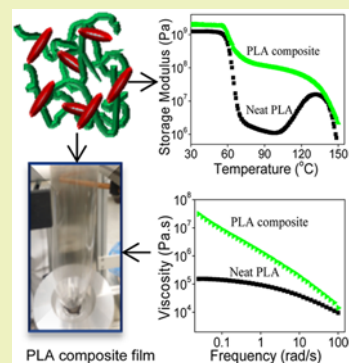


Rheological and Thermo-Mechanical Properties of Poly(lactic acid)/Lignin-Coated Cellulose Nanocrystal Composites

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S Supporting Information

ABSTRACT: Improving the processability and physical properties of sustainable biobased polymers using biobased fillers is essential to preserve its biodegradability and make them suitable for different end user applications. Herein, we report the use of spray-dried lignin-coated cellulose nanocrystals (L-CNCs), a biobased filler, to modify the rheological and thermo-mechanical properties of poly(lactic acid) (PLA) composites. The lignin coating on CNCs not only improved the dispersion of CNCs but also enhanced their interfacial interaction with the PLA matrix, resulting in a significant improvement in rheological and thermo-mechanical properties. The rheological percolation threshold concentration obtained by power law analysis for PLA/L-CNC composites was found to be 0.66 wt %, which is significantly lower than the reported values for other PLA/CNC composites. Such a low rheological percolation concentration of L-CNCs can be attributed to excellent dispersion of L-CNCs in the PLA matrix. Addition of only 0.5 wt % L-CNCs to the PLA matrix resulted in an almost 60% improvement in storage modulus, relative to neat PLA, as measured by dynamic mechanical analysis. This improvement in mechanical properties can be attributed to a significant increase in the degree of crystallinity of the PLA. Excellent dispersion and compatibility of L-CNCs with PLA allowed generation of a high density of nucleating sites resulting in an increase in the degree of crystallinity of the PLA matrix. Improvement in the storage modulus at higher loading of L-CNCs can be attributed to both high crystallinity and reinforcement by L-CNCs. We have readily prepared a fully biobased transparent and potentially biodegradable PLA film through film blowing by addition of just 0.3 wt % L-CNCs in the PLA matrix. This present study clearly demonstrates that L-CNCs can serve as excellent fillers for PLA for the development of fully biobased composites.



KEYWORDS: Cellulose nanocrystal, Dispersion, Crystallinity, Mechanical properties, Film blowing, Percolation threshold

■ INTRODUCTION

Renewable biobased polymers and composites derived from natural resources are generating great interest due to depleting fossil fuel resources and the negative environmental impact of fossil fuel-based plastic products.¹ Many biobased polymers have been developed over several decades which show great potential for different applications; however, their processing and physical properties are still not sufficient for many end user applications. The poor processing and physical properties of these polymers can be attributed to lower molecular weight, low crystallinity, and high moisture uptake. Incorporation of physical cross-link points in the polymer matrix by addition of fillers or nanofillers has shown promises to improve the melt rheology and mechanical properties.² However, the effectiveness of fillers and nanofillers strongly depends on the quality of the dispersion and distribution in the polymer matrix. Fillers derived from unsustainable sources can achieve good dispersion, but incorporation of these fillers significantly compromises the biocompatibility and biodegradability of biobased polymers. Many types of biobased fillers have also been studied in regard to modifying the properties of biobased polymers.³ Among biobased fillers, cellulose nanocrystals

(CNCs) are attractive materials to improve the performance of biobased polymers without compromising their sustainability, and inherent properties. CNCs can be obtained by acid hydrolysis of cellulose fibers,^{4,5} which is one of the most abundant natural biopolymers on Earth and has been recognized as an excellent reinforcing agent due to its excellent strength, biodegradability, high aspect ratio, and low density.^{6,7} Several studies have shown that both processing and physical properties of a polymer matrix can be modified by incorporation of CNCs. CNCs have a tendency to form agglomerates upon incorporation in a polymer matrix due to its hydrophilic nature and potential to form strong intermolecular hydrogen bonds. These properties have prevented the realization of the full potential of CNCs as a reinforcing phase. The presence of CNC aggregates in a composite act as stress concentration points which are detrimental to mechanical properties. Different approaches have been developed to improve the dispersion and interfacial adhesion of CNCs

Received: October 10, 2016

Revised: December 16, 2016

Published: January 6, 2017



within the polymer matrix including solution mixing, reactive compatibilization, ring opening polymerization, and surface modification of CNCs. Surface-modified CNCs not only improved the mechanical properties of polymer composites but also modified the melt flow behavior of polymer matrices which can significantly facilitate processing.^{8–22} Although, surface modifications of CNCs can improve compatibility and dispersion with hydrophobic polymers, such harsh chemical treatment often leads to loss in its intrinsic properties and also adds to the overall cost of the material.

An alternative approach to improve the dispersion of CNCs in a polymer matrix is through addition of a compatibilizing material such as a surfactant, starch, lignin, etc. Lignin is particularly interesting in this regard as it is biobased, formed in woody plants along with cellulose, and has been observed to improve the interfacial interaction between CNCs and hydrophobic polymers.^{23–27} Lignin is the second most abundant biobased polymer on Earth. It is an amorphous macromolecule composed of repeating phenyl propane units with aliphatic and aromatic hydroxyl groups and carboxylic acid groups. These functional groups play a significant role in improving the interaction between hydrophobic polymers and CNCs through H-bonding and van der Waal interactions. Recent studies clearly indicate that the addition of lignin improves the adhesion between biopolymers and natural fillers, such as cotton and cellulose;^{27,28} however, its efficiency depends on the compounding parameters and lignin concentration. Since lignin is also relatively difficult to disperse and the formation of a lignin–CNC complex depends on concentration of these two components, added lignin can only help in minimizing the reagglomeration of CNCs but may not play a significant role in their initial dispersion. In order to maximize the benefit of lignin to disperse CNCs in a polymer matrix, the use of lignin-coated CNCs is an attractive proposition.

