausible mechanism for this phenomenon was presented in Figure 1. CNF and PVA suspension could form physical cross-linking upon mixing.<sup>31</sup> The growth of ice crystals in the freezing–thawing process can form a gel-like structure from cross-linked aggregates.<sup>32</sup> The presence of PVA and CNF can form three types of complexes, namely PVA–PVA, PVA–CNF, and CNF–CNF, throughout the whole process. The lignin nanoparticles separated from LCNF in the system acted as spacers to support a porous network structure as revealed by FE-SEM (Figure 3). The presence of small pores in the hydrogel increased surface area and also could withstand a stronger compression force.<sup>33</sup> It is the combination of the improved reinforcement by LCNF and the porous structure by the small nanoparticles of cellulose fibrils and lignin that resulted in an improved compression strength of LCNF-PVA hydrogel (Figure 2a–c). However, results from testing single sample cannot discern the effects of lignin on hydrogel specific stiffness (Figure 4c, Table S2). Future study is needed.

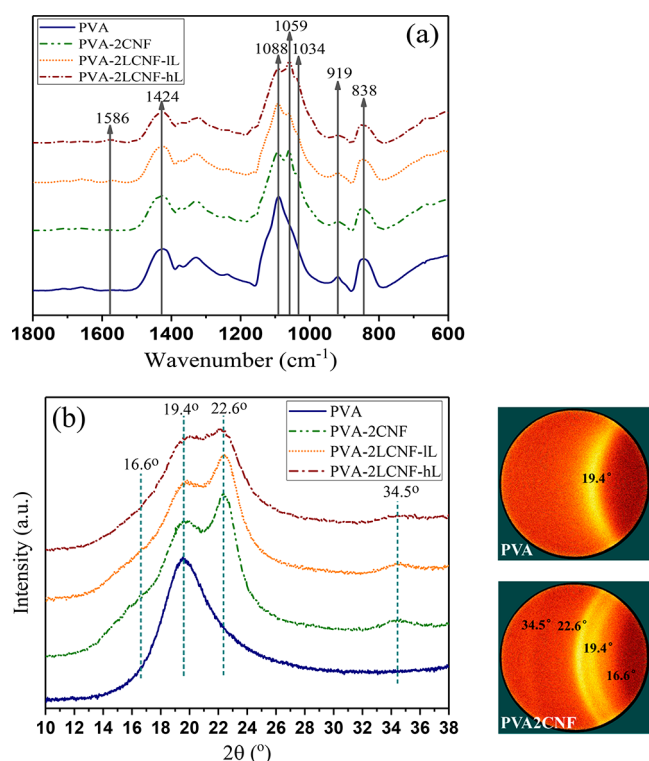
**FTIR and XRD Analysis.** As displayed in Figure 5a, the absorption bands of PVA occurring at 838, 919, 1088, and 1424  $\text{cm}^{-1}$  were attributed to the stretching of C–O, bending of  $-\text{CH}_2$ , rocking of  $-\text{CH}$ , and stretching of  $-\text{CH}$ , respectively.<sup>34</sup> The FTIR spectra illustrated the presence of CNF or LCNF in PVA-CNF (or LCNF) hydrogels, demonstrated by some characteristic peaks at 1034 and 1059  $\text{cm}^{-1}$ . These peaks were associated with the vibration stretch of C–OH bonds in



**Figure 4.** Effects of CNF or LCNF loading on (a) shear storage modulus ( $G'$ ), (b) loss modulus ( $G''$ ) measured at shear strain  $\gamma = 0.1\%$  and angular frequency  $\omega = 10$  rad/s, and (c) specific compression stiffness of reinforced PVA hydrogels measured at 20% strain. PVA loading was 4 wt % for all samples.

secondary and primary alcohols of cellulose, respectively.<sup>34,35</sup> A weak band was observed around 1586  $\text{cm}^{-1}$  in the PVA-LCNF-IL and PVA-LCNF-hL samples that was not present in PVA and PVA-CNF hydrogels. This band corresponds to the aromatic skeletal vibration of lignin.<sup>36</sup> Furthermore, the decreased peak intensities at 1088 and 838  $\text{cm}^{-1}$  for the PVA-CNF (or LCNF) hydrogels suggested changes in the crystallization of PVA due to the addition of CNF (or LCNF). This result might demonstrate the expected interaction of hydroxyl groups of PVA matrix with the hydrophilic surfaces of cellulose nanofibrils.

