Preparation and characterization of nano-cellulose with new shape from different precursor

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ABSTRACT

Three different precursor materials – 1. China cotton, 2. South African cotton, 3. Waste tissue papers were used to produce nano-cellulose by acid hydrolysis route. No chemical pretreatment has been done for the production of nano-cellulose from these precursors. Prepared nano-cellulose and their corresponding precursor materials were characterized by transmission electron microscopy (TEM), particle size analysis, X-ray diffraction (XRD) study, thermo gravimetric analysis (TGA), differential scanning calorimetric (DSC) analysis and Fourier transformed infra red (FTIR) spectroscopy. A comparative study of the characteristics was done with the properties of raw materials and with that of nano-cellulose. Shape and size of the nano cellulose generally depends on nature of the precursor and hydrolysis condition. Morphology study of nano-cellulose from different sources revealed range of length from 50 to 200 nm and diameter from 10 to 90 nm. Higher thermal stability and crystallinity of nano-cellulose were observed compared to that of precursor from TGA/DSC study.

1. Introduction

Cellulose is one of the most abundant and ubiquitous polymers on the planet Earth occurring in wood, cotton, hemp and other plant-based materials and serving as the dominant reinforcing agent in different matrices (Eichhorn et al., 2010; Iwamoto, Abe, & Yano, 2008; Mathew, Chakraborty, Oksman, & Sain, 2006). It has widespread application in biomedical, packaging, automobile sectors in the present age, but also in past for making of ropes, sails, paper, timber for housing and many other applications (Iwamoto, Nakagaito, Yano, & Nogi, 2005). Nano-scale celluloses like cellulose nano-fibrils, nano-whiskers, microfibrillated cellulose, and bacterial cellulose are high-value materials that serve as promising candidates for bio-nanocomposite production (Henriksson, Berglund, Isaksson, Lindstro, & Nishino, 2008; Henriksson, Henriksson, Berglund, & Lindstro, 2007; Iguchi, Yamanaka, & Budhiono, 2000). Nano-scale cellulose has different attractive properties like high strength and stiffness, low weight and biodegradability; thus getting more interest commercially and in research (Janardhnan & Sain, 2006; Klemm et al., 2006) Moreover cellulose nanocrystalls have liquid crystal properties and can show chiral nematic self-ordering in non-polar solvents (Heux, Chauve, & Bonini, 2000). Several processes have been used to extract highly purified nano-cellulose depending on their sources and pretreatment method. These methods include mechanical treatments like high pressure homogenizing (Jonoobi, Mathew, & Oksman, 2012; Qua, Hornsby, Sharma, & Lyons, 2011) chemical treatments like acid hydrolysis (Elazzouzi-Hafraoui, Nishiyama, Putaux, Heux, & Dubreuil, 2008; Habibi, Lucia, & Rojas, 2010) and biological treatments like enzymatic hydrolysis (Paavo et al., 2013). Several researchers prepared conventional nanocellulose from cotton (Das et al., 2009; Das, Ray, Bandyopadhyay, & Sengupta, 2010; Savadekar & Mhaske, 2012). As the content of cellulose in cotton fibres is very high (upwards 90%), generally, there is no need for pretreatment to obtain nano-cellulose.

The geometric properties of the nano-cellulose structures (shape, length and diameter) depend mainly on the origin of the cellulose and the extraction process (Boluka, Roya, & Mark, 2011). Several sources of cellulose have been used to obtain cellulose nanostructures, not necessarily conventional needle-shaped, which have high crystallinity. Recently, spherical

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cellulose nanoparticles have been synthesized by several researchers (Haafiz Mohamad, Eichhorn, Hassan, & Jawaid, 2013).

The main objective of the work is the facile synthesis and characterization of nano-cellulose with different shape which was completely different from conventional nano-cellulose like nano fibrils, nano-whiskers, microfibrillated cellulose. Physical and chemical characterization of this prepared nano-cellulose together with their thermal stability was investigated in comparison with the properties of their raw materials, in order to define their applicability and suitability to develop new fields of research.

2. Experimental

2.1. Materials

Three different raw materials:

1. China cotton (CC)
2. South Africa cotton (SAC)
3. Waste tissue paper (TP)

Sulfuric acid (Merck), NaOH (Merck).

2.2. Preparation of nanocellulose from different sources

Nano-cellulose was prepared from three different sources by acid-catalyzed hydrolysis method (Dong, Kimura, Revol, & Gray, 1996). Acid concentration was 47% sulfuric acid which was optimized by Das et al. (Das et al., 2009). Briefly, the calculated amount of raw materials were mixed with measured amount of sulfuric acid and vigorously stirred at 60 °C for 2 h. An acidic suspension of nano-cellulose resulted. The resulted suspension was centrifuged and washed with deionized water several times to reduce acid concentration. The suspension was finally neutralized with 0.5 N NaOH solutions and again washed with distilled water. The prepared nano-cellulose suspension was freeze-dried to get nano-cellulose powder. Nano-cellulose obtained from China cotton, South African cotton and waste tissue paper was referred as CNC, SANC and TANC respectively.

