

Characterization of cellulose nanocrystal with cellulose II polymorph from primary sludge and its application to PVA nanocomposites

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Abstract Cellulose nanocrystals with cellulose II polymorph (CNC-II) were obtained from primary sludge fiber (PSF) in a pulp and paper mill by sulfuric acid hydrolysis after purification to remove inorganic materials and lignin. The CNC-IIs obtained were applied as reinforcing fillers for polyvinyl alcohol (PVA). Characterization of CNC-IIs was performed using FTIR spectroscopy and X-ray diffraction. The morphology, conductivity, and tensile properties of CNC-IIs-reinforced PVA nanocomposites were also investigated. Purification treatment effectively reduced non-cellulosic material in the sludge, increasing the cellulose content from 39.87 to 76.34%. The conductivity and tensile properties of the PVA/CNC-II nanocomposite was better than those of neat PVA and PVA/PSF composite.

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Introduction

Utilization of agricultural and forestry wastes for the production of cellulose resources has increased because of its abundant availability and low cost (Brinchi et al. 2013; Neto et al. 2013; Johar et al. 2012; Dai et al. 2013; Fahma et al. 2010). Sludge from pulp and paper mills also has the potential to be used as an alternative cellulosic resource. It is mainly composed of cellulose fibers (50–60%) and inorganic materials such as minerals and ashes (Mehmood et al. 2010), which are difficult to dispose of. Efficient recycling of the sludge into value-added products can lead to environmental and economic benefits.

Cellulose fiber from sludge has been used to prepare cellulose nanofiber (CNF). Jonoobi et al. (2012) have produced low-cost CNF from sludge by dissolving cellulose produced by ultrafine grinding. The defibrillation efficiency of sludge fiber was found to be better than that of dissolving cellulose. The CNF obtained had a diameter less than 100 nm and a specific surface area of 112 m²/g. They insisted that the preparation of CNFs from sludge could be considered as an economic, energy efficient, and viable approach to generating value-added products from cellulose sludge while minimizing sludge disposal issues. Leao et al. (2012) have reported on the preparation of cellulose nanofibers from primary sludge and its effectiveness as reinforcement fillers for polymeric matrices to improve the mechanical, optical, and dielectric properties of matrix polymers.

Polyvinyl alcohol (PVA) is one of the most popular biodegradable and hydrophilic polymers and is known to have strong interactions with cellulose by forming hydrogen bonds. This strong interaction between cellulose and PVA results in miscible blends (Nishio and Manley 1988; Nishio et al. 1989). PVA has been widely used as the polymer matrix in the manufacture of composite films because of its many advantages including flexibility, resistance to solvents, and the wide spectrum of applications that can be improved by incorporating fibers (Khiar and Arof 2009). Roohani et al. (2008) have prepared and characterized cellulose nanocrystal (CNC)-reinforced PVA nanocomposites. The results obtained showed that the higher hydrolyzing degree of polyvinyl acetate caused the generation of more hydroxyl groups, resulting in stronger filler/matrix interactions compared to partially hydrolyzed samples. The reinforcing effect was found to be higher as the hydroxyl group content of the matrix increased. Peresin et al. (2010) used CNC to reinforce electrospun PVA nanofibers with different acetyl group contents. The elastic modulus of the nanocomposite mats increased significantly as a consequence of strong interactions due to the hydrogen bonds between CNC and fully hydrolyzed PVA electrospun fibers.

In the present study, CNC-IIs from primary sludge fibers (PSFs) were prepared using the sulfuric acid hydrolysis process combined with ultrasonication after the purification of primary sludge. PVA–PSF composite and PVA–CNC-IIs nanocomposites were prepared, and their morphology, transparency, conductivity, and tensile properties are compared.

Materials and methods

Materials

Primary sludge was obtained from PT. Indah Kiat Pulp and Paper Products in Serang, Indonesia. Sulfuric acid (95%) and other chemicals such as ethanol, benzene, sodium chlorite (NaClO_2), acetic acid, sodium hydroxide, and hydrochloric acid were purchased from Sigma-Aldrich.