Poly(lactic acid) (PLA) is one of the most important biobased polymers, and it shows great potential in packaging, drug delivery, and biological scaffolds applications. However, the mechanical and processing properties of PLA alone are not adequate for many of these applications. In a recent study, we reported that lignin-coated CNCs (L-CNCs) can be dispersed in PLA by high torque melt mixing and that it acts as nucleating agents for the PLA matrix in composites.²⁹ We believe the lignin coating on the CNCs helped in both initial dispersion and also avoided reaggregation of CNCs in the polymer matrix. The presence of lignin on the CNCs surface might have also allowed PLA chains to fold onto the L-CNC's surface through better compatibility. Improved interaction between lignin and PLA may also allow efficient load transfer between CNCs and the polymer matrix. Therefore, lignin-coated CNCs have the potential to be an excellent filler to improve the mechanical properties and processing behavior of PLA. In the present study, lignin-coated CNCs were dispersed and distributed in the PLA matrix using high torque melt mixing, and their rheological and thermo-mechanical properties were studied. The current work demonstrates that L-CNCs improve the mechanical performance and processing behavior of a biobased PLA with the potential of maintaining its biodegradability and biocompatibility.

EXPERIMENTAL SECTION

Materials. Commercial grade L-poly(lactic acid) (L-PLA) was procured from NatureWorks with the trade name Ingeo™ TM biopolymer 4043D. Spray-dried lignin-coated cellulose nanocrystals

(L-CNCs) were provided by American Process, Inc. (API) in powder form.^{30,31} Transmission electron microscopy (TEM) was used to determine the average length and diameter of L-CNCs, which were ~350 and ~5–7 nm, respectively (Figure S1). Before melt mixing, all the materials were dried in a vacuum oven at 90 °C for 2 h to avoid possible degradation due to moisture during processing.

Preparation of PLA/L-CNC Composites. PLA/L-CNC composites were prepared by melt mixing using a HAAKE Rheocord 90 melt mixer. PLA and L-CNCs, 66.5 g, were mixed manually by shaking them together in a jar and then adding them to the melt mixer portion wise over ~1 min at an initial temperature of 140 °C with a mixer speed of 40 rpm. The mixing was continued for 11 min during which time the temperature increased to 160 °C with a steady-state torque, after the loading spikes, of 14.7 N·m. A master-batch of 5 wt % L-CNCs was prepared and then diluted in a second melt mixing step with the appropriate amount of neat PLA to prepare 0.3, 0.5, 0.7, 1.0, 2.0, and 2.5 wt % samples of PLA/L-CNCs. The samples obtained after dilution were designated as neat PLA, PLA/L-CNCs-0.3%, PLA/L-CNCs-0.5%, PLA/L-CNCs-0.7%, PLA/L-CNCs-1.0%, PLA/L-CNCs-2.0%, and PLA/L-CNCs-2.5%, respectively.

Flat panels, 17.5 mm × 13 mm × 3 mm, of neat PLA and PLA/L-CNC composites were prepared by compression molding using a “picture frame” tool in a Wabash G30H-15-CPX hot press at 170 °C and 5 tons. Melt flow indices (MFI) and FTIR were run on as-received PLA, PLA that had been melt mixed for 20 min and then compression molded and the 0.3 L-CNC composite to verify little or no degradation of the PLA occurred during processing (Supporting Information). Disks, 25 mm in diameter, were stamped out from the panels for rheological characterization. Samples for dynamic mechanical analysis (DMA) were also machined from the PLA panels.

Films for optical microscopy were prepared by melting the PLA/L-CNC composites on a glass slide at 150 °C, followed by pressing the melted samples to form a thin film with a cover glass.

For film blowing, neat PLA and PLA/L-CNCs-0.3% pellets were prepared by melt mixing using a Haake Rheomex TW100 conical intermeshing counter-rotating twin screw extruder. Before melt mixing, PLA and L-CNCs were vacuum-dried at 90 °C for 2 h. The temperature in the first, second, third, and fourth zones of the extruder were maintained at 160 °C, and the screw speed was 40 rpm. Extruded strands were quenched in water and then cut into small pellets using Berlyn Pel-2 pelletizer.

The dried pellets were processed using a Haake Rheomex 254 single screw extruder with screw diameter of 3/4 in., L/D = 25, and compression ratio of 3:1. The extruder was equipped with a blowing head having an orifice of 5 mm diameter. The temperature of all three zones of the extruder and the die were maintained at 160 °C. The screw speed and take up line speed coupled with pressurized air were used to control the balloon stability and blow up ratio. A screw speed of 25 rpm, line speed of 170 rpm, and blow up ratio of 1:24 gave the optimum processing conditions for film blowing.

Characterization of PLA/L-CNC Composites. Rheological measurements were carried out on a TA Instruments ARG2 equipped with a parallel plate geometry using circular disks (25 mm diameter and 3 mm thick). All the samples were tested at 150 °C after drying at 80 °C to prevent hydrolysis of the specimens. Dynamic strain sweep measurements were carried out to determine the linear viscoelastic regime (LVR) at a frequency of 6.28 rad/s. Then, dynamic frequency sweep measurements (0.01–100 rad/s) were carried out for all the samples at a strain value of 1% (LVR). Dynamic mechanical analysis was carried out on a TA Instruments ARG2 fitted with a rectangular geometry fixture in torsion mode to study the effect of L-CNCs on the viscoelastic properties of PLA composites. The scans were recorded in the temperature range of 30–150 °C at a heating rate of 3 °C/min at a frequency of 6.28 rad/s. A minimum of two samples of each composite were tested, and the data was found to lay over each other. A TA Instruments Q2000 differential scanning calorimeter (DSC) was used for recording DSC scans (heating and cooling) under N₂. About 8–10 mg of sample in a closed aluminum pan was placed in the DSC. The sample was first heated from room temperature to 200 °C at a heating rate of 10 °C/min and then held at that temperature for 5 min to

