Carbohydrate Polymers 127 (2015) 202–208

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Cellulose nanocrystals isolated from oil palm trunk

Junidah Lamaming[a], Rokiah Hashim[a,*], Othman Sulaiman[a], Cheu Peng Leh[a], Tomoko Sugimoto[b], Noor Afeefah Nordin[a]

[a] Division of Bioresource, Paper and Coatings Technology, School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
[b] Forestry and Forest Products Research Institute, I Matsunosato, Tsukuba 305-8687, Ibaraki, Japan

ARTICLE INFO

Article history:
Received 7 February 2015
Received in revised form 4 March 2015
Accepted 8 March 2015
Available online 30 March 2015

Keywords:
Cellulose nanocrystals
Oil palm trunk
Raw fibers
Hot water treated fibers
Thermal properties
Crystallinity

ABSTRACT

In this study cellulose nanocrystals were isolated from oil palm trunk (*Elaeis guineensis*) using acid hydrolysis method. The morphology and size of the nanocrystals were characterized using scanning electron microscopy and transmission electron microscopy. The results showed that the nanocrystals isolated from raw oil palm trunk (OPT) fibers and hot water treated OPT fibers had an average diameter of 7.67 nm and 7.97 nm and length of 397.03 nm and 361.70 nm, respectively. Fourier Transform Infrared spectroscopy indicated that lignin and hemicellulose contents decreased. It seems that lignin was completely removed from the samples during chemical treatment. Thermogravimetric analysis demonstrated that cellulose nanocrystals after acid hydrolysis had higher thermal stability compared to the raw and hot water treated OPT fibers. The X-ray diffraction analysis increased crystallinity of the samples due to chemical treatment. The crystalline nature of the isolated nanocrystals from raw and hot water treated OPT ranged from 68 to 70%.

1. Introduction

As an agricultural plant, the oil palm tree (*Elaies guineensis*) has become one of the major crops that contributes to economic growth of Malaysia. The total biomass of 95 million tons are generated annually, this lignocellulosic material provides a continuous supply for the new oil palm biomass industry (MPOB, 2012). This new industry has converted such underutilized bio-fiber into promising value-added products such as fertilizer, mattress filling, medium density fiberboard, molded wares, composite material, pulp and paper, and other potential products. Oil palm bio-fibre waste is lignocellulosic materials, and it is rich in cellulose. The trunks become available during the replanting season on a cycle of every 25 to 30 years. Holocellulose composition in oil palm trunk range from 72 to 78% (Abdul Khalil, Siti Alwani, Ridzuan, Kamarudin, & Khairul, 2008; Hashim et al., 2010; Lamaming et al., 2013, 2014). This makes the trunks suitable to be used as raw material for the production of cellulose nanofibers.

Cellulose is a poly β-1,4,D anhydroglucopyranose that displays a regular network of inter and intramolecular hydrogen bonding organized into perfect stereoregular configurations called microfibrils (Janardhanan & Sain, 2006). Naturally, cellulose composed of two main regions that are amorphous and crystalline. The crystalline regions were accessible by using strong acid hydrolysis to remove the amorphous regions. It is insoluble in water but can be degraded by microbial and fungal enzymes (Li et al., 2009). Synthesizing cellulose from lignocellulosic materials is very useful in various applications such as a potential use as reinforcing the component in high-performance composite materials (Zuluaga, Putaux, Restrepo, Mendragon, & Gañán, 2007; Faria, Cordeiro, Belgacem, & Dufresne, 2006). Research on cellulose nanofibers has been gaining much interest this past year with different isolation methods and raw materials. There are different methods for isolation of the cellulose microfibers being reported including mechanical, chemical, chemo-mechanical, and enzymatic isolation processes (Jonoobi, Khazaeian, Md Tahir, Azry, & Oksman, 2011).

Utilizing oil palms waste as a source for natural cellulose fibers will significantly benefit for the agricultural use, fiber resource, food, and energy needs. It will also help the environment because the products are considered as sustainable green materials. This will also tackle the problem of oil palm waste being left out in the field or burned and contribute to the economy by turning it into valuable products. The nanocellulose can be used in nanocomposite materials as reinforcing filler for the automotive industry, predominantly for interior applications, construction, electronics, cosmetics, packaging and also in biomedicine purposes (Abdul Khalil, Bhat, & Ireana Yusra, 2012; Tang, Du, Li, Wang, & Hu, 2009).

* Corresponding author. Tel.: +60 4 653 5217; fax: +60 4 6573678.
E-mail addresses: hrokiah@usm.my, hrokiah1@gmail.com (R. Hashim).

http://dx.doi.org/10.1016/j.carbpol.2015.03.043
0144-8617/

Application of nanocellulose in polymer reinforcement is still new and further research is needed. One of the applications is incorporating nanocellulose with polyvinyl alcohol (PVA), polylactic acid (PLA), starch, and polycaprolactone but also with polyethylene or polypropylene (Panaitescu et al., 2011). The PVA biocomposite film that was produced is water soluble, biodegradable, and can be used in manufacture medicine cachets, yarn for surgery, and controlled drug delivery systems because it has no toxic effect on the human body (Tang et al., 2009).

