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PREPARATION AND CHARACTERIZATION OF FUNCTIONAL NANOCOMPOSITES BASED ON LIGNIN NANOPARTICLES AND CELLULOSE NANOCRYSTALS FROM HOLISTIC RAPID-FORMIC ACID FRACTIONATION OF BAMBOO

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ABSTRACT

The urgent need for using renewable resources instead of fossil sources has attracted extensive research activities on the development of biodegradable materials from biomass. Due to the highly recalcitrant nature of lignocellulose, it is essential to develop an efficient fractionation approach which may facilitate the subsequent conversion. Herein, in a holistic rapid-formic acid fractionation of bamboo chip under the optimized conditions at 145 °C for 45 min of cooking, with a solvent ratio of 85:15 (formic acid:water, v/v), wood:solvent ratio of 1:7, relatively pure hemicelluloses, lignin and cellulose were sequentially obtained as fractionated streams. The bamboo-originated cellulose, as a raw material, was easily converted into cellulose nanocrystals (CNCs) using TEMPO oxidation in a short time in comparison to wood Kraft pulp. The dissolved lignin was processed into nanoparticles (lignin-NPs), which exhibited sphere morphology and a uniform particle size distribution. Dispersions of CNCs and lignin-NPs were prepared and further filtrated to result in nanocomposite membranes. The nanocomposite membranes, in varied compositional ratios of CNC and lignin-NP, were elaborately characterized with SEM, TG-DSC, and mechanical property analysis. These all-bamboo-originated nanocomposite membranes showed to possess superior tensile strength and thermal stability as

compared to pure CNC-based membrane. This study presents a promising and green pathway in achieving novel high value-added wood-based nanomaterials.

Keywords: Bamboo chips; Formic acid fractionation; Cellulose nanocrystals; Lignin nanoparticle; Nanocomposite

INTRODUCTION

Nowadays, numerous methods for producing cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) has been reported. Nanocellulose is commonly produced from market wood pulp by mechanical fibrillation, chemical treatments, and enzymatic treatments; as well as a combination of two or several of the aforementioned approaches^[1-3]. Different preparation procedures results in different types of nanocellulose. The typical method for the fabrication of CNCs is to subject cellulosic materials to strong acid hydrolysis, such as sulfuric acid or other mineral acids, followed by mechanical fibrillation^[4, 5]. However, CNCs production using strong acids remained some issues, such as environmentally unsustainable, the recovery of the acid and expensive market pulp fiber. Among the various methods for fabrication of CNFs, chemical pretreatments, such as the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation^[3, 6], can significantly overcome the high energy input of mechanical fibrillation method. However, as the result of the limited reaction efficiency, relatively long reaction time (about 10 to 24 h, or even longer) or a higher chemical reagent input was also required. There is no doubt that these preparation procedures for nanocellulose substantially increase the production cost and negatively affects commercial utilization.

As the most abundant aromatic polymer and the second-most abundant biopolymer after cellulose, the conversion of low value lignin by-product to its valorization is one of the key factors for developing an economically feasible integrated lignocellulose biorefinery^[7]. The preparation of lignin-nanoparticles (lignin-NPs) has been considered as the best way to build a promising versatile material platform for various downstream utilizations, especially in the emerging nanomaterial fields for enhancing the UV barrier^[8], antibacterial^[9] and antioxidant properties^[10]. Lignin-NPs have been fabricated by different methods, such as precipitation methods initiated with acids^[11], CO₂ saturation^[12], solvent exchange^[13], and dialysis^[14], as well as by sonication^[15] and water-in-oil microemulsion methods^[16]. Among the various available methods reported so far, acid precipitation is a technically and economically feasible route to achieve the green chemistry goals of benign products and processes.

All the methods lead to different types of lignocellulosic nanomaterials (e.g., nanocellulose and lignin-NPs) depend

on the treatment of raw materials. For the fabrication of nanocellulose, the first step of the raw lignocellulosic biomass is the delignification to remove lignin and hemicellulose in order to overcome the recalcitrance and facilitate the subsequent processing. Sulfite, chlorite, diluted-acid, or alkaline solution was very common to be used in the delignification process which was usually tedious and detrimental to the environment^[17, 18]. Toward the manufacture on an industrial scale, it is important to obtain high purity cellulose and lignin with an effective fractionation method and facilitate the subsequent preparation of nanomaterials. Nowadays, as a new type of organosolv treatment protocol, formic acid rapid-delignification under pressure results in an efficient fractionation of lignocellulosic biomass into purity cellulose, lignin without high chemical reactivity and hemicellulosic sugar^[19, 20]. Equivalent delignification using known ethanol pulping and alkaline pulping can only be achieved at a higher temperature with longer reaction time. To increase the technical and economic feasibility, a sustainable integrated biorefinery platform could be achieved based on the formic acid rapid-fractionation, and the various components obtained can be converted into nanocellulose and lignin-NPs as well as nanocomposite.

