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# High Shear Homogenization of Lignin to Nanolignin and Thermal Stability of Nanolignin-Polyvinyl Alcohol Blends

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A new method to prepare nanolignin using a simple high shear homogenizer is presented. The kraft lignin particles with a broad distribution ranging from large micron- to nano-sized particles were completely homogenized to nanolignin particles with sizes less than 100 nm after 4 h of mechanical shearing. The <sup>13</sup>C nuclear magnetic resonance (NMR) and <sup>31</sup>P NMR analysis showed that there were no major changes in the chemical composition between the starting kraft lignin particles and the

nanolignin obtained after 4 h of mechanical treatment. The nanolignin particles did not show any change in molecular weight distribution and polydispersity compared to the original lignin particles. The nanolignin particles when used with polyvinyl alcohol (PVA) increased the thermal stability of nanolignin/PVA blends more effectively compared to the original lignin/PVA blends.

## Introduction

Lignin is one of the most abundant renewable resources in the world, next only to cellulose and hemicelluloses in the extent of occurrence.<sup>[1]</sup> The lignin fraction of biomass is an amorphous polymer that can be derived typically from up to three different monolignol units, coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol. These monomers are incorporated into lignin as phenylpropanoids such as guaiacyl, syringyl, and *p*-hydroxyphenyl units, and are linked together by different ether and carbon-carbon bonds forming a three dimensional network.<sup>[2]</sup> The type of lignin produced depends on the plant species. While softwood lignin is derived mainly from guaiacyl units, hardwood lignin is derived primarily from guaiacyl-syringyl units.<sup>[3]</sup> Large amounts of lignin are produced each year as a by-product in spent cooking liquor from the production of kraft pulps. Of this, only a small fraction is recovered and used for chemical and material applications whereas approximately 98% is directly burned in recovery furnaces for energy production and recovery of pulping chemicals.<sup>[4]</sup> The low-value

use of lignin and high capital cost associated with pulping chemical recovery furnaces has spurred research to convert lignin to various valuable products. Lignin derivatives have been shown to have antioxidant activity in human red blood cells,<sup>[5]</sup> antiviral activity in vitro,<sup>[6]</sup> antibiotic, and anticarcinogenic activities.<sup>[7]</sup> Lignosulfonates have also been used as binders,<sup>[8]</sup> dispersant agents for pesticides,<sup>[9]</sup> emulsifiers,<sup>[10]</sup> and heavy-metal sequestrants.<sup>[11]</sup> Lignin has also been used to modify the technical properties of various polymeric materials and has been used as an alternative to phenols in phenolic resins<sup>[12]</sup> and blends with polyolefin polymers.<sup>[13]</sup> It has also been used for making lignin-based thermoplastic polyesters,<sup>[14]</sup> precured polyurethanes,<sup>[15]</sup> active carbons, and carbon fibers.<sup>[4]</sup>

Preparation of lignin-based nanoparticles can provide a new approach for a high-value-added application of lignin-based products. Nanoparticles have a large surface area for a given volume and they often behave in a way different to micron-sized particles.<sup>[16]</sup> When mixed with various polymers, nanofillers may interact intimately with the polymer matrix when compared to their corresponding micro-sized or bigger particles.<sup>[17]</sup> Being evenly distributed in polymer matrices, these nanoparticles can increase the mechanical performance, thermal stability, and barrier properties of the resulting composites.<sup>[18]</sup> Jiang et al.<sup>[19]</sup> obtained nanolignin by fabricating colloidal lignin-poly(diallyldimethylammonium chloride) (PDADMAC) complexes through self-assembly. They dissolved purified lignin in a sodium hydroxide solution, which was slowly added to a PDADMAC solution under vigorous stirring, leading to the formation of colloidal lignin-PDADMAC complexes with different mass ratios. The use of this nanolignin significantly enhanced the thermal and mechanical properties of the natural rubber matrix. Qian et al.<sup>[20]</sup> used acetylated lignin (ACL) as an amphiphilic polymer to prepare lignin nanospheres through self-assembly. ACL was completely dissolved in tetrahydrofuran

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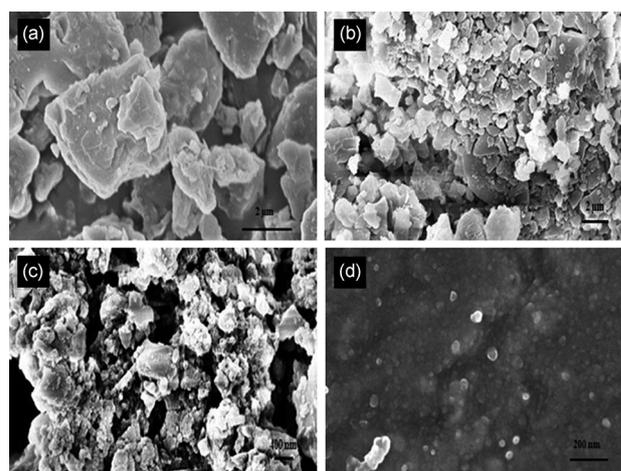
(THF) and thereafter colloidal lignin spheres were formed by gradual hydrophobic aggregation of molecules when water was added to the ACL/THF solution. In all reported nanolignin studies, lignin has to be either dissolved in a caustic aqueous solution or an organic solvent and then precipitated by adding water in the presence of a polyelectrolyte as stabilizer. Clearly, the polyelectrolyte will affect the lignin properties and its sustainability. Also, apart from characterizing the morphology or size determination, a detailed chemical or thermal characterization of nanolignin is lacking.