2.3. Charaterization

TEM analysis: Samples were examined under transmission electron microscopy (TEM, JEOL, Japan) equipment for microscopic analysis. A droplet of diluted suspension of nano-cellulose sample was deposited on a carbon microgrid (400 mesh) prior to examination and allowed to dry.

Particle size analysis: Particle size analysis of the different nano-cellulose was done with a dynamic light scattering particle size analyzer (Yobin Horiba, LB-550). A very dilute solution was made by taking nano-cellulose in deionized water. Then the solution was sonicated for good dispersion. Then, the sonicated solution was placed in the particle size analyzer to get particle size distribution.

XRD study: X-ray diffraction (XRD) analysis of nano-cellulose from various sources were conducted using X-pert PRO XRD Cu K$_\alpha$ radiation (wavelength 0.154 nm), operated at 40 kV/40 mA. The samples were scanned in fixed time (FT) mode with a counting time of 2s under diffraction angle 2θ in the range of 1°–60°.

DSC study: Runs were carried out in a DSC Q2000 V24.4 (TA instrument) from room temperature to 400 °C at a heating rate of 10 °C/min under nitrogen atmosphere at flow rate 50 ml/min. The experiment was done by first heating, cooling, second heating cycles.

TGA: The thermal stability of samples was determined by means of thermo gravimetric analyzer using a TGA Q500 (TA Instruments)

at a heating rate of 10 °C under nitrogen atmosphere, from room temperature to 500 °C.

FTIR spectroscopic study: FTIR of the all nano-cellulose samples were done by SHIMADZU instrument. Scans were carried out on wave number from 4000 cm^{-1} to 600 cm^{-1}.

3. Results and discussion

Hydrolytic cleavage of glycosidic bonds between two anhydroglucose units was observed during acid hydrolysis of the precursor material to produce cellulose with nanometric dimension. This action is counteracted by rearrangement of the tangling chain ends, which is favoured by release of internal strain. In this way amorphous portion gets dissolved by the acid hydrolysis, leaving behind the crystalline regions. Acid hydrolysis followed by mechanical treatment results in disintegration of the cellulose structure into nano crystalline cellulose particles. Effective production of nano-cellulose with different shape was resulted due to effective acid hydrolysis with mechanical agitation from different precursor. Rectangular and square shaped nano-cellulose crystals were observed for CNC and TNC samples from TEM analysis (Fig. 1a–c). The approximate ranges of diameter of CNC and TNC were from 30 to 60 nm and 10 and 90 nm respectively. However, TEM image of SANC showed smaller and finer particles of completely different shape from other samples. The diameter range of this sample was from 2 to 10 nm and the shape was irregular. Interestingly, the range of diameter distribution varied considerably among the sources; that is the diameter range of SANC aggregates was from 2 and 10 nm, was smaller than those from CNC and TNC, ranging from 30 to 60 nm and 10 to 90 nm, respectively.

The particle size and particle size distribution depend on the structure of the source sample, acid concentration, temperature, time, procedure of hydrolysis and the mechanical treatment. Fig. 2 showed the particle size analysis of different nano-cellulose samples. Although the size distribution of each sample varied from ~4 to 15 nm, but the distribution pattern was different. As evident from TEM study (Fig. 1) that SANC showed finer particles, a lower range of distribution for SANC was observed from Fig. 2. The highest volume (%) showed the particle range of 7–9 nm for SANC and 9–10 for CNC and TNC. From TEM study, it was also evident that the particle size was larger for CNC and TNC in comparison to that observed in particle size analysis study. That might occur due to the high agglomeration affinity of CNC and TNC. Similar observation was reported by Das et al. (Das et al., 2009; Das, Ray, Bandyopadhyay, & Sengupta, 2010). The suspension of nano cellulose was dried to nano-cellulose powder and subjected to XRD analysis. The XRD graphs of the precursor and the prepared nano cellulose particles are shown in Fig. 3.

The crystallite size was calculated (Das et al., 2009) by using the Scherrer equation in (1),

$$L_{h,k,l} = K\lambda = \beta \cos\theta \tag{1}$$

where $K = 0.94$, based on the full width at half maximum of 002 reflection. The cellulose I peak responsible for 002 reflections was at $2\theta = 22.2°$. The % crystallinity was also calculated (Das, Ray, Bandyopadhyay, & Sengupta, 2010) as per the formula in (2),

$$\% \text{Crystallinity} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \tag{2}$$

The changes in the % crystallinity and the crystallite size perpendicular to 002 plane are summarized in Table 1. In case of China cotton, the crystallinity of CNC increased (92.4%) compared to source China Cotton (82.4%), implying that dissolution of amorphous china cotton raised the crystallinity of the CNC particles. In South African Cotton also, removal of amorphous fractions increased the crystallinity of the SANC particles (97.8%) with respect to their source