Diffraction patterns of PVA and PVA-CNF (or LCNF) hydrogels are shown in Figures 5b and 5c. The pure PVA hydrogel showed a diffraction peak at  $2\theta = 19.4^\circ$ , being assigned to the orthorhombic lattice structure of semicrystalline PVA.<sup>24</sup> With the incorporation of CNF (or LCNF) into the PVA system, some new diffraction peaks formed, which are located at around  $16.6^\circ$ ,  $22.6^\circ$ , and  $34.5^\circ$ , corresponding to the



**Figure 5.** (a) FTIR spectra and (b) X-ray diffractograms of pure PVA and PVA reinforced by 2 wt % CNF (or LCNF) hydrogels. PVA loading was 4 wt % for all samples.

(110), (200), and (004) reflection planes of typical cellulose I structure, respectively.<sup>37</sup> Note that the diffraction peaks of PVA became weaker with the increase in lignin and CNF or LCNF contents (Figures 5b and S3). This suggests the strong interactions between the hydroxyl radicals of PVA with CNF and LCNF, as well as the complexation between them which destroyed the well-organized PVA structure. Furthermore, the presence of lignin in PVA-LCNF hydrogels had no effect on the cellulose crystal structure of composite hydrogels but weakened the intensity of diffraction peaks.

## CONCLUSIONS

LCNF-reinforced PVA hydrogels were successfully produced in an aqueous medium without adding initiators or chemicals. By respectively incorporating three kinds of cellulose nanofibrils (i.e., CNF, LCNF-IL, and LCNF-hL) to PVA aqueous systems, the viscoelastic properties and specific compression stiffness of the composite hydrogels were remarkably improved, especially using the LCNF with a high lignin content of 17%. The well-dispersed LCNF in the polymer matrix acted as multifunctional cross-linking agents to enhance the interactions between LCNF and PVA. Lignin, especially the lignin nanoparticles separated from LCNF during LCNF production, served as nanospacers, which effectively prevented the aggregation of polymers and increased the PVA porosity. Both the mechanical and rheological properties of LCNF reinforced PVA hydrogels can be tailored by varying the LCNF loading and lignin content. Because LCNFs can be more sustainably produced than CNF with high yield and without bleaching, this study has practical significance in improving the utilization of lignocellulosic materials for a variety of applications.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b04172.

**Figure S1** AFM topographic images of CNF (a), LCNF-IL (b), and LCNF-hL (c), respectively. **Figure S2** Strain dependence of shear storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of CNF or LCNF reinforced PVA (4 wt % loading) hydrogels: (a) PVA-CNF; (b) PVA-LCNF-IL; (c) PVA-LCNF-hL measured at angular frequency  $\omega = 10$  rad/s. **Figure S3** Typical fits of compression stress–strain data by an exponential growth function  $y = A[\exp(B \cdot x) - 1]$  (fitting parameters are listed in Table S1). **Figure S4** AFM image of the suspension of hydrogel 4PVA-2LCNF-hL showing the presence of free lignin particles as a spacer between cellulose nanofibrils as well as within the PVA matrix. **Figure S5** X-ray diffractograms of PVA (4 wt % loading) hydrogels reinforced by CNF or LCNF at varied loadings. **Table S1** Fitting results of hydrogel compression stress and strain data using an exponential function:  $y = A[\exp(B \cdot x) - 1]$ . **Table S2** Hydrogel stiffness at different strain rates calculated from the fitted stress function:  $y' = A \cdot B \cdot \exp(B \cdot x)$  (PDF)

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: jzhu@fs.fed.us. Tel.: +1-608 231 9520.

### ORCID

J.Y. Zhu: 0000-0002-5136-0845

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was partially supported by US Forest Service, the National Natural Science Foundation of China (Project No. 31470599), and the Doctorate Fellowship Foundation of Nanjing Forestry University. We also would like to acknowledge Dr. Goyal Gopal and his colleagues of International Paper Company for complementarily providing us the unbleached mixed hardwood pulp samples, and Jane O'Dell, Carlos Baez, and Sara Fishwild of our Laboratory for assisting in rheology testing, XRD analyses, and mechanical testing, respectively.

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