Physial Properties of Nanocellulose Extracted from Empty Fruit Bunch

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Abstract. The high content of cellulose in lignocellulosic waste can be further utilized to produce nanocellulose (NCC). Conventional method of dissolving lignocellulosic waste in acid solvent is detrimental to the environment. Thus, a new method for utilizing lignocellulosic waste using environmental friendly solvent should be developed. NCC can be produced by dissolution of palm oil empty fruit bunch (EFB) in green solvent, natural deep eutectic solvent (NADES). In this study, palm oil EFB was used to produce NCC by dissolving in NADES and analysed for its characterization. Atomic force microscope (AFM) and transmission electron microscope (TEM) were used to evaluate the NCC’s morphology and dimension. Under AFM analysis, the average height of NCC produced was 15.574±3.658 nm while the obtained diameter is 53.179±24.237 nm. Using TEM analysis, the NCC produced was a needle-like particles with average diameter of 17.842±2.859 nm, while the length is 185.486±91.776 nm. Based on TGA results, NCC produced has a thermal stability at 224 °C. From the results obtained, the dissolution of cellulose in NADES is able to produce nanocellulose with similar properties as nanocellulose produced using conventional method.

1. Introduction

Globally, Malaysia has played important role in palm oil industry and generates the economies of this country which consequently produced about 280 000 tonnes of empty fruit bunch (EFB) annually [1,2]. The high content of cellulose (44.4%), hemicellulose (30.9%) and lignin (14.2%) in EFB has raised interest for nanocellulose production in utilizing EFB as source of raw materials [2,3].

Various methods can be used for preparation of nanocellulose (NCC) from lignocellulosic fibres such as mechanical treatment, chemical treatment and chemo-mechanical treatment process. The most commonly used and studied method is acid hydrolysis [2]. However, the usage of acid hydrolysis is not environmental friendly as it is toxic, hazardous, time consuming and requires corrosion resistant reactors [4]. These drawbacks encourage the discovery and usage of more efficient and green method to prepare nanocellulose. Thus, ionic liquids (IL) have been given interest as one of the method used for preparing nanocellulose as this solvent possess high thermal and chemical stability, non-flammable and miscible with other solvents[5]. However, IL are expensive due to the highly synthesis cost. Thus, the usage of IL is replaced with deep eutectic solvent (DES) [6].
Natural deep eutectic solvent (NADES) comprises of two or three naturally occurring compounds (a mixture between HBD and HBA components) is also known as the sub-class of DES [7]. Natural compounds that is usually used to synthesize NADES is natural primary metabolites such as amino acids, organic acids and sugars [8]. In this study, the characteristics and thermal stability of NCC produced from dissolution of cellulose in NADES will be investigated.

2. Experimental

EFB was obtained from Taclico Company Sdn. Bhd. Chemicals used for this study were sodium chlorite (NaClO₂), acetic acid (>95%), sodium hydroxide (NaOH), citric acid 1-hydrate (99.5-100%), choline chloride (99%), and ethanol (95%) which were purchased from Modern-Lab Chemicals Sdn. Bhd., Malaysia and A.R. Alatan Sains (K) Sdn. Bhd., Malaysia.

2.1. Preparation and chemical treatment of EFB

EFB was grounded using small grinder and then sieved to obtain particle size of 250μm. 10 g of EFB was treated in 200 mL of alkaline solution for 1 to 2 hours at 85°C, and then rinsed with distilled water until pH 7 was obtained. 3% (w/v) NaOH solution was used for alkaline treatment in order to remove lignin [9,10]. Alkaline-treated EFB was bleached with bleaching solution (1:30) at 70°C for 1 hour. 1% (w/v) of NaClO₂ was prepared with an acidity of pH 4 and was used as bleaching solution [11]. The mixture was rinsed with distilled water repeatedly until pH 7 was obtained.

2.2. Preparation of NADES

Hydrogen bond acceptor (HBA) was mixed together with hydrogen bond donor (HBD) for NADES preparation. The mixture was vigorously stirred and heated for 1 to 2 hours at 80°C until clear liquid NADES was observed [12] 10 wt% of water was added to aid the mixture homogenization [13]. In this study, the NADES synthesized with a ratio of 2 choline chloride (HBA) to 1 citric acid (HBD).