Owing to its biodegradability, renewability, abundance, and low cost, lignin is considered to be a good candidate as functional filler and reinforcement for a variety of polymers. Several studies have shown that the use of lignin or lignin derivatives can improve the mechanical and thermal properties of the polymeric materials.<sup>[21,22]</sup> Polyvinyl alcohol (PVA) is a nontoxic, highly polar, water-soluble, and biodegradable polymer,<sup>[23]</sup> which has been used in blends and composites with various polymers. PVA is widely used for packaging purposes, as emulsifier, and as a sizing and coating in textile and paper industries.<sup>[24]</sup> The use of lignin with PVA has been reported to form miscible blends and provide good thermal and mechanical performance, which has been attributed to the formation of strong intermolecular hydrogen bonds between the hydroxyl groups of PVA and lignin.<sup>[21,22]</sup> In this study, a new strategy to produce nanolignin using a simple mechanical treatment is discussed. The structure and composition of the nanolignin has been investigated using <sup>13</sup>C NMR and <sup>31</sup>P NMR spectroscopy, thermogravimetric Analysis (TGA) and differential scanning calorimetry (DSC). A further goal was to investigate the thermal stability of a nanolignin/PVA blend system.

## Results and Discussion

Several SEM images were acquired for each lignin fraction and subsequently used to determine the size of lignin particles. Quantitative imaging analyses were conducted using an open-source freeware application (Gwyddion). Representative SEM images of the kraft lignin and lignin mechanically sheared for different time periods are shown in Figure 1. According to the SEM images, the kraft lignin particles were irregular in shape with a broad distribution ranging from large micron-sized to nano-sized particles. Figure 2 shows the histogram of the size distribution (here, size refers to the longest dimension of each lignin particle) of lignin particles at different time periods of mechanical shearing. More than 50% of the starting kraft lignin particles were larger than 500 nm with some particles as long as 6–7 μm. This decreased to less than 2% after 2 h of shearing, with 75% particles having a diameter less than 100 nm. Clearly, the size distribution became narrow as the duration of mechanical shearing increased. After 4 h of mechanical shearing, lignin particles were completely homogenized to sizes less than 100 nm.

The quantitative <sup>13</sup>C NMR spectra obtained for kraft lignin and the lignin mechanically sheared for 4 h are shown in Figure 3. The aromatic region of the <sup>13</sup>C NMR spectra for this softwood lignin can be divided into the protonated aromatic



**Figure 1.** SEM images of the lignin mechanically sheared for different time periods (a) 0, (b) 1, (c) 2, and (d) 4 h.

(125–106 ppm), the condensed aromatic (140–125 ppm), and the oxygenated aromatic (157–140 ppm) regions. The oxygenated aromatic region includes the C3 and C4 carbon atoms on the aromatic ring, whereas the protonated aromatic region (125–106 ppm) consists of the C2 and C6 methine carbon atoms and any protonated C5 carbon atoms. The condensed aromatic region primarily includes the C1 and C5 carbon atoms from condensed aromatic ring linkages such as β-5' and 5-5' substructures present in lignin. The aliphatic region (90–57.5 ppm) of the <sup>13</sup>C NMR spectra displays signals of aliphatic side-chain carbon atoms with C–O bonds including Cα, Cβ, and Cγ. Spectra for both kraft and mechanically sheared lignin had peaks specifically assigned to guaiacyl units appearing between 150–148.5 (C3 in etherified guaiacyl units), 148.5–146.7 (C4 in etherified guaiacyl units), 146.2 (C4 in nonetherified guaiacyl units), 137–134 (C1 in etherified guaiacyl units), 133–130 (C1 in nonetherified guaiacyl units), 122–117 (C6), 117–113 (C5), and 113–108 (C2). The prominent peaks in the aliphatic region had chemical shifts at 60.2 (Cγ in β-O-4 linkages) and 55.4 ppm (methoxyl groups).<sup>[25,26]</sup> Comparison of Figure 3a and b reveals that the <sup>13</sup>C NMR spectra for kraft and mechanically sheared lignin did not exhibit any remarkable differences in signal intensities originating from various lignin moieties within both the aromatic and aliphatic regions and methoxy groups.

<sup>31</sup>P NMR spectra of the lignin samples were analyzed to determine structural changes after homogenization. Figure 4 represents the <sup>31</sup>P NMR spectra and Figure 5 summarizes the <sup>31</sup>P NMR analysis results of the kraft lignin and the lignin mechanically sheared for 4 h. The <sup>31</sup>P NMR data confirmed that the lignin samples belong to the *p*-hydroxyphenyl–guaiacyl type.<sup>[27]</sup> The <sup>31</sup>P NMR results show almost no change in the condensation or the guaiacyl content of the lignin samples after mechanical treatment, whereas a slight difference was observed for the aliphatic hydroxyl groups, phenols, *p*-hydroxyphenyl group, and carboxylic group after mechanical treatment. However, these changes are within 5% error associated with the <sup>31</sup>P NMR technique and, therefore, cannot be consid-