Methods

Purification of primary sludge

Purification treatment was conducted using the method proposed by Fahma et al. (2010) with some modification to isolate the cellulose fiber from primary sludge prior to acid hydrolysis. The primary sludge was extracted with ethanol/benzene (1:2 v/v) for 48 h to remove the extractive components (resins, oils, fats, and waxes) and then washed with ethanol to remove benzene, followed by washing with distilled water. The extractive-free fibers were bleached with 1.25 wt% sodium chlorite solution in acetate buffer ($\text{pH} = 4\text{--}5$) at 70 °C for 4 h, and washed repeatedly with distilled water until neutral. To remove inorganic materials, the fibers were treated with 1 M aqueous hydrochloric acid solution followed by repeated washing with distilled water until neutral. Subsequently, they were oven-dried at 50 °C. The resultant cellulose fibers (1 g) were then treated with a 17.5% sodium hydroxide aqueous solution (w/w) (25 mL) for 2 h at 20 °C and washed several times with distilled water until neutral. During this solid-state process, cellulose fibers were swollen in alkali and recrystallized into cellulose II polymorph.

CNC-II preparation

The cellulose fibers obtained above were hydrolyzed with sulfuric acid solution (50% v/v) at 45 °C for 30 min (denoted as CNC-II-30) and 60 min (CNC-II-60) with constant agitation. The cellulose fiber–sulfuric acid solution ratio was 1:20. Distilled water was added and centrifuged. The supernatant was removed and the precipitated reactant was diluted with distilled water, followed by centrifugation. This process was repeated until a constant pH (6.5) was obtained for the precipitated reactant. Subsequently, the reactant was sonicated for 60 min to improve the dispersion in water and then stored in a refrigerator at 4 °C.

Chemical composition analysis

The chemical composition of the primary sludge before and after purification was determined in accordance with TAPPI standards (TAPPI T204 om-88 1988a; TAPPI T222 om-88 1988b; TAPPI T211 om-93 1993). The holocellulose content was measured by the acid chlorite method (Browning 1967), and the α -cellulose

content was determined by treating the holocellulose with 5 wt% potassium hydroxide solutions (Browning 1967).

The elemental compositions of the primary sludge before and after purification were determined by energy-dispersive X-ray spectroscopy (EDS; JEOL JED 2300/2300F, Japan).

Characterization of purified primary sludge and CNC-II

Fourier transform infrared (FTIR) spectra were acquired using an FTIR (ABB MB 3000, Canada). Samples were vacuum-dried at 80 °C for 1 h, and the standard KBr pellet method was employed for all measurements. Wide-angle X-ray diffraction (WAXD) was measured in reflection mode (Shimadzu XRD-7000 MaximaX, Japan). Nickel-filtered Cu-K α radiation (wavelength of 0.154 nm) was used at 40 kV and 30 mA. The diffraction intensity profiles were collected in the 2θ range 10°–40°.

Preparation of nanocomposite films

CNC-II and PSF-reinforced PVA nanocomposite films with contents of 1, 3, and 5% CNC-IIs and PSFs were prepared using the casting method. A suspension of CNC-II and PVA obtained by stirring at 800 rpm and 80 °C for 1 h was casted on Teflon. The obtained films were then vacuum-dried at 40 °C for 24 h.

Characterization of nanocomposite films

The transmittances of the nanocomposite films were measured from 250 to 850 nm using a UV–Vis Spectrophotometer (Ocean Optic 2000, USA). The electrical conductivity was measured with an LCR Hi-Tester (Hioki 3522-50, Japan) in the frequency range 1–1000 kHz. The nanocomposite film was placed between the capacitor plates and then the conductance (G) was measured. The electrical conductivity value was determined from the following equation (Khair and Arof 2009):

$$\sigma = \frac{l}{A} \times G$$

where σ is the electrical conductivity (S/cm), l is the sample thickness (cm), A is the sample area, and G is the conductance (S). Tensile properties of ten specimens were measured with a Shimadzu Autograph AG-IS 1 kN (Japan) at crosshead speed of 5 mm/min, according to ASTM D882-75b.