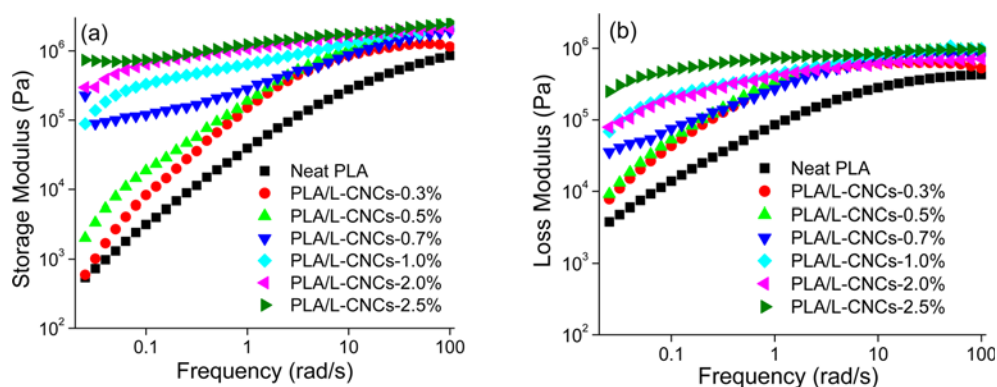


Figure 1. Storage (G') and loss modulus (G'') of PLA/L-CNC composites at 150 °C as a function of frequency.

remove the thermal history of the material. The sample was then cooled to 25 °C at a rate of 10 °C/min and again heated to 200 °C at the same rate. The degree of crystallinity, X_c , was calculated based on the enthalpy of melting (ΔH_m) measured from the area of the endothermic peak, using the following equation:

$$X_c = \frac{\Delta H_m}{(1 - \text{mass of L-CNC}) \times \Delta H_m^0} \times 100 \quad (1)$$

For the X_c calculation, 93.0 J/g was used as the heat of fusion (ΔH_m^0) for 100% crystalline PLA.³² The second heating scans obtained for PLA/L-CNC composites were used to calculate X_c , except for the annealed and quenched samples, where the first heating scans were used. For the annealed and quenched samples, X_c was calculated by subtracting the ΔH_c value from ΔH_m , and the resulting ΔH_m value was used to calculate X_c of these samples. Since no exothermic peak was observed during cooling, the ΔH_m value was used to calculate X_c of the PLA/L-CNC composites. XRD scans were also recorded to investigate the effect of L-CNCs on crystal morphology of the PLA (Supporting Information). A Micromaster optical microscope was used to investigate the distribution of L-CNCs in the PLA matrix. Images were taken at 10× magnification and analyzed using ImageJ software. Morphology of the PLA composites was investigated using a FEI NOVA nanoSEM field emission scanning electron microscope (FEI company, Hillsboro, OR) operating at 5 kV accelerating voltage, with an ~3.5–4.0 mm working distance, and 50 μm aperture. Sample strips were frozen in liquid N₂ and snapped to produce pieces with free broken surfaces. All samples were sputter coated for 60 s with Pt prior to imaging.

RESULTS AND DISCUSSION

Rheological Behavior of PLA/L-CNC Composites. The rheological properties of PLA/L-CNC composites at 150 °C as a function of frequency (ω) are shown in Figure 1. Addition of L-CNCs led to a dramatic increase in both storage (elastic, G') and loss (viscous, G'') moduli of PLA/L-CNC composites. The effect is more prominent in the low frequency region. Neat PLA and the composites with low L-CNCs loading (up to 0.5 wt %) show terminal flow behavior, whereas at higher L-CNCs loading (>0.5 wt %) terminal flow behavior was not observed. The terminal flow behavior of fully relaxed homodispersed polymer chains are very well-known in the literature and obeys the power law relations, $G' \sim \omega^2$ and $G'' \sim \omega$, in the low frequency region. For neat PLA, the power law index values obtained for G' and G'' are 1.58 and 0.97, respectively. The deviation from the theoretical exponent values of 2 for G' and 1 for G'' can be attributed to the polydispersity of the commercial PLA resin and the presence of the two lactide forms (L-lactide and D-lactide).¹⁵ However, a wide range of power law index values have been reported in the literature for PLA and its

composites. Incorporation of L-CNCs in the PLA matrix gradually weakens the low-frequency power-law dependence of G' and G'' on ω and thus decreases the slope of G' and G'' vs ω curves. Similar to the viscoelastic moduli, the complex viscosity also exhibits a strong dependency on added L-CNCs (Figure 2). The complex viscosity of the PLA/L-CNC composite

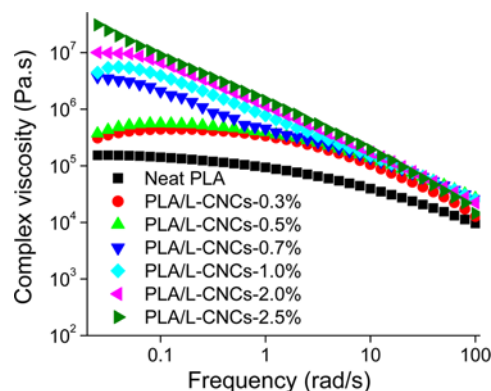
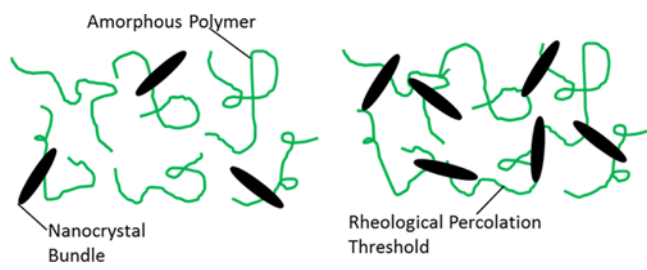


Figure 2. Complex viscosity at 150 °C as a function of frequency for PLA/L-CNC composites.