2.3. Dissolution of EFB

Dissolution of EFB in NCC was performed based on the method used by previous work [14,15]. Treated EFB was mixed and stirred in NADES at a ratio of 1:40 at 85°C for 6 hours. Cold distilled water was added to quench the reaction. Ethanol was used at first washing of the mixture using centrifuge at 8000 rpm for 10 minutes and then repeated with distilled water to collect NCC suspension until there was no more cloudy suspension obtained. NCC suspension was then dried for characterization and solubility measurement based on the equation (1) shown below.

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\text{Solubility (\%) = } \frac{\text{Weight of dried NCC}}{\text{Initial weight of treated EFB}} \times 100
\]

2.4. Atomic Force Microscope (AFM)

Morphology or the dimensional image of NCC obtained was characterized using AFM. Sample was prepared by dropping a drop of diluted aqueous suspension of NCC on the surface of an optical glass substrate and was left to dry at ambient temperature. Sample was analyzed by the equipment at ambient temperature using tapping mode [16].

2.5. Transmission Electron Microscope (TEM)

The diameter, length and structure of the NCC was analysed using transmission electron microscope. A copper grid coated with a thin film of carbon was used as sample holder where a drop of diluted NCC suspension was placed there and left for self-drying at room temperature.
3. Results and Discussions

3.1. Solubility of NCC in NADES
NADES is known to be able to accept or donate electron or proton, thus making it an outstanding dissolution agent [17]. In earlier research, fructose was converted to HMF effectively when NADES consisting of citric acid and choline chloride were used [18]. This proved the ability of NADES to hydrolyze carbohydrates, which was cellulose into NCC. Table 1 shows that the dissolution of treated EFB in NADES provides a solubility value of 2.74 % to produce NCC. NADES is formed by the interaction between HBA and HBD, which creates the competition of forming hydrogen network between cellulose molecules, and consequently disrupt cellulose hydrogen bonding to create smaller particles size of NCC.

| Temperature, (°C) | Time, (h) | Solubility, (%) |
|------------------|-----------|-----------------|
| NADES: treated EFB, 40:1 | 85 | 6 | 2.74 |

3.2. Physical characterization of NCC
Microscopy analysis using AFM and TEM are used for NCC’s physical characterization and morphology analysis. The roughness of NCC able to be determined by AFM analysis and based on figure 1, the NCC particles tend to overlap with one another. The dense appearance in figure 1 is due to the overlap and aggregation of NCC deposited on the glass slide holder [19].

![AFM amplitude scanning of NCC](image)

Based on figure 2, the topography image of NCC is captured and describes the summary of NCC dimension using AFM. In this analysis, the average height achieved by NCC is 15.574 ± 3.658 nm while the obtained diameter is 53.179 ± 24.237 nm. Based on literature, cellulose nanocrystal usually have a width of 2-30 nm and several hundreds of nanometers in length [20]. The width values obtained from the AFM analysis shows that the NCC particles formed through dissolution of EFB in NADES can be classified as nanocellulose crystals.
Transmission electron microscope (TEM) provides a high-resolution images [21]. From the image captured by TEM in figure 3, NCC produced from dissolving EFB in NADES shows a needle-like structure, similar to NCC produced from maize straw [22]. TEM shows that the average diameter of NCC was 17.842 ± 2.859 nm, while the length is 185.486 ± 91.776 nm. Comparing to similar raw material sources, Burhani and his team produces NCC from oil palm EFB with a diameter of 43 ± 8 nm and average length of 147 ± 23 nm [23]. NCC produced in this study has smaller width compared to Burhani’s team. This shows that the interfibrillated hydrogen bonds in cellulose fiber were broken down by NADES due to hydrogen bonding competition [20,24].
4. Conclusions
Dissolution of lignocellulosic materials in a green solvent, NADES is shown to be able to produce nanocellulose with similar characteristics as nanocellulose obtained through conventional method using acid solvent based on the results obtained through AFM and TEM. Even though the solubility of nanocellulose in NADES is quite low compared to conventional method, this value can be improved by additional vigorous mechanical treatment during dissolution process. Thus, NADES can be a potential solvent for producing nanocellulose with further improvement on the method of dissolution.

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