Results and discussion

Chemical composition of primary sludge before and after purification

The chemical compositions of the primary sludge before and after purification are shown in Table 1. The cellulose content after purification increased from 39.87 to 76.34% because the non-cellulosic components (i.e., extractives, hemicellulose, lignin, and ash) were removed during the purification process. The lignin and ash contents decreased remarkably. Primary sludge generally contains inorganic materials such as kaolin, clay, and calcium carbonate (Girones et al. 2010; Gomez and de Alda 2008). Table 2 shows the elemental analysis results of the primary sludge before and after purification by EDS. The mass of C and O increased by 6.42 and 3.32% after purification, respectively. The mass of Ca decreased remarkably, whereas the masses of Al, Si, S, and Zr did not change significantly.

FTIR spectroscopy

FTIR spectra of the primary sludge, purified primary sludge, and CNC-IIs are shown in Fig. 1. The peaks near 3500 cm^{-1} in all spectra are representative of OH groups and suggest the presence of cellulose (Johar et al. 2012). The peak intensity at 1420 cm^{-1} due to lignin decreased in the purified sludge, CNC-II-30, and CNC-II-60, which might be due to the removal of lignin during the purification process (Fahma et al. 2011). In typical FTIR spectra of cellulose, peaks at 750 and

Table 1 Chemical composition of primary sludge before and after purification

Component	Mass (%)	
	Before purification	After purification
Extractives	4.49	0.61
Hemicellulose	20.49	12.88
Cellulose	39.87	76.34
Lignin	21.62	2.76
Ash	33.47	4.96

Table 2 EDS data of primary sludge before and after purification

Element	Mass (%)	
	Before purification	After purification
C	38.58	45.00
O	43.65	46.97
Al	1.11	1.29
Si	1.50	1.32
S	0.41	0.31
Ca	10.63	0.25
Zr	4.12	4.86

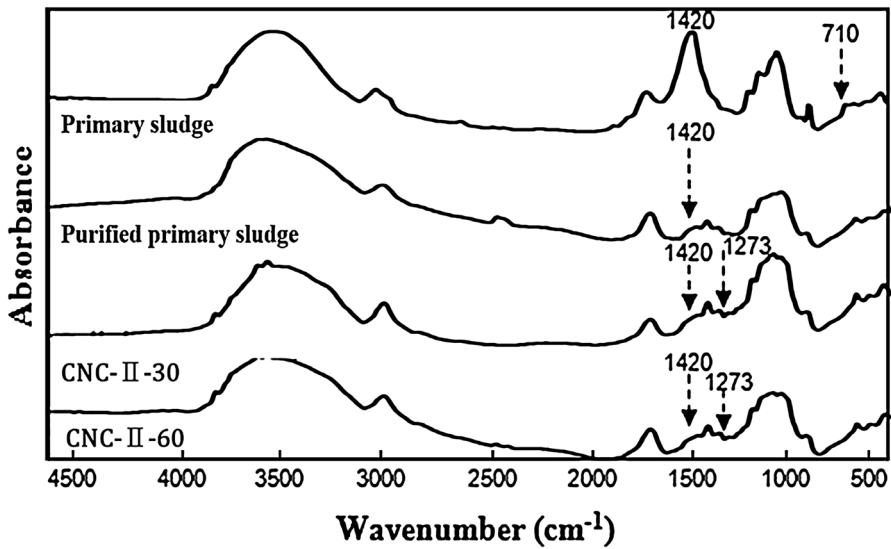


Fig. 1 FTIR spectra of primary sludge, purified primary sludge, and CNC-IIs

710 cm^{-1} are representative of cellulose I α and I β , respectively, but no peak at 750 cm^{-1} was detected in any FTIR spectrum. Meanwhile, only the peak at 710 cm^{-1} was seen in the sludge spectra, indicating that the I β crystalline polymorph of cellulose was dominant in the sludge (Zuluaga et al. 2009; Fahma et al. 2011). The peak at 710 cm^{-1} was not detectable in the spectra of CNC-II-30 and CNC-II-60, suggesting transformation from cellulose I to cellulose II.