increases gradually up to 0.5 wt % L-CNC loading and then increases dramatically as the loading was further increased. This increase in complex viscosity is primarily due to the dramatic increase in G' , as shown in Figure 1. At L-CNC loadings higher than 0.5 wt %, the nanocrystals restrict the motion of PLA chains which results in a significant increase in G' and thus viscosity. Frequency also has a prominent effect on viscosity of the PLA/L-CNC composites. The complex viscosity of neat PLA and the composites decreases with increasing frequency exhibiting non-Newtonian behavior. The shear thinning behavior observed can be attributed to disentanglement and orientation of L-CNCs and PLA chains in the flow direction reducing the viscous resistance. Dramatic change in PLA moduli and complex viscosity in the loading range of 0.5–0.7 wt % L-CNCs (Table 1) clearly indicates transition from liquid to solid-like viscoelastic behavior of the PLA composites. The liquid to solid-like transition of the composites arises through the formation of an interconnected network of polymer chains and nanofiller particles (Scheme 1). The nanofiller acts as physical cross-linking points, and above a specific nanofiller loading, known as the rheological percolation threshold concentration, all polymer chains become connected which inhibits mobility of individual chains under shear force. As

Table 1. Change in Low-Frequency Slopes of G' and G'' vs ω and Cole–Cole Plot for PLA/L-CNC Composites

sample designation	slope of G' vs ω	slope of G'' vs ω	slope of Cole–Cole plots
neat PLA	1.58	0.97	1.52
PLA/L-CNCs-0.3%	1.44	0.96	1.49
PLA/L-CNCs-0.5%	1.46	0.95	1.47
PLA/L-CNCs-0.7%	0.23	0.55	0.96
PLA/L-CNCs-1.0%	0.44	0.43	1.12
PLA/L-CNCs-2.0%	0.33	0.43	0.86
PLA/L-CNCs-2.5%	0.16	0.26	1.09

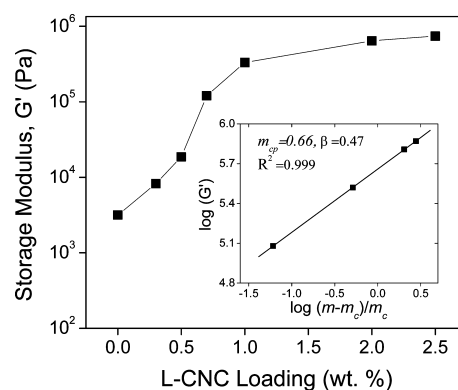
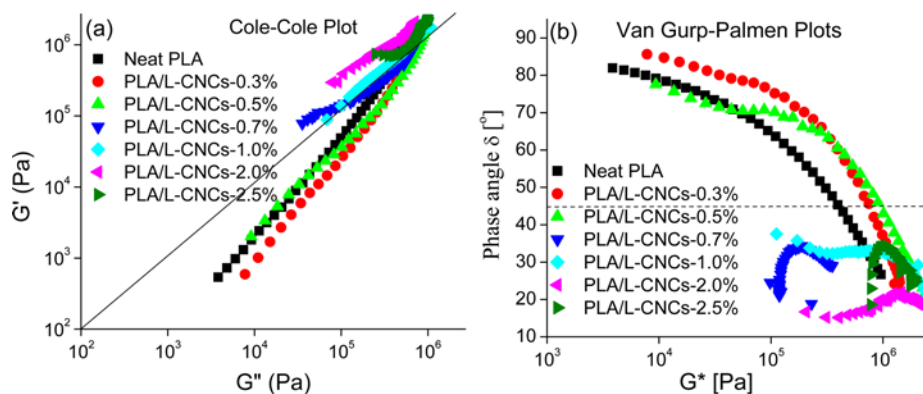
Scheme 1. Scheme of Formation of Percolating Network Structure in PLA/L-CNC Composites

mobility of the polymer chains becomes restricted, the polymer matrix exhibits a significant change in its flow behavior.

Cole–Cole plots, i.e., frequency dependence of G' vs G'' , are an important tool to identify structural changes in a polymer matrix due to the incorporation of fillers.^{33–35} Polymer composites near the percolation threshold show a dramatic change in the slope of G' vs G'' curves due to the formation of a network structure. Below the percolation threshold, rheological and processing behavior of the composites is very similar to the neat polymer. However, above the percolation threshold the presence of fillers impedes the motion of the polymer chains resulting in a change in rheological properties. Figure 3a shows G' vs G'' curves for neat PLA and PLA/L-CNC composites. It is shown that the slope of the G' vs G'' curve decreases with increasing L-CNCs loading (Table 1). When the L-CNCs loading exceeds 0.5 wt %, the slope of the curves change drastically, indicating a significant change in the microstructure of the composites. Similar observations can also be drawn from van Gurp–Palmen plots (Figure 3b), where the phase angle (δ) is plotted against complex modulus (G^*).^{36,37} The phase angle is the phase difference between the applied strain and measured stress. For purely elastic material, the stress and strain waves are

always in phase ($\delta = 0^\circ$). On the other hand, a purely viscous material exhibits the two waves out of phase ($\delta = 90^\circ$). Figure 3b shows that for neat PLA and the composites containing L-CNCs up to 0.5 wt %, the G'' dominates over G' , and curves approach a phase angle of 90° indicating viscous behavior. However, at higher L-CNC loading (>0.5 wt %), all of the composites exhibit a phase angle value below 45° indicating dominance of G' over G'' . The drop in phase angle is directly related to the development of the solid-like structure in the PLA matrix through formation of physically cross-linked structures as depicted in Scheme 1.^{36,37}

Although, it is clear that network-like structure or rheological percolation in PLA/L-CNC composites occurs between 0.5 and 0.7 wt % L-CNCs loading, for many practical applications, it is important to know the onset of percolation concentration, also known as the critical L-CNC concentration. The low frequency G' data can be fitted to a power-law equation to determine critical L-CNC concentration (Figure 4). In general, the power

**Figure 4.** Storage modulus as a function of L-CNC loading for PLA/L-CNC composites at a frequency of 0.1 rad/s.**Figure 3.** Determination of percolation threshold concentration (a) storage modulus (G') vs loss modulus (G'') and (b) phase angle (δ) vs complex modulus (G^*) plots for PLA/L-CNC composites.