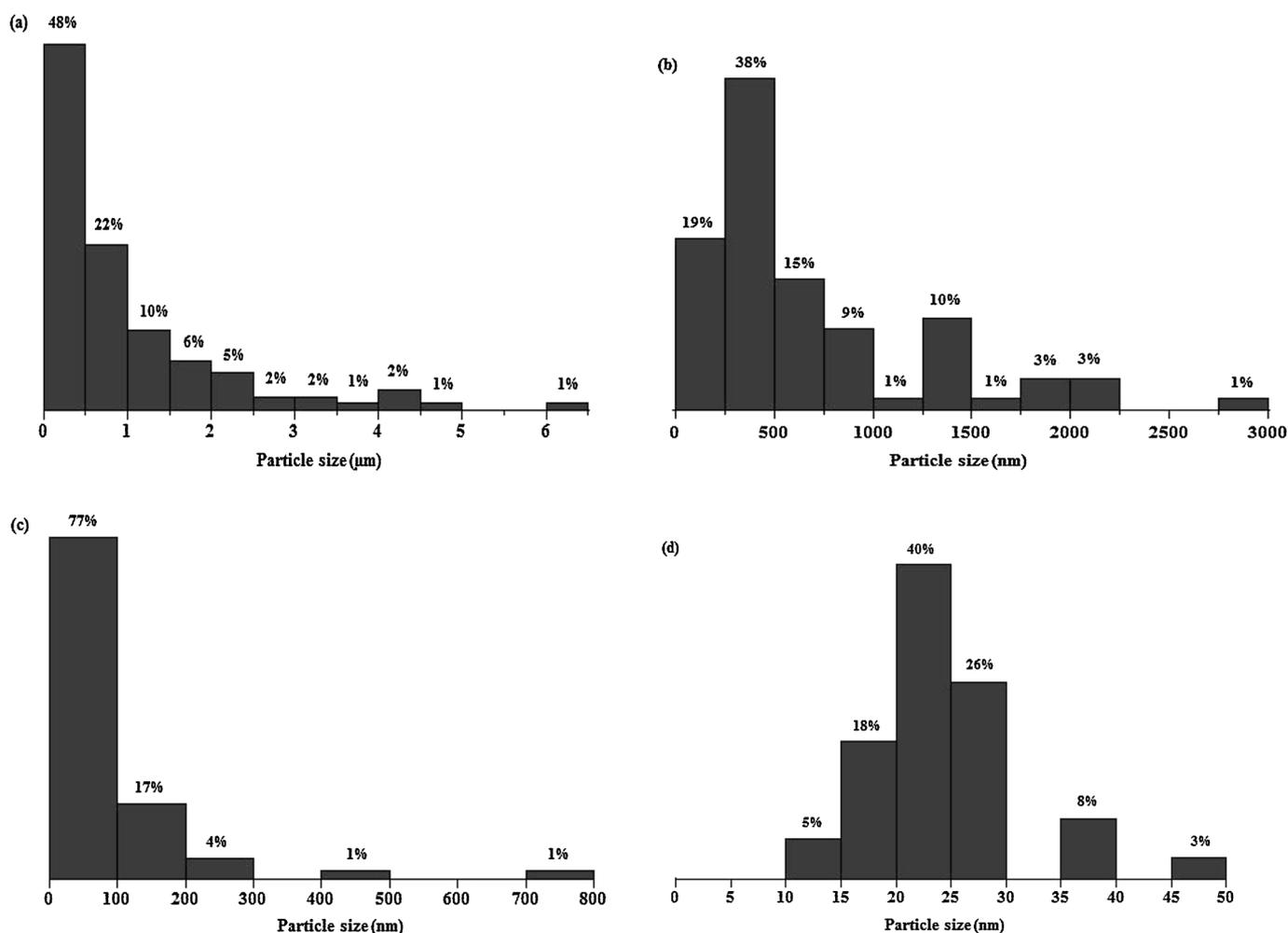


Figure 2. Histograms of the size distribution of lignin particles mechanically sheared for different time periods: (a) 0, (b) 1, (c) 2, and (d) 4 h.

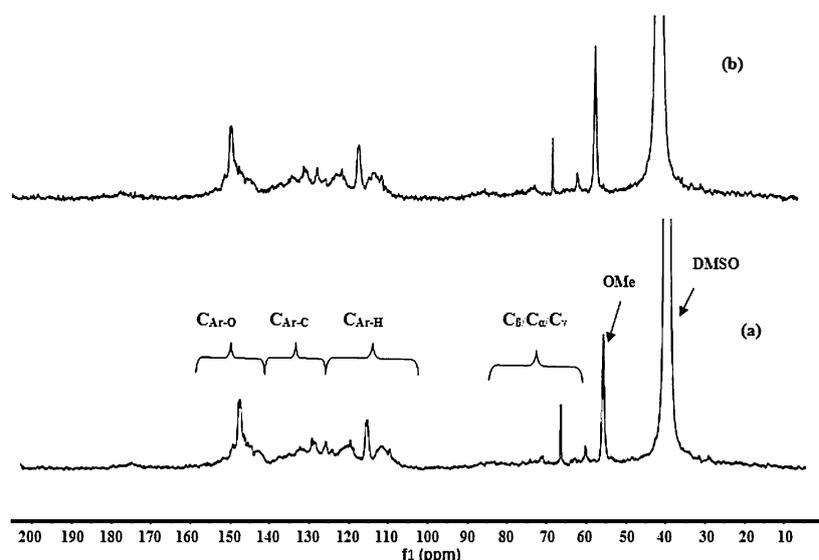


Figure 3. Quantitative <sup>13</sup>C NMR spectra of the lignin samples mechanically sheared for (a) 0 and (b) 4 h.

<sup>13</sup>C NMR and <sup>31</sup>P NMR analysis, there were no major changes on the core lignin structures after mechanical treatment. Number average and weight average molecular weights ( $M_n$  and  $M_w$ ) and polydispersity ( $D$ ) values for the lignin sheared for various time periods are presented in Table 1.  $M_w$ ,  $M_n$ , or  $D$  did not show any change with mechanical treatment. This confirms in combination with NMR results that there is not much change in the molecular structure of lignin samples during mechanical shearing.