X-ray diffraction analysis

The X-ray diffraction patterns in Fig. 2 show that the sludge was mainly composed of cellulose and calcium carbonate phases. This finding agrees with the finding of Girones et al. (2010) that sludge is primarily composed of cellulose fibers and inorganic materials. The calcium carbonate peak disappeared after the purification treatment. The three peaks at $2\theta = 14.80^\circ$ (110), 16.20° ($1\bar{1}0$), and 22.70° (200) confirmed that only cellulose I was present in the primary sludge sample. Purification treatment changed the three peaks to 12.34° (110), 19.95° ($1\bar{1}0$), and 21.85° (200), indicating the formation of the cellulose II structure (Yue 2011; Neto et al. 2013). This change occurred because of alkaline treatment during purification. As reported by Kim et al. (1990) and Zugenmaier (2008), the structure of cellulose I can be converted to cellulose II when treated with a high concentration of sodium hydroxide. The X-ray diffraction patterns of CNC-II-30 and CNC-II-60 also showed the structure of cellulose II.

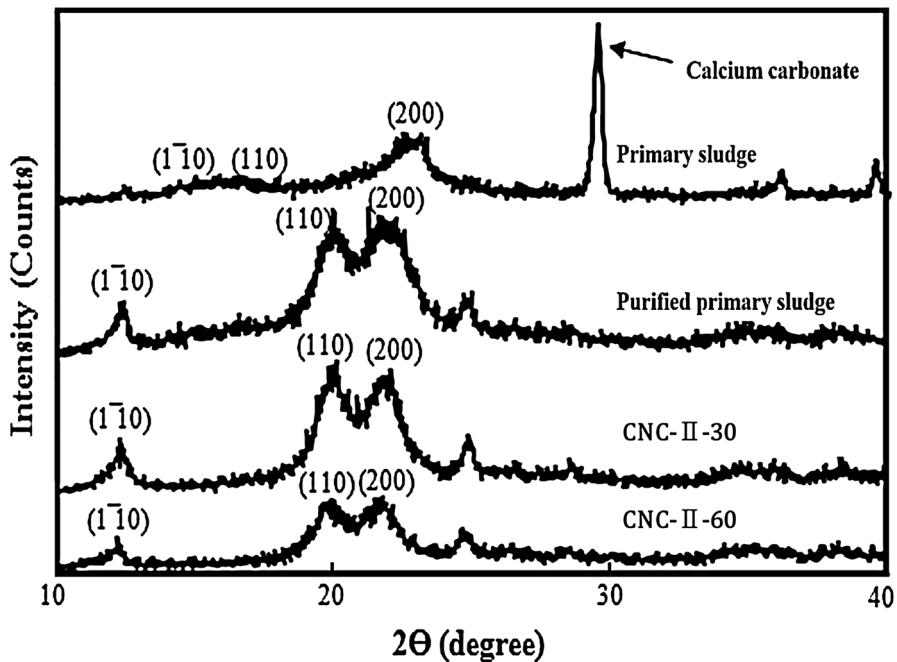


Fig. 2 WAXD profiles of primary sludge, purified primary sludge, and CNC-IIs

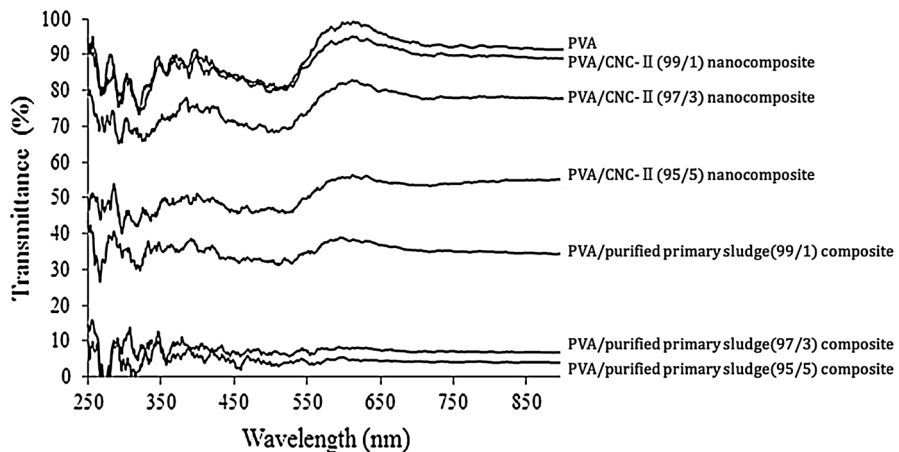


Fig. 3 UV-Vis spectra of neat PVA film and composites with purified primary sludge and CNC-IIs

Physical and tensile properties of CNC-II-reinforced PVA nanocomposite

Figure 3 shows the UV-Vis transmittance spectra of the nanocomposites. PVA film is a transparent polymer with a transmittance of 93% at 600 nm (wavelength). The 1 and 3% CNC-II-reinforced PVA nanocomposites had transmittances of 80%. On the

other hand, the nanocomposite reinforced with 5% CNC-IIIs had a transmittance of 54%. Uniform distribution of the CNC-IIIs in the PVA matrix brings about the transparent nature of the nanocomposites (Fortunatia et al. 2013a). The composite films reinforced with 1, 3, and 5% fiber of the purified sludge had low transparent values, namely 35, 6, and 4%, respectively. This may be due to poor distribution of the fibers in purified sludge in the PVA matrix.