To achieve full utilization of lignocellulosic biomass and easy integration of nanomaterials production into current biorefinery concept, we developed a combined method for the fabrication of novel biodegradable nanocellulose and lignin-NPs as well as nanocomposite from lignocellulosic biomass based on formic acid rapid-fractionation. It is conceived that the formic acid rapid-fractionation will contribute to efficient fabrication of nanocellulose through TEMPO-mediated oxidation. Efficient recovery of formic acid can be accomplished by evaporation to achieve environmental sustainability. The dissolved lignin and hemicellulose sugars can be easily separated by diluting the spent acid liquor. The precipitated non-sulphonated lignin can be directly used for producing lignin-NPs based on a pH change from basic to acidic aqueous medium. The properties of the resultant nanocellulose (e.g., structure, morphology and crystallinity) and the lignin-NPs (e.g., morphology, size and zeta potential against various pH) were comprehensively investigated. In an attempt to achieve a multifunctional nanocomposite and facilitate their application, dispersions of CNCs and lignin-NPs were prepared and further filtrated to result in nanocomposite membranes. The main objective of the study is to demonstrate the feasibility of the combined process to integrate production of nanocomposite toward the manufacture on an industrial scale and large-commercial application.

EXPERIMENTAL

Materials

Bamboo (*Neosinocalamus affinis*) chips (20–30 mm long, 10–20 mm wide, and 3–4 mm thick) were obtained from Sichuan Province in China and selected as the raw materials in this study. According to the NREL LAP method, the moisture content of the selected bamboo chips used in this study was 9.43% based on an oven dried weight. The primary chemical compositions of the bamboo chips were as follows: Klason lignin 25.56%, acid-soluble lignin 1.87%, xylan 21.96%, glucan 39.63%, ethanol-toluene extractives 2.10%, and ash 2.2%.

Methods

100 g of dry bamboo chips was treated at a temperature of 145 °C for 45 min using 85% (v/v) formic acid at a liquid/solid ratio of 7:1 (mL/g) in a jacketed Hastelloy alloy sealed reactor. When the reactions finished, the solid fraction (crude pulp, mainly cellulose) was filtered from the process liquor and washed with 85% formic acid and deionized water (85 °C) three times, respectively. The obtained pulp was screened with an 8-cut flat-screen to remove the rejects. The filtrate and the washing liquids were mixed together as spent liquor, and then evaporated in a rotary evaporator to recover formic acid. Then 10 volumes of distilled water were poured into the concentrated liquor to precipitate the dissolved lignin. The precipitate was centrifuged off, washed twice with distilled water, and dried. The supernatant was collected and concentrated using a rotary evaporator. The residue obtained was a hemicellulose-rich fraction.

Cellulose fiber obtained was bleached to 87 %ISO by a ECF (elemental chlorine free) sequence (D₁EPD₂P), where D stands for a chlorine dioxide stage, EP for an alkaline extraction with peroxide stage, and the P for a peroxide stage, according to our previous research^[19]. TEMPO-mediated oxidation process according to the literature method^[6]. The carboxylate content of nanocellulose was determined according to the literature method^[6].

Initially 1.0 g precipitated lignin was mixed with 150 mL milli-Q water, and the pH was increased stepwise to hit a final target pH value of 12.00 by adding 0.1 M NaOH under constant stirring. The sample was equilibrated for 5 min. Finally, lignin-NPs were formed by addition of 0.1 M HCl to reach the final pH value of 5.00.

Nanocomposite films were prepared by mixing nanocelluloses and lignin-NPs suspension followed diluted to 0.1% (w/v) during magnetic stirring at room temperature for 30 min. The total amount of dry substance in each film was kept constantly at 300 mg. The compositional weight ratios of nanocellulose/lignin-NP in nanocomposite film were 100, 10, 5, 2, and 1, respectively. About 300 mL of the suspension was filtrated on a nylon membrane filter with 0.1 μm pore size and 90 mm diameter (Sterlitech, USA). A nanocomposite film was obtained after drying in vacuum desiccator at 40 °C at a pressure of 88 mbar for 4.0 h.