The thermal stability and degradation behavior of lignin are very important parameters in determining their potential applica-

ated as a significant change. The aliphatic hydroxyl, phenolic, and carboxylic contents are comparable. According to the

tions. Figure 6a shows the decomposition of the various lignin particles and Figure 6b shows the corresponding derivative

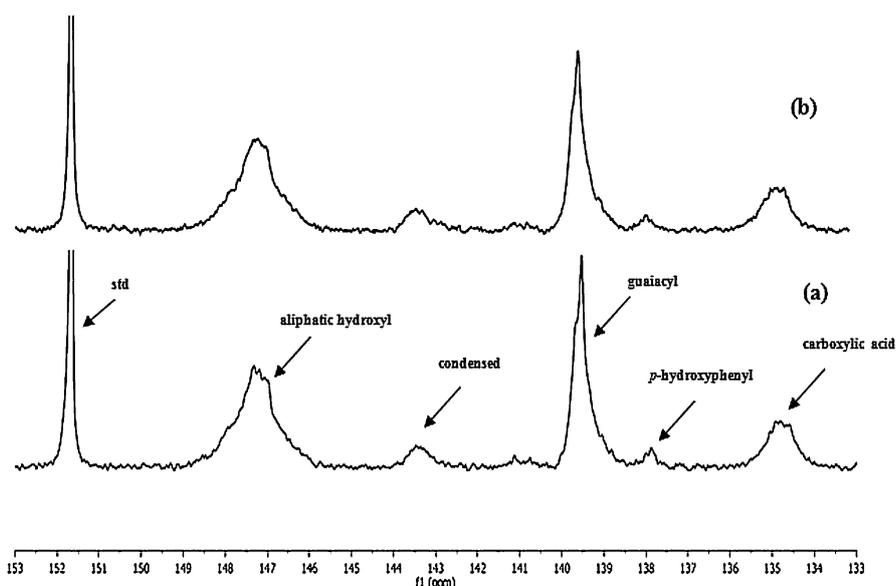


Figure 4. Quantitative  $^{31}\text{P}$  NMR spectra of the lignin samples mechanically sheared for (a) 0 and (b) 4 h.

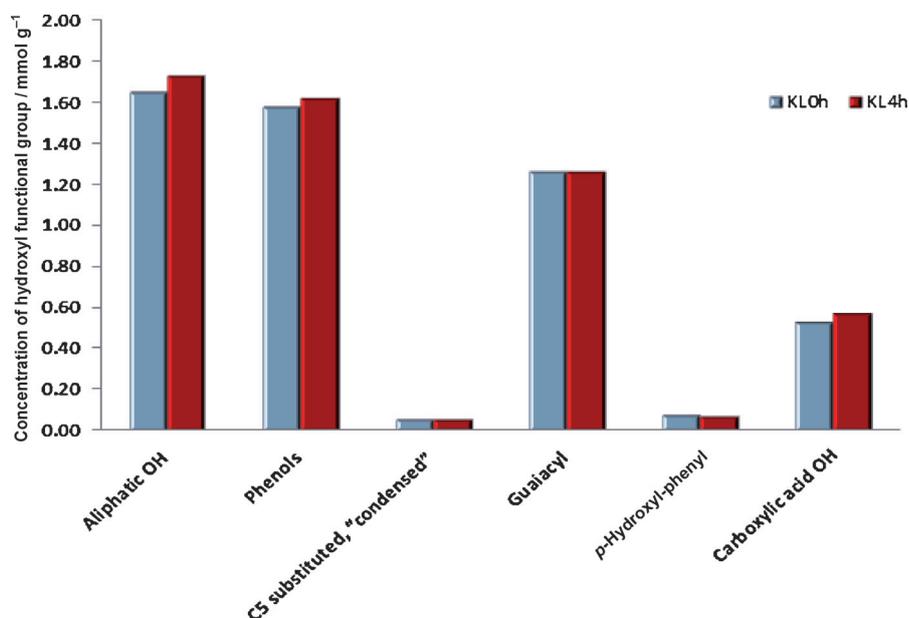


Figure 5. Structural characteristics calculated from the  $^{31}\text{P}$  NMR spectra of the lignin samples mechanically sheared for (a) 0 and (b) 4 h.

Lignin samples	$M_n$	$M_w$	$D (M_w/M_n)$
KL0h	$2.00 \times 10^3$	$5.11 \times 10^3$	2.56
KL0h	$2.10 \times 10^3$	$5.16 \times 10^3$	2.46
KL2h	$2.11 \times 10^3$	$5.31 \times 10^3$	2.52
KL4h	$2.01 \times 10^3$	$5.24 \times 10^3$	2.61

weight curves. The TGA results were analyzed to obtain  $T_{max}$  the maximum value on the derivative weight curve, which in-

dicates the temperature at which the degradation rate is fastest.  $T_{max}$  of the degradation of purified kraft lignin without mechanical treatment (KL0h) was 354 °C, whereas the mechanically sheared lignin had  $T_{max}$  values of 380, 378, and 382 °C for KL1h, KL2h, and KL4h, respectively. Apparently, the rate of thermal degradation of lignin particles decreased with the increase in duration of mechanical treatment, with the lignin particles sheared for 4 h showing the lowest rate of thermal degradation. These results indicate that the mechanically sheared lignin particles were thermally more stable than the starting kraft lignin. DSC was used to determine the glass transition temperature ( $T_g$ ) for various lignin samples. Figure 7 shows the DSC thermograms of mechanically untreated kraft lignin and samples mechanically sheared for different time periods.  $T_g$  for KL0h was 120 °C, whereas the mechanically sheared lignin showed a  $T_g$  at approximately 150 (KL1h and KL2h) and 154 °C (KL4h). Smaller transitions were observed for the KL1h and KL2h particles around 120 °C in the DSC curve similar to kraft lignin without mechanical treatment. It is possible that there are larger particles retained in both KL1h and KL2h samples without much mechanical treatment. However, this smaller transition almost disappeared after 4 h of mechanical treatment, indicating that most of the lignin particles were homogenized to nanoparticles. The