law describes the rheological behavior of an incipient gel within the viscoelastic region. Considering formation of a gel-like structure of polymer composites near percolation, the power-law relationship as shown below (eq 2) was used.³⁸

$$G' \propto (m - m_c)^\beta \quad (2)$$

where G' is the storage modulus, m is volume fraction of the L-CNCs, m_c and β are the rheological percolation threshold concentration and the critical exponent that describe the fractal properties of the percolating medium, respectively. The density of L-CNCs and PLA was taken 1.5 and 1.24 g/cm³, respectively, to convert mass fraction to volume fraction. Linear regression analysis was used to fit the double logarithmic plot of G' and L-CNC loading. The critical rheological percolation concentration (m_{cp}) and critical exponent β obtained from the best fit line are 0.66 wt % and 0.47, respectively. As per the authors' knowledge, except Bagheriasl et al.,¹⁸ all other studies on PLA/CNC composites reported a much higher percolation threshold concentration for CNCs.^{14,15} Bagheriasl et al.¹⁸ prepared PLA/CNC composites using low aspect ratio (6 ± 2) CNCs and found rheological percolation at fairly low CNC loading, 0.68 wt %. They attributed such low percolation concentration to the excellent dispersion of CNCs which was achieved through sonication followed by solution mixing. In the present study, an even lower percolation threshold concentration of the PLA/L-CNC composite prepared by simple melt mixing is obtained which clearly shows the importance of the lignin coating in achieving good dispersion of CNCs in the polymer matrix. To estimate the extent of L-CNC dispersion, we calculated the effective aspect ratio of L-CNCs in the polymer matrix using the relationship between critical rheological percolation concentration (m_{cp}) and average aspect ratio (A_f) of filler as follows:³⁹

$$A_f = \frac{3m_{\text{sphere}}}{2m_{cp}} \quad (3)$$

where $m_{\text{sphere}} = 0.29$ is the percolation concentration for randomly packed three-dimensional interpenetrating spheres⁴⁰ and $m_{cp} = 0.0066$ is the onset of rheological percolation concentration for the PLA/L-CNC composites. The aspect ratio of L-CNCs obtained from eq 3 is ~ 65 , which is very close to the value reported for the L-CNCs used in this study. This result indicates that the L-CNCs are very well dispersed and distributed in the PLA matrix and thus significantly influence the rheological properties of the PLA/L-CNC composites. Such a low rheological percolation threshold concentration and high effective aspect ratio of L-CNC in the PLA matrix clearly suggest that the lignin coating helps in achieving good dispersion of CNCs by promoting initial dispersion and preventing reaggregation of the CNC after initial dispersion and distribution.

Dynamic Mechanical Analysis (DMA). Figure 5 shows the plots of storage modulus (G') vs temperature for neat PLA and the composites having varying L-CNCs loadings. The composites show significantly higher G' than the neat PLA at all loadings of L-CNCs. It is interesting to note that all of the composites exhibit higher modulus in both the glassy and rubbery regions as compared to neat PLA. Upon heating, all of the composites exhibit a large drop in G' at 50–70 °C corresponding to the glass transition region, followed by a relatively gradual drop across the rubbery plateau, up to the melting point except for the neat PLA. Reduction in G' with

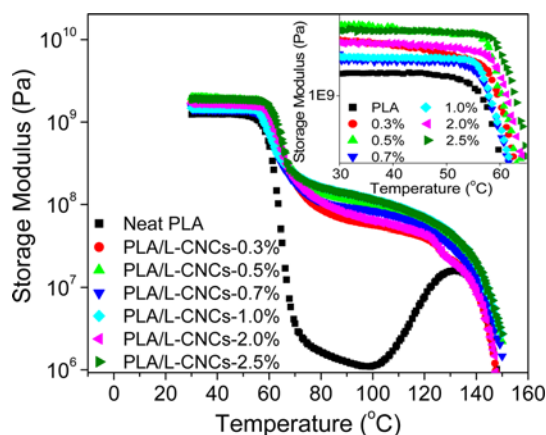


Figure 5. DMA scans at 1 Hz for neat PLA and PLA/L-CNC composites showing change in storage modulus as a function of temperature (inset shows increase in storage modulus in glassy region).

respect to temperature is related to softening of the PLA at higher temperature. As the temperature exceeds the softening point, mobility of the PLA chains increases leading to a sharp decrease in modulus at temperatures between 50 and 70 °C. The sharp increase in storage modulus of neat PLA at temperatures around 100 °C arises due to cold crystallization in PLA,⁴¹ which can be easily seen in the DSC scans of PLA. Similarly, the loss modulus (G'') was also found to increase with increasing L-CNC loading.

The effect of L-CNCs on the damping behavior of PLA, i.e., plot of $\tan \delta$ vs temperature is shown in Figure 6. The PLA/L-

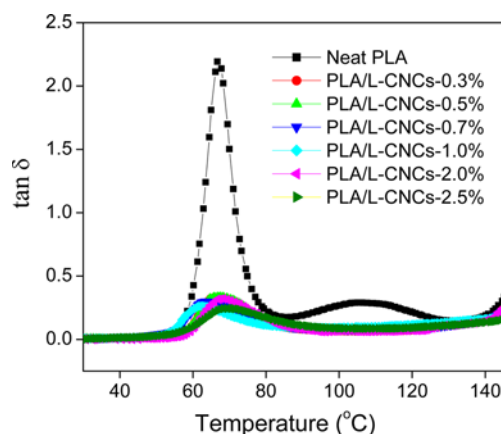


Figure 6. Plot of $\tan \delta$ vs temperature for neat PLA and PLA/L-CNC composites at 1 Hz.

CNC composites exhibit a dramatic decrease in the $\tan \delta$ peak height relative to the neat PLA. The height of the $\tan \delta$ peak is associated with the chain mobility of the amorphous region in the polymer composites. As shown in Figure 6, the height of $\tan \delta$ plots decreased in the composites on addition of L-CNCs, whereas the peak position remains unchanged. The lack of a shift in the $\tan \delta$ peak position indicates that L-CNC had no effect on the glass transition temperature (T_g) but significantly affected the chain mobility in the amorphous region due to confinement effect resulting in the reduction in $\tan \delta$ peak height. The increase in crystallinity upon addition of L-CNCs also has an impact in dropping the intensity of $\tan \delta$ due to a reduction in the amorphous content.