Fourier transform infrared spectroscopy (FTIR) was recorded by Thermo Scientific™ Nicolet™ iSTM 50 FTIR Spectrometer (United States). Each spectra was collected with ATR mode in the transmittance or absorbance mode from an accumulation of 36 scans in the range of resolution from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . The zeta potentials were measured using a Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK). Thermogravimetric analysis (TGA) was performed on a Thermal Gravimetric Analyser (Q600, TA instruments, N_2 flow 100 mL/min, heating rate 10 $^\circ\text{C}/\text{min}$). The surface morphologies and chemical composition of samples were investigated by use of a scanning electron microscope (SEM; Zeiss SUPRA 55) with an accelerating voltage of 20 kV.

RESULTS AND DISCUSSION

One-step rapid-fractionation using formic acid efficiently separates bamboo into its main components, namely cellulose pulp, lignin, and a hemicellulose-rich fraction. It was found that 42.2 g cellulose pulp, 31.5 g crude lignin, and 8.5 g hemicellulosic sugars could be obtained from 100.0 g of oven-dried bamboo chips, demonstrating that the rapid-fractionation using formic acid exhibited a good selectivity towards cellulose. To achieve valorization of main compositions and easy integration production into current biorefinery concept, the one-step rapid treatment strategy followed by TEMPO oxidation and acid precipitation for cellulose and lignin, respectively, were employed to produce nanocellulose and lignin-NPs. Furthermore, a nanocomposite film can be facilely synthesized by using the suspension of nanocellulose and lignin-NPs obtained from the integrated process. The characterization and property of the nanomaterials obtained will be discussed in the following text.

Characterization of nanocellulose

Cellulose fibers were isolated by a rapid-formic acid fractionation process combined with bleaching treatment prior to subjecting to nanofibrillation. In the present study a commercial bleached Kraft pulp (KP) was applied as a reference for the preparation of nano-sized cellulose. To facilitate discussion, code names of these nanocellulose samples from reference KP and bleached formic acid pulp (FP) with different reaction time (5 h or 24 h) of TEMPO-mediated oxidation were used as (KP-CNFs, 24 h), (FP-CNCs, 5 h) and (FP-CNCs, 24 h), respectively. Fig. 1a shows the FTIR spectra of three nanocellulose samples along with that of the original fibers. As can be seen, several absorption peaks were found in all spectra. The main feature shown is that there was a strong band in the spectra of three samples at 1604 cm^{-1} corresponded to the antisymmetric stretching of COO^- in carboxylate salts, while this band in the spectra of both original Kraft pulp

(KP) and formic acid pulp (FP) was very weak. This suggests that the carboxyl groups were introduced on the nanocellulose samples after modification of KP and FP by TEMPO-mediated oxidation, which is in agreement with previous report^[21]. The amount of carboxyl groups in the nanocellulose samples and original fibers was calculated and shown in Fig. 1b. The results indicated that the carboxyl group content ranged from 0.27 to 1.78 mmol/g for the nanocellulose sample from FP, while ranged from 0.16 to 1.58 mmol/g for the sample from KP. Furthermore, the carboxylate content of the three samples at each time point of TEMPO-mediated oxidation showed a rapid rise during the first 5 h, followed by a slight increase up to 24 h and then leveled off. Under the same reaction conditions, the carboxylate content of the nanocellulose products from FP could reach 1.63 mmol/g with a 5 h reaction time, while that of the KP-CNF could only reach 1.58 mmol/g with a 24 h reaction time.

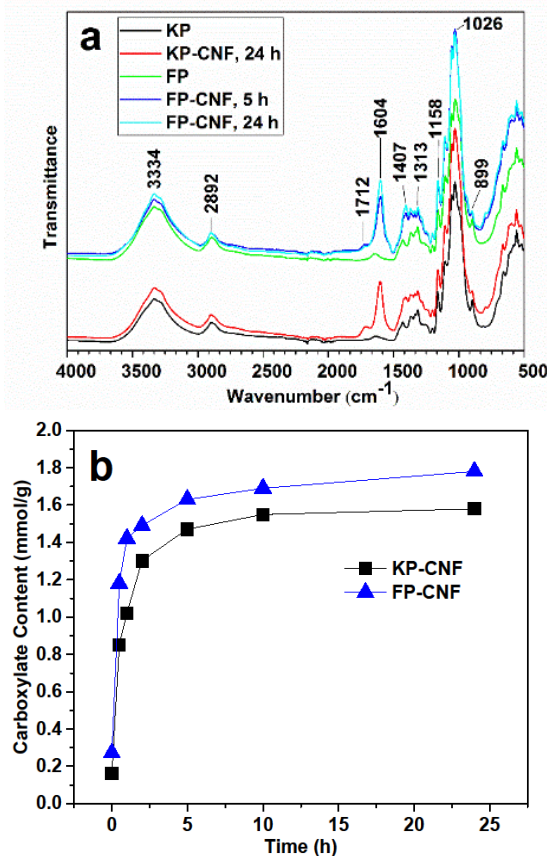


Fig. 1. (a) FTIR and (b) Carboxylate contents of nanocellulose samples compared with that of the original fibers.