Figure 4 shows the conductivity values of the PVA film and the nanocomposite films with purified primary sludge and CNC-IIIs. The conductivities of the composites with CNC-II were higher than that of neat PVA, which was higher than those of the purified sludge embedded in PVA (at different levels). The conductivity increased with increasing fiber content in CNC-II-reinforced nanocomposites, but decreased in the composite with cellulose fiber of the purified sludge.

Figure 5 shows the tensile properties of the composites. The tensile strength and tensile modulus of the 1 and 3% CNC-II-reinforced nanocomposites were higher than those of the neat PVA films. In particular, 3% CNC-II addition remarkably increased the elongation at break. This indicates that the homogeneous dispersion of CNC-II enhanced the formation of hydrogen bonds between PVA and CNC-II (Fortunatia et al. 2013a). Yue (2011) reported that the change of cellulose I to cellulose II can increase tensile properties. The tensile properties of the PVA/PSF composite were lower than those of the nanocomposites with CNC-IIIs, indicating that the larger surface area and reduced size might be the cause for the beneficial effects of CNC-IIIs on tensile properties. Fortunati et al. (2013b) reported the PVA/CNC nanocomposite with CNC extracted from Okra fibers. Young's modulus and elongation at break of the PVA/CNC nanocomposite with 1, 2, and 5% CNC ranged from 700 to 120 MPa and 10–130%, respectively. They suggested that 5 wt% CNC addition is ideal to improve mechanical interaction between the PVA and cellulose structures.

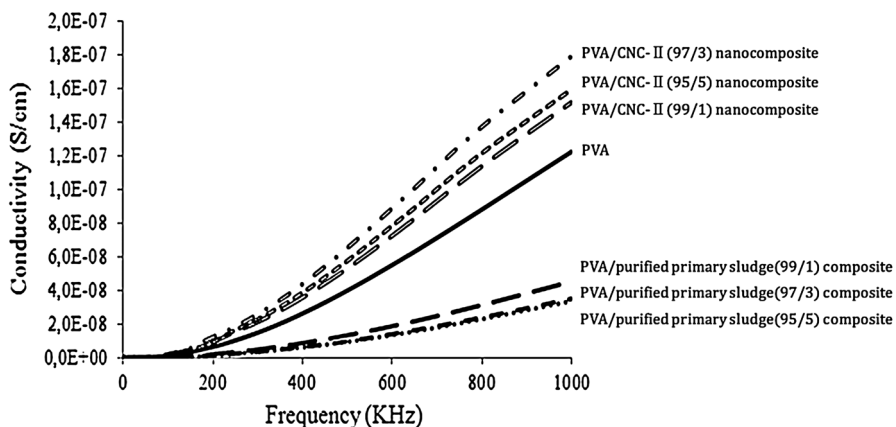


Fig. 4 Conductivity values of neat PVA film and composites with purified primary sludge and CNC-IIIs

