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Isolation and characterization of cellulose nanowhiskers from oil palm biomass microcrystalline cellulose

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ABSTRACT

The objective of this study is to compare the effect of two different isolation techniques on the physicochemical and thermal properties of cellulose nanowhiskers (CNW) from oil palm biomass obtained microcrystalline cellulose (MCC). Fourier transform infrared analysis showed that there are no significant changes in the peak positions, suggesting that the treatments did not affect the chemical structure of the cellulose fragment. Scanning electron microscopy showed that the aggregated structure of MCC is broken down after treatment. Transmission electron microscopy revealed that the produced CNW displayed a nanoscale structure. X-ray diffraction analysis indicated that chemical swelling improves the crystallinity of MCC while maintaining the cellulose I structure. Acid hydrolysis however reduced the crystallinity of MCC and displayed the coexistence of cellulose I and II allomorphs. The produced CNW is shown to have a good thermal stability and hence is suitable for a range of applications such as green biodegradable nanocomposites reinforced with CNW.

1. Introduction

In recent years, there is a growing interest in the development of biodegradable products using innovative processing technologies from renewable resources that offer sustainability and reduced dependence on fossil fuel (Cherian et al., 2011; Deepa et al., 2011). In this context, a renewable biopolymer resource that has high potential as a raw material for sustainable production is cellulose which occurs in abundance in nature, relatively cheap and biodegradable (Deepa et al., 2011; D. Liu, Zhong, Chang, Li, & Wu, 2010). Cellulose is a linear homopolymer of glucose $(C_6H_{10}O_5)n$ linked by 1, 4-β-glycosidic bonds with cellobiose, a dimer, as its repeating unit which is bound together by lignin and hemicelluloses (Filson & Dawson-Andoh, 2009; Li et al., 2009).

In nature, cellulose molecular chains are biosynthesized, self-assembled and repeatedly aggregated along cellulose chains to form microfibrils, which are composed of crystalline and amorphous domains (Eichhorn, 2010; Fernandes et al., 2011; Nishiyama, 2009). Cellulose I only exists in two allomorphs which are the crystalline structure in nature (Filson & Dawson-Andoh, 2009). The fiber bundles of cellulose molecules are stabilized laterally by hydrogen bond between hydroxyl groups (Nishiyama, 2009). Cellulose fibers obtained from different sources or their derivatives have been used in a different type of products for a long time. However, it has only been known that acid hydrolysis of cellulose fibers yielded very crystalline rodlike cellulose nanocrystals (CNC), also called cellulose nanowhiskers (CNW) or nanocrystalline cellulose (NCC) or even monocrystal despite their nanoscale dimension (Bras et al., 2010; Brito, Pereira, Putaux, & Jean, 2012).

CNW has gained considerable interest because of their unique and attractive features i.e. cost effectiveness, high aspect ratio, and light weight (H. Liu, Liu, Yao, & Wu, 2010). Indeed the tensile strength of whiskers is far above those of current high-volume content reinforcements, allowing the processing of the highest attainable composite strengths (Bondeson, Mathew, & Oksman, 2006; D. Liu et al., 2010). They are also ideal as reinforcement's materials in a transparent polymeric matrix because they do not cause light scattering. This is due to their lateral dimensions smaller than the wavelength of visible light e.g. bacterial cellulose fibrils (Yano et al., 2005).

CNW can be prepared by acid hydrolysis of any natural source of cellulose. The controlled acid hydrolysis readily degrades the amorphous regions of the cellulose microfibrils, leaving the crystalline segments intact and leading to the formation of single crystals (Rånby, 1951; Samir, Alloin, & Dufresne, 2005). The length and

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width of the CNW mainly depend on the cellulose source and the acid hydrolysis conditions (Brito et al., 2012). It is difficult to obtain uniformly dispersed CNW from natural plant fibers because the nano-phase has a strong tendency to form larger structures via aggregation and agglomeration (D. Liu et al., 2010). However, when subjected to mechanical dispersion or ultrasonification, it permits the dispersion of CNW aggregates, resulting in the production of stable colloidal suspensions (Filson & Dawson-Andoh, 2009; Pandey, Chu, Kim, Lee, & Ahn, 2009). As reported earlier (Filson & Dawson-Andoh, 2009; Petersson, Kvien, & Oksman, 2007), proper treatment of microcrystalline cellulose (MCC) with sulfuric acid (H_2SO_4) provides not only isolated cellulose whiskers but also yields a negatively charged surface resulting from the esterification of hydroxyl groups by sulphate ions forming a stable colloidal dispersion. Another alternative way to produce CNW from MCC is chemical swelling and ultrasonic treatment method proposed by Oksman, Mathew, Bondeson, and Kvien (2006).