Properties of lignin nanoparticles

The dissolved lignin and hemicellulose in the spent liquor can be separated simply through precipitation by diluting the spent liquor with distilled water. The precipitated lignin was further used for producing

lignin-NPs based on a pH change from basic to acidic aqueous medium. The obtained lignin-NPs suspensions were analyzed for particle size and zeta potential. The variation of the hydrodynamic diameter and ζ -potentials of the lignin-NPs with increasing pH are shown in Fig. 2a and Fig. 2b, respectively. The lignin-NPs dispersions were stable in a broad pH range from 5.0 to 8.0, with a diameter of about 100 nm and ζ -potentials of around -25 mV. At pH < 5.0, the magnitude of the electrical double layer repulsion decreased significantly, resulting from the protonation of charged functional groups, which resulted in aggregation of the lignin-NPs. It is suggested that the electrostatic repulsion plays a dominant role of in the stabilization of the dispersion. When the pH >9, the particle size decreased to about 50 nm. The decrease in particle size can be attributed to the onset of the disassembly of the particle toward dissolution, where the complete dissolution occurred at pH > 12.0.

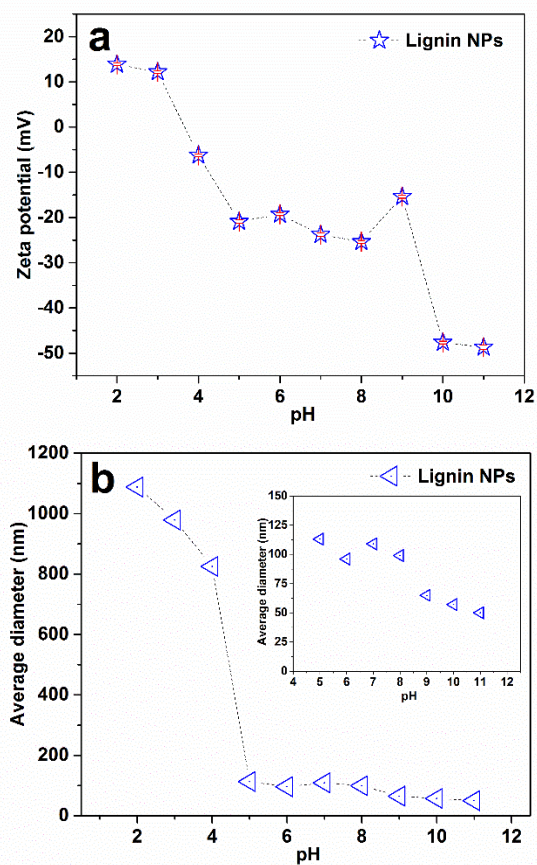


Fig. 2. Surface charge related properties of lignin-NPs: (a) ζ -potentials of the lignin-NPs as a function of pH. (b) Effect of pH of average hydrodynamic diameter of lignin-NPs

Characterization of functional nanocomposite films

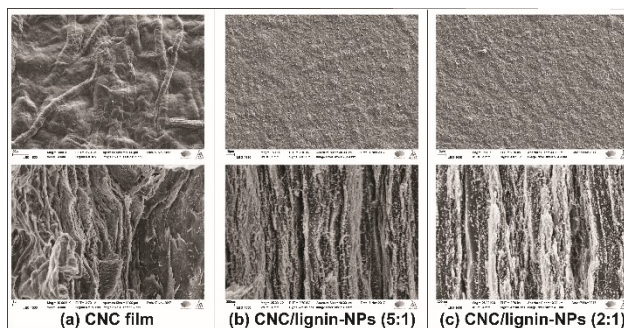


Fig. 3. SEM images of nanocomposite film: surface (top row) and cross section (bottom row).

SEM images (Fig. 3) of the cross-section of selected nanocomposite showed a multilayer network with numerous layers of CNCs surrounded by lignin-NPs compared to the pure CNCs film. This architecture indirectly suggested the lignin-NPs were homogeneously dispersed in the CNCs matrix without any visible aggregations. SEM image of the surface of pure CNCs film shows the uneven and rough surface in an interconnected web structure, while those obtained from nanocomposite presented a very smooth surface after the addition of different amount of lignin-NPs.