It is well-known that fillers play an important role in determining the mechanical properties of a material. Prediction of a composite's modulus through micromechanics models helps in understanding the effect of filler reinforcement on the mechanical properties of the materials. The modified Halpin–Tsai equation is one of the most used empirical approaches to predict the modulus of particulate-filled polymer composites.⁴² Assuming that L-CNCs are randomly oriented in the PLA matrix, we can calculate the modulus of a composite with the modified Halpin–Tsai equation.⁴³ The elastic modulus (E_{PLA}) for PLA and the composites was calculated using the relationship between elastic (E') and shear modulus (G'). A Poisson ratio (ν) of 0.36 was used for PLA.⁴⁴

$$E = G' \times 2(1 + \nu) \quad (4)$$

Halpin–Tsai equation

$$E_c = \left[\left(\frac{3}{8} \right) \left(\frac{1 + 2(l_{\text{L-CNC}}/d_{\text{L-CNC}})\eta_L V_{\text{L-CNC}}}{1 - \eta_L V_{\text{L-CNC}}} \right) + \left(\frac{5}{8} \right) \left(\frac{1 + 2\eta_T V_{\text{L-CNC}}}{1 - \eta_T V_{\text{L-CNC}}} \right) \right] E_{\text{PLA}} \quad (5)$$

where

$$\eta_L = \frac{(E_{\text{L-CNC}}/E_{\text{PLA}}) - 1}{(E_{\text{L-CNC}}/E_{\text{PLA}}) + 2(l_{\text{L-CNC}}/d_{\text{L-CNC}})}$$

$$\eta_T = \frac{(E_{\text{L-CNC}}/E_{\text{PLA}}) - 1}{(E_{\text{L-CNC}}/E_{\text{PLA}}) + 2}$$

where E_c , E_{PLA} , and $E_{\text{L-CNC}}$ are the moduli of the composites, PLA and L-CNC, respectively; $l_{\text{L-CNC}}/d_{\text{L-CNC}}$ is the ratio of the length to the diameter, i.e., the aspect ratio for the L-CNCs, and $V_{\text{L-CNC}}$ is the volume fraction of L-CNCs in the composites. To fit eq 5 to the experimental results for the PLA/L-CNC composites, the weight fraction was transformed to the volume fraction with the densities of PLA, 1.24 g/cm³, and L-CNCs, 1.5 g/cm³.⁴⁵ The values of the composite modulus can be estimated taking the aspect ratio of ~58 and $E_{\text{L-CNC}}$ of ~115 GPa for L-CNCs.⁶ The modulus of L-CNCs used in this study represents an average value of the modulus in the axial direction. The calculated and the experimental storage modulus of PLA/L-CNC composites were plotted against L-CNC loading and are shown in Figure 7. The experimental results

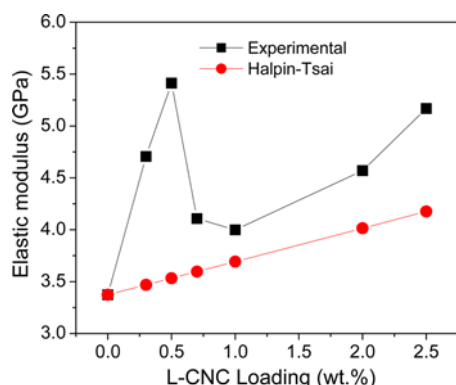


Figure 7. Experimental and calculated values of storage modulus of PLA/L-CNC composites as a function of L-CNC loading. The calculated value was determined using Halpin–Tsai equation (eq 5).

for the PLA/L-CNC composites are higher than those predicted values at all L-CNC loadings. The effect is more pronounced at lower L-CNC loading. At L-CNC loading of 0.3 and 0.5 wt %, the composites displayed ~40% and 60% improvement over the neat PLA matrix, respectively. On further addition of L-CNCs, the composites initially exhibited a reduction in G' ; however, G' improved at higher L-CNC loadings.

The observed improvement in G' of PLA composites can be attributed to restricted polymer chain mobility due to (1) an increase in degree of crystallinity, (2) restricted mobility of polymeric chains in the presence of L-CNCs,^{46,47} or (3) a synergistic effect of (1) and (2). The degree of crystallinity (X_c) of PLA was calculated from the second DSC heating scans of neat PLA and the composites (Table 2). The X_c increased and

Table 2. Thermal Properties of PLA and PLA/L-CNC Composites

sample designation	T_g (°C) ^a	ΔH_m (J/g) ^b	T_c (°C) ^b	X_c (%) ^b
neat PLA	57.9	5.4	129.3	5.8
PLA/L-CNCs-0.3%	58.3	37.1	112.5	40.0
PLA/L-CNCs-0.5%	55.9	35.8	114.8	38.6
PLA/L-CNCs-0.7%	55.7	35.0	118.0	37.9
PLA/L-CNCs-1.0%	60.0	32.0	113.2	34.8
PLA/L-CNCs-2.0%	56.9	30.0	114.6	32.9
PLA/L-CNCs-2.5%	56.5	31.5	117.2	34.7

^aDetermined during the first heating scan on extruded samples (10 °C/min). ^bDetermined during the second heating scan on extruded samples (10 °C/min).

cold crystallization temperature (T_c) decreased in the composites relative to neat PLA. The maximum change in the X_c and T_c was observed at 0.3 wt % L-CNC loading, where the X_c of the PLA increased from ~6 to 40% and T_c decreased from ~129 to 112 °C. However, at the highest filler loading, i.e., 2.5% L-CNC, X_c was 34% and T_c was 117 °C. The dramatic improvement in crystallization behavior of PLA at low loading can be attributed to the excellent dispersion and improved interfacial interaction between L-CNCs and PLA chains. Excellent dispersion of L-CNCs led to a high number of nucleating sites resulting in a high degree of crystallinity. At higher L-CNCs loading, reduction in the degree of crystallinity was due to agglomeration of L-CNCs as shown in optical micrographs (Figure 8) of the PLA/L-CNC composites. The optical micrographs suggest that the composites contain aggregates in the range from ~0.1 to 30 μm (Figure 8b–d) and that the number and size of aggregates increases with increasing L-CNC loadings. However, the aggregate size for the as-received spray dried L-CNCs is ~30 μm (Figure 8a). SEM imaging of cryo-fractured surfaces of the composites (Figure 9) also confirms the uniform distribution of L-CNCs in the PLA matrix of 0.3, 1.0, and 2.0 L-CNC at the nano scale. These results also show the efficiency of the mixing process that allowed opening of L-CNC bundles leading to the better dispersion and higher numbers of nucleating sites.