$T_g$  values reported in the literature for several types of lignins are between 110–150 °C.<sup>[28,29]</sup> Softwood lignins have been shown to have a lower thermal mobility or softening due to their more cross-linked structure.<sup>[30]</sup> It has been shown that  $T_g$  of lignin increases due to several factors such as increased cross-linking<sup>[31]</sup> or higher degree of intermolecular association due to more hydroxyl groups.<sup>[32]</sup> However, in our experiments the NMR results did not show any change in the molecular structure of lignin particles or degree of condensation with mechanical treatment. The thermal results for nanolignin are quite interesting and provide scope for future research.

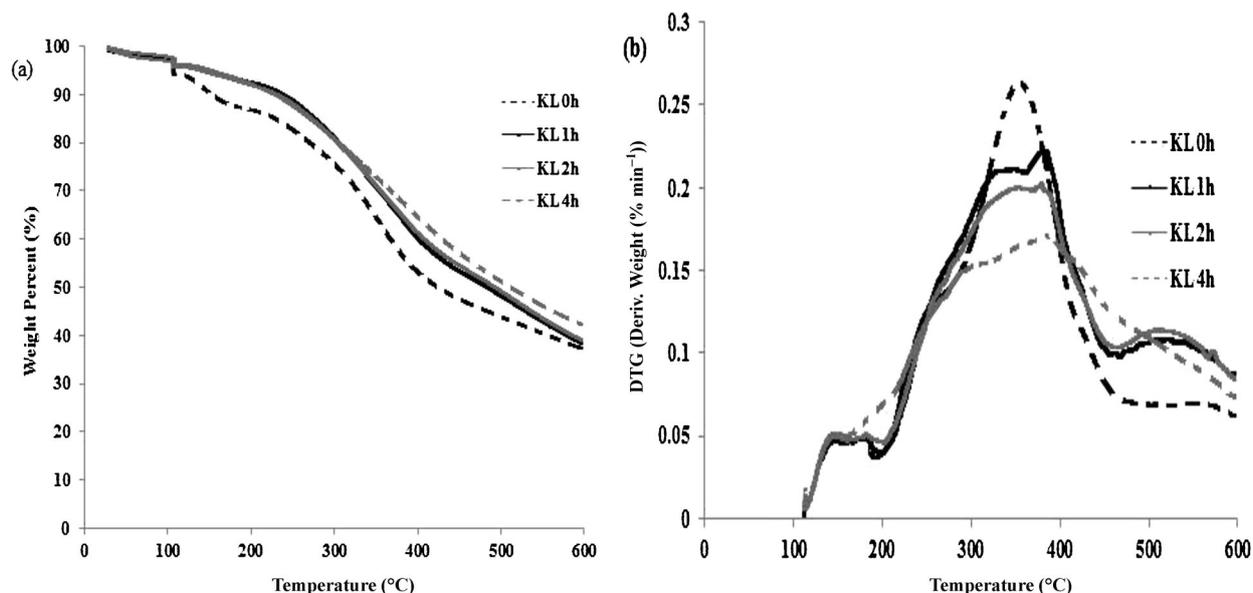


Figure 6. (a) TGA and (b) DTG curves of the lignin samples mechanically sheared for different time periods.

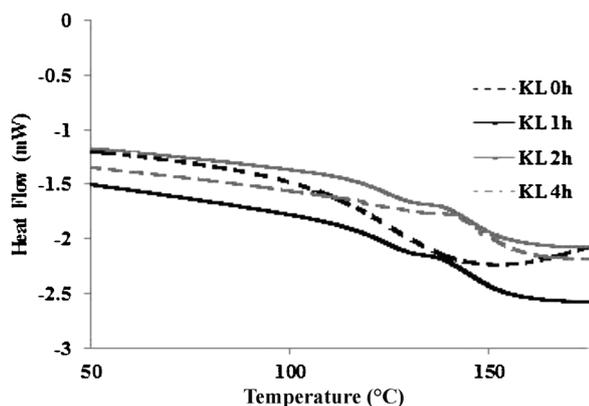


Figure 7. DSC curves of the lignin samples mechanically sheared for different time periods.

The unique combination of nanomaterial characteristics such as size, its inherent thermo-mechanical properties, and