Table 1. Young's modulus, tensile strength, elongation at break, and thickness of composite films with different ratio of CNCs/lignin-NPs

CNC/lignin-NPs (wt/wt)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
100	63.15±4.2	2.52±0.2	4.94±0.01
10	82.70±0.3	2.62±0.2	6.53±0.02
5	91.84±0.3	2.86±0.3	7.24±0.01
2	69.70±4.3	1.39±0.3	6.23±0.1
1	66.03±3.7	1.62±0.1	5.62±0.02

The measured values of the tensile strength, the elongation at break, the Young's modulus and thickness for various lignin-NPs contents in CNCs films are reported in Table 1. The addition of lignin-NPs tended to increase the tensile strength and Young's modulus of the nanocomposite films. It is indicated that incorporation of lignin-NPs could result in a significant improvement in the tensile strength of the nanocomposite films. At the CNCs/lignin-NPs ratio of 5, the tensile strength, Young's modulus and elongation at break of the nanocomposite film increased up to 91.84 MPa, 7.24 GPa and 2.86%, which were much higher than the pure CNCs film without lignin-NPs. This may be due to the strong hydrogen bonding and van der Waals forces which allow good interfacial adhesion between CNCs and lignin-NPs^[8, 22].

Thermal analysis was subsequently conducted with the selected sample films using thermogravimetric analysis

(TGA). As shown in Fig. 4, TGA results show that the thermal stability of the nanocomposite films was significantly improved with the increase of incorporated lignin-NPs content, as compared to those of the pure CNCs film. The nanocomposite samples are observed to have similar decomposition profiles and the degradation of the nanocomposites takes place in two stages. The enhanced thermal stability of these nanocomposite samples could be obviously revealed in the two decomposition temperatures, which corresponds to the degradation of the polymer backbone. The thermal stability of the nanocomposite filled with a CNCs/lignin-NPs ratio of 2, is better than those of nanocomposite under the CNCs/lignin-NPs ratio of 5.

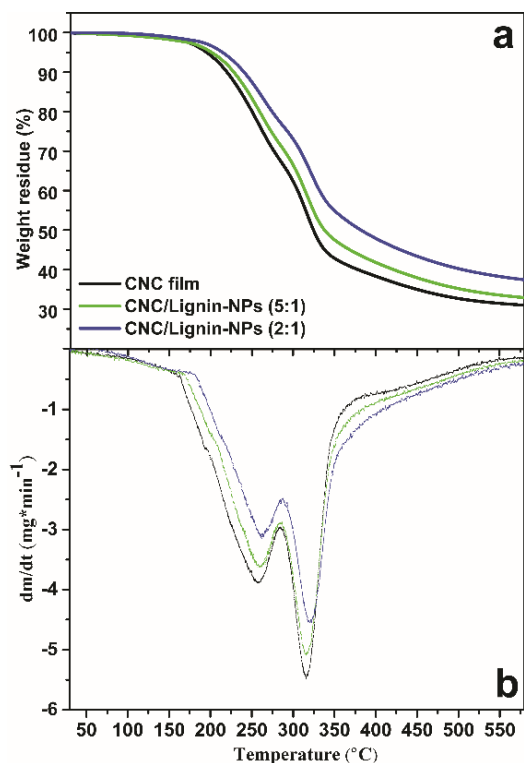


Fig. 4. Thermal stability of different nanocomposites produced under the various CNCs/lignin-NPs ratio: (a) TGA weight loss; (b) TGA temperature derivative weight loss.

CONCLUSIONS

To increase the technical and economic feasibility, using a combined process based on formic acid rapid-fractionation, it achieves full utilization of lignocellulosic biomass and easy integration of nanomaterials production to convert raw lignocellulose into nanomaterials. Pure cellulose, lignin and hemicelluloses were firstly fractionated. It is indicated that formic acid rapid-fractionation contributed to efficient fabrication of nanocellulose through TEMPO-mediated oxidation in a relatively short time in comparison to wood

Kraft pulp. The precipitated non-sulphonated lignin was directly used for producing lignin-NPs which exhibited sphere morphology and a uniform particle size distribution. The all-bamboo-originated nanocomposite membranes based on the CNCs and lignin-NPs showed to possess superior properties. These all-bamboo-originated nanocomposite membranes showed to possess superior tensile strength, thermal stability, and effective antibacterial activity as compared to pure CNCs-based membrane. The full transformation of lignocellulose with this combined process is of great significance for the building of a promising versatile material platform in the emerging nanocomposite fields to meet the green chemistry principles and the commercial cost target.

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