The modulus of the PLA composites at 35 °C were found to increase with loading up to 0.5% L-CNC and then drop sharply at 0.7% L-CNC loading. Above 0.7% L-CNC loading, the modulus increased gradually with increasing L-CNC loading. The enhanced modulus for the 0.3 and 0.5 wt % composites can be attributed to mechanical percolation, which is a well-known phenomenon in semicrystalline polymers.^{48–50} An

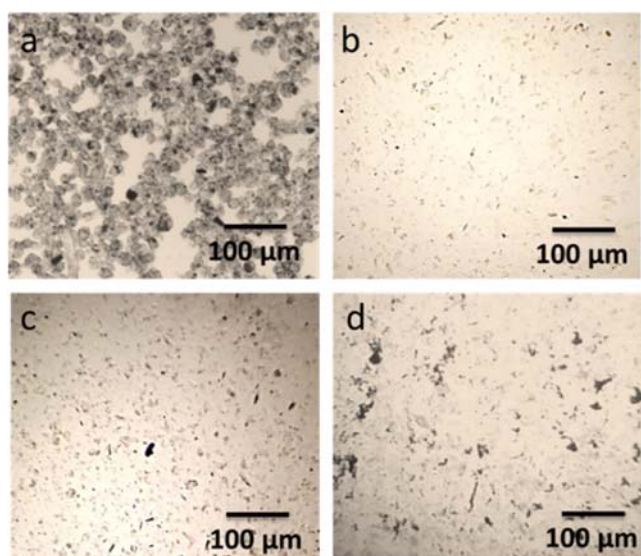


Figure 8. Optical microscope images of (a) spray-dried L-CNC powder and (b–d) for PLA/L-CNC composites containing 0.3, 1.0, and 2.0% (w/w) L-CNCs, respectively, showing the distribution of L-CNCs in composite films. Scale bar: 100 μm .

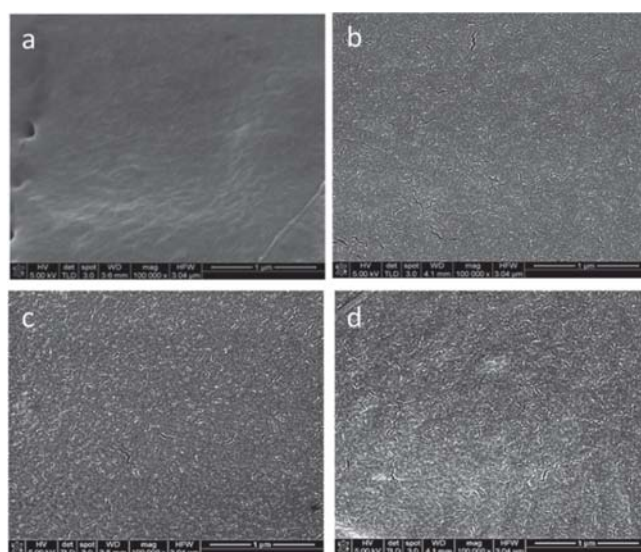


Figure 9. SEM images of (a) neat PLA and (b–d) for PLA/L-CNC composites containing 0.3, 1.0, and 2.0% (w/w) L-CNCs, respectively, showing the distribution of L-CNCs in PLA. Scale bar: 1 μm .

increase in the degree of crystallinity of a polymer matrix leads to an increase in modulus because individual crystals act as restriction sites. Above a critical volume fraction of crystals, or degree of crystallinity, the polymer matrix forms a network structure, and at this point, mechanical properties change drastically. In the present case, PLA exhibits mechanical percolation above 38% crystallinity (Figure S2). Above this point, the PLA crystals and chains form a network structure which leads to a significant improvement in modulus. The sudden drop in modulus at 0.7% L-CNCs can be attributed to a drop in crystallinity below the mechanical percolation threshold. Thus, it can be suggested that at lower L-CNC loading the higher G' is attributed to the high crystallinity of PLA composites, whereas at higher L-CNC loading both crystallinity

and chain restriction by L-CNCs play a role in improving the G' of the PLA matrix.

To better understand the role of crystallinity and the L-CNCs on thermo-mechanical properties of PLA, we prepared a crystalline PLA sample through annealing and a completely amorphous PLA/L-CNC composite through quenching. Annealing was performed at 90 $^{\circ}\text{C}$ for 12 h and the quenched sample was prepared by heating a sample to 150 $^{\circ}\text{C}$ and then immediately cooling it in ice-cold water. Figure 10a and b shows DSC and DMA scans for the annealed and quenched samples. The quenched sample exhibits a strong cold crystallization peak, and the annealed samples exhibits a broad low intensity cold crystallization peak on the first heating. The cold crystallization peak intensity of the quenched sample was very high, as it was almost completely amorphous. The degree of crystallinity calculated from the heat of fusion showed that the annealed sample was $\sim 23\%$ crystalline, whereas the quenched sample showed no crystallinity other than that induced on the first heating cycle.

The increase in degree of crystallinity of neat PLA after annealing led to a significant increase in its G' because the crystals act as restriction sites. The G' of the crystalline PLA was found to be in the range of the PLA/L-CNC composites (Figure 10b). In spite of lower crystallinity ($\sim 23\%$), similarity of the modulus of the annealed sample to that of the PLA/L-CNC composites can be attributed to short-range ordering of the PLA chain in the amorphous region⁵¹ as supported by the increase in T_g of the annealed sample (Figure 10a). Short range ordering strengthened the amorphous region and increased the overall modulus of the annealed sample. Therefore, at low L-CNC loading, the increase in crystallinity appears to be the dominant factor for the improvement in the modulus of the PLA/L-CNC composites. However, at higher L-CNC loading, the presence of L-CNC also contributes to the modulus of the composites. The amorphous sample (see DSC Figure 10) containing 0.7% L-CNC, prepared by quenching, still exhibits a higher modulus than the $\sim 6\%$ crystalline neat PLA matrix which suggests that the L-CNCs act as restriction sites and enhance the modulus of the sample. Thus, it is clear that at low loading crystallinity is the major factor, but at high loading, both crystallinity and L-CNCs contribute to the improvement in modulus of the composites. Such dramatic improvement in mechanical properties of PLA on addition of L-CNC suggests that lignin-coated CNCs are an excellent biobased filler to improve the mechanical properties of the PLA matrix.