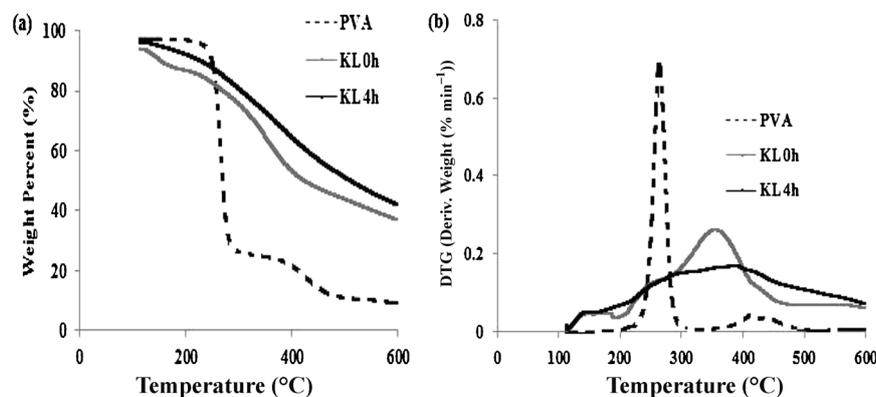
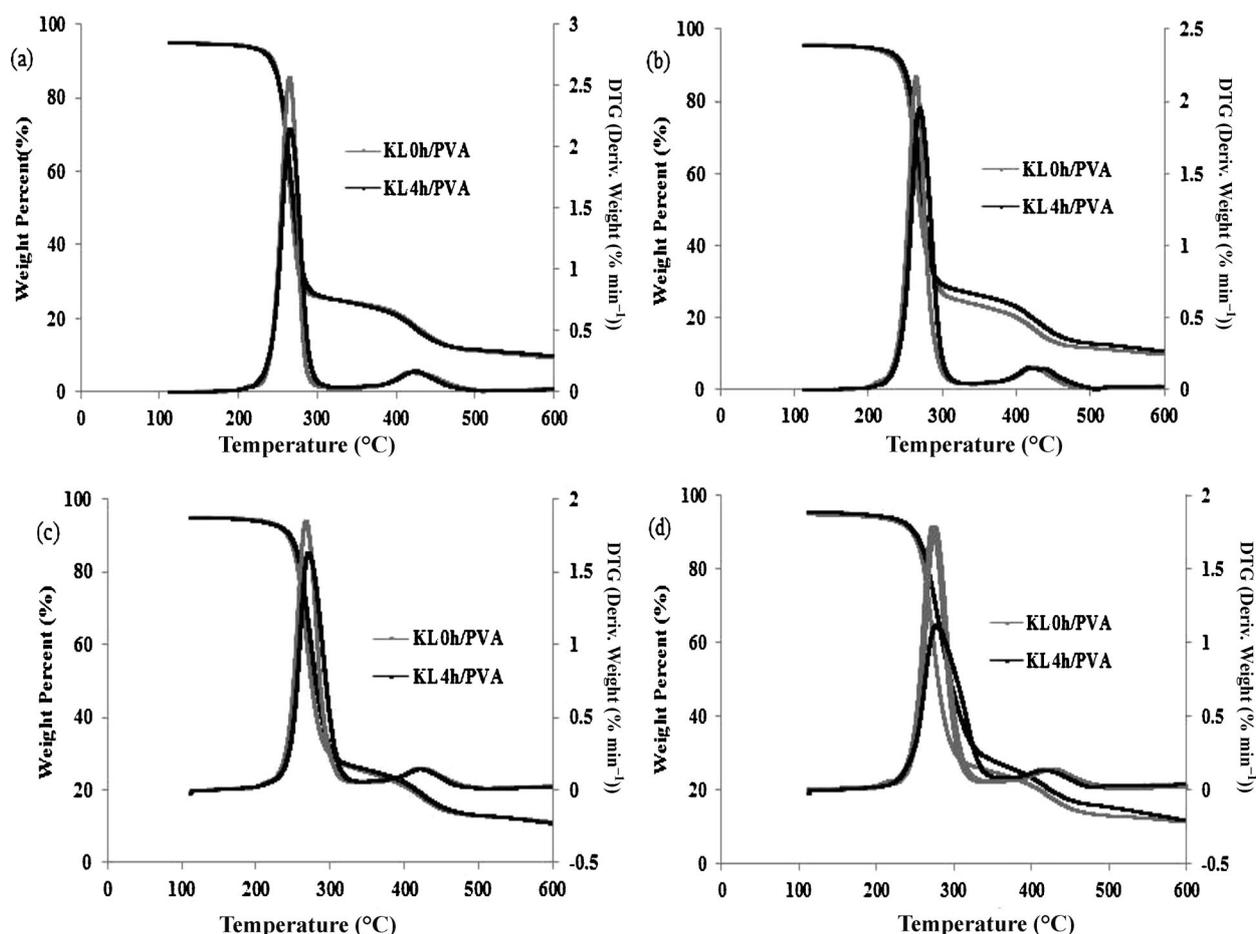


Figure 8. (a) TGA and (b) DTG curves of pure PVA compared to lignin (KL0h) and nanolignin (KL4h).

suitable concentrations necessary to facilitate changes in the polymer matrix have generated substantial interest in the field of nanocomposites. Figure 8 shows the TGA and DTG (derivative thermogravimetry) curves of pure PVA compared to KL0h and KL4h. Evidently, lignin is more thermally stable compared to PVA.  $T_{max}$  of the degradation rate for pure PVA obtained from the DTG curve is 262 °C, whereas it is 354 and 382 °C for the PVA composites with original lignin and mechanically treated (for 4 h) lignin, respectively. The major weight loss of about 75% for pure PVA occurred between 200 and 315 °C, which can be attributed to the decomposition of PVA. The weight loss also increased from 390 to 470 °C, a temperature range in which PVA forms polyene structures and further degradation continues by chain scission and formation of compounds of low molecular weight.<sup>[33]</sup> The total weight loss at 470 °C was 88% for PVA, whereas that of KL0h and KL4h were 54% and 46%, respectively. Figure 9 shows the thermal stability of a nanolignin (KL4h)/PVA blend compared to mechanically untreated kraft lignin (KL0h)/PVA composites. Table 2 shows the

$T_{onset}$  defined as the temperature at which the sample weight was 93% of the sample mass at 105 °C, and  $T_{max}$  values of the various composites. The  $T_{onset}$  and  $T_{max}$  values of the nanolignin composites are higher than that of the mechanically untreated kraft lignin composites. Figure 10 shows SEM images of the cross sections of pure PVA films and KL0h/PVA and KL4h/PVA films. The fracture cross section of KL0h/PVA showed poor dispersion of the mechanically untreated kraft lignin in PVA.