The present paper describe, for the first time to our knowledge, the isolation and detailed characterization of CNW from MCC obtained from completely chlorine free oil palm empty fruit bunch (OPEFB) pulp. The isolation and characterization of MCC from OPEFB has previously been reported by the present authors (Haafiz, Eichhorn, Hassan, & Jawaid, 2013). OPEFB is the fibrous mass left behind after separating the fruits from sterilized fresh fruit bunches (Shinoj, Visvanathan, Panigrahi, & Kochubabu, 2011). This highly cellulosic material is presently used as fuel, fertilizers or mulching material (Hassan, Salema, Ani, & Bakar, 2010). OPEFB fibers are already recognized as a natural reinforcing component but their use as a viable bioresource to produce CNW has not received attention yet, despite increasing efforts to find high-added value application for this fiber. In addition, CNW characterization was compared by using two different isolation techniques, acid hydrolysis and chemical swelling treatment. The aim of this comparison was to address the question of the influence of the different isolation technique on the properties of the CNW obtained.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC) was produced from oil palm empty fruit bunch (OPEFB) chlorine free pulps. The production of MCC was described in detail in our previous paper (Haafiz et al., 2013). All chemicals were used as received and were secured from Merck, Malaysia.

2.2. Preparation of CNW

2.2.1. Acid hydrolysis

Colloidal suspension of CNW in water was prepared as described in detail elsewhere (Bondeson et al., 2006; Li et al., 2009). For 5 g of MCC were hydrolyzed in 64% H_2SO_4 (96% purity) solution with an acid to MCC ratio of 8.75 ml/g at 40 °C for 60 min with strong agitation. The on-going hydrolysis was stopped by adding 4–5 times cold distilled water based on the volume of the reacting mixture. The diluted suspension was centrifuged using Universal 32 Hettich (Newport Pagnell, England) at 5000 rpm for 15 min to get the precipitates. The precipitate was suspended in distilled water, followed by centrifugation. This process was repeated until the supernatant solution became turbid and further the colloidal suspension was collected and sonicated for 30 min. Sonication was done in cold water bath to avoid heat-up. Subsequently, the suspension was stored in a refrigerator at 4 °C and designated CNW.

2.2.2. Chemical swelling

MCC was swelled and partly separated to whiskers by chemical and ultrasonification treatments using the same method as described by Pereda, Amica, Rácz, and Marcovich (2011) based on original procedures described by Oksman et al. (2006). *N*,*N*-Dimethylacetamide (DMAc) (99% purity) with 0.5% lithium chloride (LiCl) (99% purity) solution was used as swelling agent. The initial concentration of MCC in DMAc/LiCl was 10 wt%. The MCC was agitated using a mechanical stirrer inside a water bath for 12 h at 70 °C. The slightly swelled particles were then sonicated in a Branson 2510 bransonic bath for 3 h over a period of 5 days, with long intervals between each sonication treatment to separate the cellulose nanowhiskers. The resultant cellulose nanowhiskers were repeatedly washed with distilled water then freeze-dried and noted as CNW/S.

3. Characterization

3.1. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was measured by direct transmittance by means of the KBr pellet technique using a Perkin Elmer 1600 infrared spectrometer (Nicolet AVATAR 360) at 32 scans with a resolution of 4 cm^{-1} and within the wave number range of 370–4000 cm^{-1}. The position of significant transmittance peaks was determined using the "find peak tool" provided by Nicolet OMNIC 5.01 software.

3.2. Microscopic analysis

3.2.1. Scanning electron microscopy

Scanning electron microscopy (SEM) was carried out using a SEM-EDX Oxford INCA 400 model at an acceleration voltage of 15 kV. The samples were sputter-coated with gold to avoid charging.

3.2.2. Transmission electron microscopy

The dimensions of the prepared samples were obtained from transmission electron microscopy (TEM) model LEOLIBRA at an accelerating voltage of 120,000. The 5 μL suspension samples were placed on a carbon-coated grid and allowed to dry at room temperature. The TEM images were obtained using soft imagine system software.

3.3. X-ray diffraction

X-ray diffraction (XRD) was carried out to study the crystallinity of the samples using an X'Pert X-ray diffractometer (SIEMENS XRD D5000) and Ni-filtered Cu Kα radiation at an angular incidence of 10–60° (2θ angle range). The operating voltage and current were 40 kV and 50 mA, respectively. The crystallinity of the samples was calculated from diffraction intensity data using the empirical method for native cellulose (Rosa, Rehman, De Miranda, Nachtigall, & Bica, 2012; Tang et al., 2013). The crystalline-to-amorphous ratio of materials was determined using Eq. (1).

$$C_rI \quad (\%) = \frac{I_{002} - I_{am}}{I_{002}} \tag{1}$$

where C_rI is the crystallinity index, I_{002} is the maximum intensity (in arbitrary units) of the diffraction from the 0 0 2 plane at $2\theta = 22.6°$, and I_{am} is the intensity of the background scatter measured at $2\theta = 19°$.