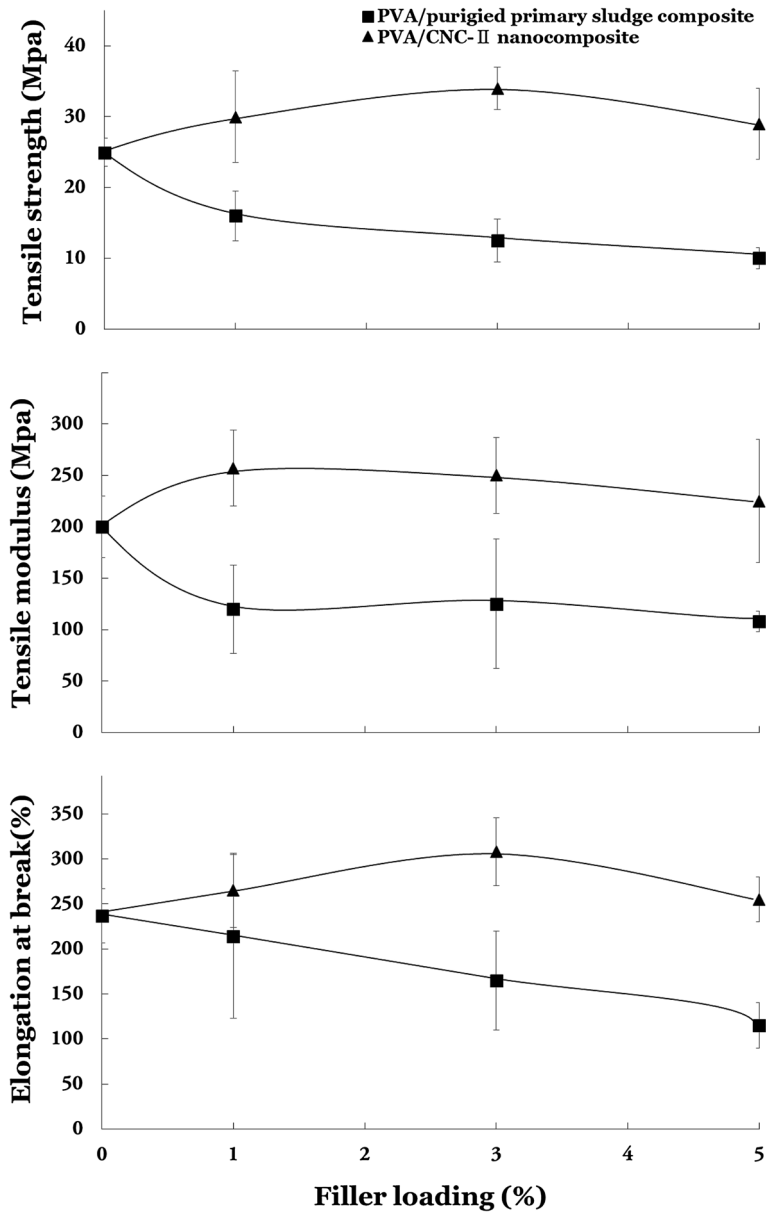


Fig. 5 Tensile strength, tensile modulus, and elongation at break of PVA film and composites with purified primary sludge and CNC-IIs

Conclusion

CNC-IIIs were successfully prepared by the sulfuric acid hydrolysis of cellulose fiber in primary sludge after purification. The non-cellulosic materials such as lignin, hemicellulose, and inorganic materials in primary sludge were remarkably reduced after purification treatment. During alkali treatment in the purification process, crystalline polymorphs of cellulose I changed to cellulose II, which is more stable and less reactive than cellulose I. The physical and tensile properties of CNC-II-reinforced nanocomposites were improved relative to those of the neat PVA film and the composite reinforced with PSFs.

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