**Figure 9.** TGA and DTG curves of the nanolignin (KL4h)/PVA blend compared to lignin (KL0h)/PVA composites at different concentrations: (a) 2.5%, (b) 5%, (c) 7.5%, and (d) 10%.

Sample	$T_{\text{onset}}$ [°C]	$T_{\text{max}}$ [°C]
2.5% KL0h/PVA	240	262
2.5% KL4h/PVA	244	264
5% KL0h/PVA	243	262
5% KL4h/PVA	247	267
7.5% KL0h/PVA	245	265
7.5% KL4h/PVA	249	270
10% KL0h/PVA	249	270
10% KL4h/PVA	252	276

However, it can be seen that nanolignin particles were well dispersed in the PVA matrix with little agglomeration. The evenly distributed nanolignin–PVA matrix can form miscible blends with the formation of strong intermolecular hydrogen bonds between them and provide good thermal stability.

## Conclusions

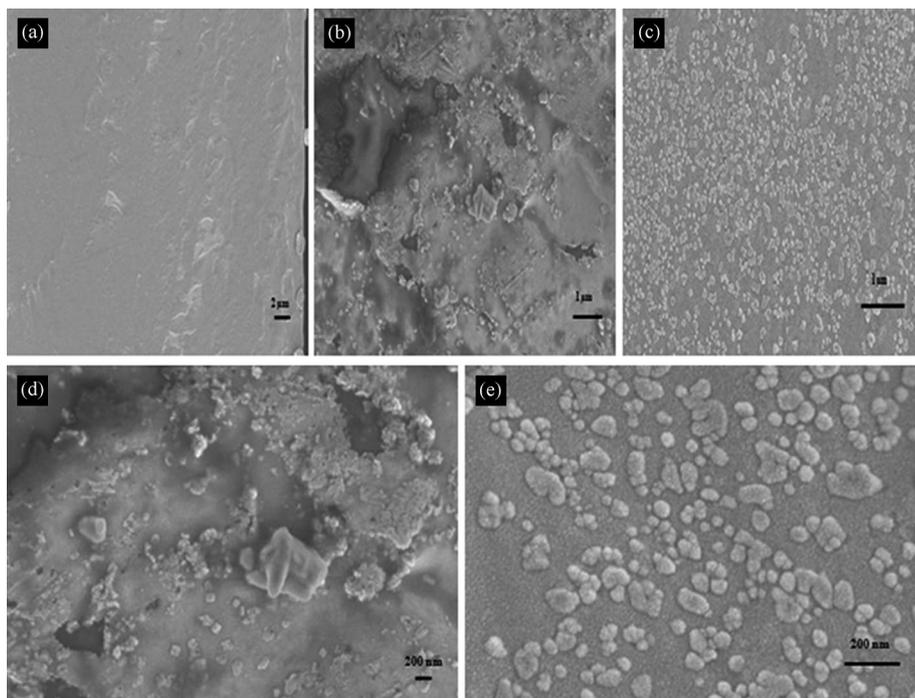
Nanolignin was successfully prepared by applying a simple mechanical treatment using a high shear homogenizer. Lignin par-

ticles were completely homogenized to diameters less than 100 nm after 4 h of mechanical shearing. The  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR analysis showed that there were no major changes on the core lignin structures for starting kraft lignin particles and nanolignin obtained after 4 h of mechanical treatment. The aliphatic hydroxyl, phenolic, and carboxylic contents are comparable and there was no apparent cleavage of aryl-*O*-ether linkages during mechanical treatment. The thermal stability properties of a nanolignin/polyvinyl alcohol (PVA) blend system were higher than that of mechanically untreated kraft lignin/PVA system. The nanolignin particles were well dispersed in the PVA matrix with little agglomeration, but the original lignin was poorly dispersed in the PVA matrix.

## Experimental Section

**Materials:** Softwood kraft black liquor was received from a commercial kraft pulp mill. PVA (98–99% hydrolyzed,  $M_w$  31000–50000) was purchased from Sigma–Aldrich. All other chemicals used were ACS reagent grade from Sigma–Aldrich (St. Louis, MO).

**Isolation of kraft lignin:** The kraft lignin was isolated from the cooking liquor following published methods.<sup>[25,34]</sup> In brief, kraft black liquor was first filtered through a Whatman #4 filter paper



**Figure 10.** SEM images of a PVA and 2.5% lignin/PVA composite: (a) pure PVA, (b) KL0h/PVA composite, (c) KL4h/PVA composite, (d) KL0h/PVA composite (high resolution), and (e) KL4h/PVA composite (high resolution).

on a Büchner funnel. Disodium ethylenediaminetetraacetate ( $\text{EDTA-2Na}^+$ , 0.5 g per 100 mL of black liquor) was added to facilitate metal ion removal. The pH value was adjusted to 6 using aqueous sulfuric acid (2 M), and the solution was stirred for 1 h. The pH value of the liquors was further lowered to 3.0 to facilitate lignin precipitation. The samples were then frozen overnight. After thawing the solution, the precipitates were collected on a medium sintered glass funnel and washed several times with cold water by suspending the precipitates in water and stirring vigorously at 0 °C. The precipitates were collected, air dried, and extracted with pentane for 8 h in a soxhlet extractor to remove sulfur and other impurities and further dissolved in a 9:1 dioxane/water solution and stirred for 1 h. The solutions were centrifuged and the collected supernatants were filtered over Celite on a medium sintered glass funnel. Dioxane was removed by rotary evaporation and the purified kraft lignins were freeze dried. These purified kraft lignins (KL0h) were then used for subsequent analyses and chemical derivatization.