Research on the cellulose nanocrystal isolation using empty fruit bunch has been reported by a few researchers (Fahma, Iwamoto, Hori, Iwata, & Takemura, 2010; Jonoobi et al., 2011; Mohamad Haafiz, Eichhorn, Hassan, & Jawaid, 2013). Fahma et al. (2010) isolated the cellulose nanocrystal from an empty fruit bunch by using acid hydrolysis and Jonoobi et al. (2011) isolated the nanocrystal using chemo-mechanical process. The latter researcher using acid hydrolysis as described by Chuayjuljit, Su-uthai, and Charuchinda (2010) with followed the original procedure of Battista (1950). However, no studies could be found yet on the cellulose nanocrystal isolated from other parts of oil palm biomass, an especially trunk. For this reason, the aim of this study was to isolate the cellulose nanocrystal from oil palm trunk using chemo-mechanical treatments. The morphological and structural characteristics of isolated nanocrystal were evaluated through Scanning electron microscope (SEM) and Transmission electron microscope (TEM). The chemical components of the fibers were measured before and after chemical treatments according to TAPPI standard. The properties of the cellulose nanocrystal isolated from the trunk were characterized using thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD) analysis.

2. Experimental

2.1. Preparation of samples

Old oil palm trunks obtained from a plantation in Kuala Selangor were harvested and sawn into discs before the bark was removed. The trunks were then chipped and dried before being ground to particles and pass screening process of 1000 μm using a Willey Mill. Two types of materials were prepared from oil palm trunk, namely raw fibers and water-treated fibers soaked in hot water having a temperature of 60 °C ± 3 °C. For water treatment, the fibers were soaked with a thermostat control unit using hot distilled water for 6 h before they were filtered on a Buchner Funnel. This treatment was done because hot water removes a substantial amount of extractives in oil palm trunk and reduces the need to use ethanol/toluene solvents in producing the cellulose nanocrystal.

2.2. Isolation of the cellulose nanocrystal

The isolation of the cellulose nanocrystal was done following the procedure of Fahma et al. (2010) with a slight modification. About 20 g of raw oil palm trunk fibers was weighed. Extractives of raw oil palm trunk fibers were removed by Soxhlet extraction for 4 h using ethanol/toluene (v/v 2:1). Then, the extracted fibers were bleached four times in sodium chlorite ($NaClO_2$) solution under acidic conditions (pH 4 to 5) at 70 °C for 1 h then washed with deionized water. Hemicelluloses were removed by soaking the fibers with 6 wt% potassium hydroxide (KOH) solution at 20 °C for 24 h and rinsing with deionized water until pH 7. Then, the cellulose fibers were hydrolyzed in 210 mL of sulfuric acid (H_2SO_4) solution (64%) under strong agitation at 45 °C for 1 h. The hydrolysis was terminated by adding 400 mL of cold water. The precipitate was resuspended in water with strong agitation, centrifuged and dialysed for 3 days until the pH became constant. It was then homogenized, sonicated, and freeze dried. The step was repeated for water-treated fibers by skipping the Soxhlet extraction step.

2.3. Chemical analysis of the specimens

The chemical components of the oil palm trunks fibers before and after water treatments were investigated. Preparations of extractive free samples were conducted according to TAPPI 264 cm-97 (TAPPI, 1997) with a modification of the solvent ethanol-toluene ratio of 2:1. Holocellulose content was done based on the method of Wise, Murphy, and D'Addieco (1946). The cellulose content was extracted from the percentage of holocellulose with 17.5% sodium hydroxide. Lignin content of the samples was analyzed according to TAPPI 222 om-02 (TAPPI, 2002). Total starch content was carried out using a total starch kit manufactured by Megazyme International Ltd, Bray, Ireland. Measurement was conducted in triplicate, and the recorded data were found to be reproducible.

2.4. Microstructure study of the samples

An LEO Supra 50 Vp field emission scanning microscope (FESEM) with ultra-high resolution was used to study the effect of the water and chemo-mechanical treatments on the fiber morphology. All samples were gold-sputtered using sputter coater model Polaron SC 515 ± 20 nm to avoid charging.

2.5. Transmission electron microscope

The structure and size of the nanocrystal were observed by transmission electron microscopy (TEM) using a Philips CM 12 electron microscope. A drop of diluted oil palm trunk nanocrystal.

A total of 10 fibers of each material were measured, and the result was reported as the mean value of the data from each set of measurements.

2.6. Spectroscopic study by Fourier transform infrared

The presence of any changes in functional groups during treatment in the samples was scanned by FT-IR Spectroscopy. The samples were pounded to made a thin pellet that is the mixture of approximately 5 mg of particles samples and 95 mg of finely ground KBr. Spectra were viewed using a Nicolet infrared spectrophotometer (Avatar 360 FT-IR E.S.P) machine. The spectra produced are transmittance mode between wave numbers of 4000 cm^{-1} and 500 cm^{-1}.

2.7. X-ray diffraction analysis of the samples

Structural and phase analyzes of the samples were measured by using an X-ray diffractometer with Ni-filtered Cu*K*α radiation (wavelength of 1.5406 Å). The operating voltage and current were generated of 40 kV and 30 mA, respectively. The samples was scanned at 2°/min with a 2θ angle range from 5° to 50°. The crystallinity index value was computed according to Segal, Creely, Martin, and Conrad (1959) to quantify the crystallinity of the samples. The crystallinity index (C_{Ir}) is defined by:

$$C_{Ir}(\%) = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \quad (1)$$

where I_{002} is the peak intensity corresponding to crystalline and I_{am} is the peak intensity of the amorphous fraction.

2.8. Thermogravimetric analysis

Thermogravimetric analysis was performed to determine the thermal decomposition of the oil palm trunk fibers after each