Blown Film Processing of Neat PLA and PLA/L-CNC Composite.

PLA is primarily used in packaging applications, such as thin films, which are produced by the film blowing process. The thickness of the film is primarily controlled by the balloon diameter (Figure 11a) and throughput rate. The stability of the balloon is important for continuous production of polymer films. Among different factors, melt strength is the most important for dictating balloon size and stability. Some studies have reported that modified PLA and PLA blended with different fillers and plasticizers can be successfully used for the film blowing process.^{52,53} During the present study, we found that a very low loading of L-CNCs significantly enhances the melt viscosity and rate of crystallization of PLA matrix through excellent dispersion and interfacial interaction. Hence, we used L-CNCs to improve the film blowing properties of the PLA matrix. Figures 11a and b show blown film processing of neat PLA and PLA containing 0.3 wt % L-CNCs. The film blowing process for neat PLA was regularly interrupted by collapsing or

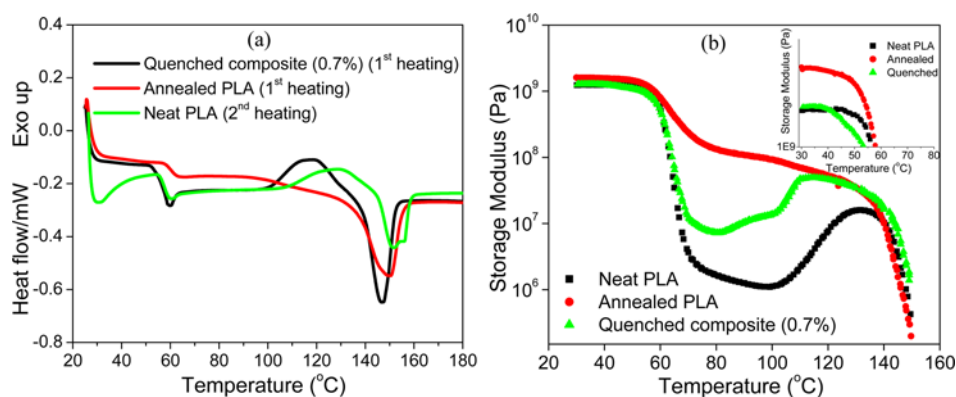


Figure 10. (a) DSC and (b) DMA scans for annealed PLA at 90 °C, quenched composites, and neat PLA. The DSC scan for the quenched sample (black) show a strong exothermic peak due to cold crystallization during heating cycle (inset in (b) shows change in storage modulus in glassy region).

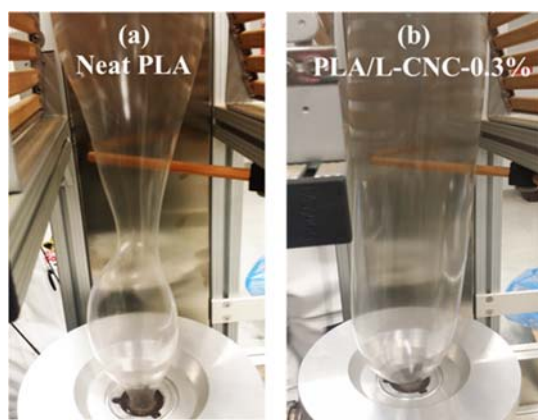


Figure 11. Picture of (a) neat PLA showing unstable balloon (with die temperature at 160 °C) and (b) PLA/L-CNC-0.3% composite with stable balloon (with die temperature at 160 °C).

bursting of balloons which diminished the quality of the film and increased the overall cost of the film. On the other hand, the balloon of the PLA/L-CNC film was very stable, and continuous production of the film was achieved. The continuous production of films can significantly lower the production cost and can help to reduce the overall cost of PLA films. Both PLA and PLA/L-CNC film were highly transparent as required for packaging applications. Thus, through application of a small amount of L-CNCs, continuous and fully biobased PLA films can be produced for end user applications.

CONCLUSION

Lignin-coated CNCs, a biobased filler, were used to prepare PLA composites by a simple melt mixing process. Incorporation of L-CNCs into the PLA matrix resulted in significant improvement in rheological properties as both the complex viscosity and moduli increased in the presence of L-CNCs. A dramatic improvement in melt viscosity and storage modulus in the low frequency region of the composite containing 0.7 wt % L-CNCs showed a liquid-like to solid-like transition indicating formation of a network structure. The rheological percolation concentration for the formation of an L-CNCs network was determined using a power law and was found to be 0.66 wt %, while the corresponding L-CNCs aspect ratio of ~ 65 was determined. Percolation at such a low loading is attributed to

excellent dispersion and distribution of L-CNCs in the polymer matrix due to good compatibility between the lignin and PLA matrix. Thermo-mechanical properties showed that excellent dispersion of L-CNCs and a high degree of crystallinity of PLA composites led to a significant improvement in storage modulus of the composites. Crystallization behavior of the PLA matrix was also found to improve significantly in the presence of L-CNCs. The ability of lignin-coated CNCs to improve the rheological and mechanical properties of the PLA matrix suggests that it can be an excellent filler for the development of PLA-based composites for biomedical and packaging applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b02458.

Information as mentioned in the text. (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge partial support of this work by the U.S. Forest Service Grants 11-JV-11111101-050 and 11-JV-11111129-030 and Dr. Kim Nelson from American Process Inc. for providing L-CNCs. We also acknowledge support from DOD Grant W911NF-14-1-0084 for the purchase of the PANalytical Empyrean XRD.

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