**Preparation of nanolignin:** Nanolignin was prepared using a mechanical homogenization method. Purified dried kraft lignin (KL0h, 2 g) were first soaked and dispersed in deionized water (400 mL). The lignin suspension was treated for 1, 2, and 4 h using a high shear homogenizer (IKA Ultra-Turrax T-50 Homogenizer) at 15 000 rpm and was named KL1h, KL2h, and KL4h, respectively. For each treatment, the homogenizer was operated in runs of short duration of 30 min each. Sufficient time was allowed between the run to allow for the temperature to cool down to ambient temperature and the mass of bubbles caused by agitation to settle down.

**Scanning electron microscopy (SEM):** The surface morphology of the lignin fraction after each treatment and PVA–nanolignin/lignin composites was studied by using a scanning electron microscope (LEO 1530 SEM, Carl Zeiss NTS, Peabody, MA, USA) at 15 kV. Drops of the lignin suspension (0.05 w/w%) were dried on polished Al

mounts and sputter-coated with Au to provide adequate conductivity. Composites were quickly frozen using liquid  $\text{N}_2$  and fracture surfaces were then mounted on an Al stub and dried. Fracture surfaces were coated with Au to provide adequate conductivity.

**Nuclear magnetic resonance (NMR) analysis of lignin:** NMR experiments were performed using a Bruker Avance III 400 MHz spectrometer operating at a frequency of 100.59 MHz for the  $^{13}\text{C}$  nucleus. Quantitative  $^{13}\text{C}$  NMR were acquired using dimethyl sulfoxide ( $\text{DMSO-D}_6$ , 0.5 mL) as the solvent for lignin (100 mg) using an inverse gated  $^1\text{H}$  decoupling sequence with a 12 s pulse delay and 8192 scans. For quantitative  $^{31}\text{P}$  NMR, the lignin samples (25.0 mg) were dissolved in a solvent of pyridine and deuterated chloroform (1.6:1.0 v/v, 500  $\mu\text{L}$ ) mixture and derivatized using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. The spectrum was acquired using a 90° pulse, 25 s pulse delay, and 128 scans. *N*-hydroxy-5-norbornene-2,3-dicarboximide was used as an internal standard.

**Gel permeation chromatography (GPC) analysis of lignin:**  $M_w$  and  $M_n$  of the lignin samples were determined by GPC following published methods.<sup>[25,35]</sup> The lignin samples (100 mg) were dissolved in mixture of pyridine and acetic anhydride (1:1 v/v, 4.0 mL) while stirring at room temperature for 24–36 h. The reaction mixture was diluted with ethanol (30 mL), stirred for 30 min, and then concentrated under lower pressure using rotoevaporation. The addition and removal of ethanol was repeated seven times to remove traces of acetic acid and pyridine from the sample. The acetylated samples were dissolved in chloroform (2 mL) and added dropwise to diethyl ether (100 mL) to precipitate the lignin, which was followed by centrifugation. The precipitate was washed with diethyl ether and centrifuged three times. The air-dried acetylated samples were then dried for 24 h in a vacuum oven at 40 °C and then dissolved in THF over night prior to GPC analysis.

Molecular weight determination was conducted using a Polymer Standards Service GPC SECurity 1200 system equipped with four Waters Styragel columns (HR0.5, HR2, HR4, HR6) at 30 °C and an Agilent isocratic pump, Agilent autosampler, Agilent degasser, Agilent refractive index detector, and Agilent UV detector (270 nm). THF was utilized as the mobile phase (1.0  $\text{mL min}^{-1}$ ) with an injection volume of 20  $\mu\text{L}$ .

**Preparation of PVA–nanolignin/lignin composites:** PVA was completely dissolved in water by continuous mechanical stirring for 30 min in water bath kept at 90 °C. The aqueous PVA solution (10% w/w) and lignin (KL0h)/nanolignin (KL4h) suspension were mixed through manual stirring and degassed. Each mixture was poured onto a polystyrene petri dish to air dry over night. The films were stored in a desiccator at 50% relative humidity for two days prior to testing. For all films, the total weight of the solute

was kept constant. The mass amounts of KL0h or KL4h in the PVA matrix in the resultant films was 2.5%, 5%, 7.5%, and 10%.

**Thermal analysis:** TGA of the lignin samples and prepared films were performed using a TA TGA Q50 (TA Instruments, New Castle, DE, USA). The samples ( $\approx 5$  mg) were initially heated to 105 °C at a heating rate of 10 °C min<sup>-1</sup> and kept isothermally for 20 min before being heated to 600 °C at a heating rate of 10 °C min<sup>-1</sup>.  $T_g$ s were analyzed using a TA DSC Q20 (TA Instruments, New Castle, DE, USA). The lignin samples ( $\approx 5$  mg) were heated to 105 °C at a rate of 5 °C min<sup>-1</sup> and then kept isothermally for 40 min prior to being quenched to 25 °C. The DSC thermograms were then recorded by heating the samples to 200 °C at a heating rate of 10 °C min<sup>-1</sup>.

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**Keywords:** biomass · composites · lignin · nanoparticles · thermal stability

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