Carbohydrate Polymers 184 (2018) 74–81

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Silylation and characterization of microcrystalline cellulose isolated from indonesian native oil palm empty fruit bunch

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ARTICLE INFO

Keywords:
Cellulose
OPEFB
Silylation
Surface modification

ABSTRACT

Silylation of microcrystalline cellulose (MCC), isolated from Indonesian native oil palm empty fruit bunch (OPEFB), using aminosilane compound synthesized through aminolysis of 3-glycidoxypropyltrimethoxysilane (GPTMS) with ethylenediamine (EDA) has been conducted in this study. Generally, there are three steps performed to isolate MCC before silylation process, i.e. bleaching, alkaline treatment and acid hydrolysis. All products resulted from bleaching, alkaline and acid hydrolysis treatments were characterized using Fourier Transform Infrared (FTIR) spectroscopy. Two conditions were optimized in this study which they were an acid concentration in hydrolysis process and aminosilane ratio in silylation process. The preliminary study regarding optimizing acid hydrolysis process by varying sulfuric acid concentration was obtained an optimum sulfuric acid concentration by 45% having highest crystallinity index (CI) measured using x-ray diffraction (XRD) data. The morphological structure of MCC was rod-like crystalline structure confirmed by transmission electron microscopy (TEM). The silylating agent was varied in this study with the ratio to MCC by 1:1, 3:1 and 5:1 mmol g^{-1}. Based on loading analysis, the aminosilane with ratio 1:1 mmol g^{-1} was noted as optimum concentration having high loading yield by 79.2%. Effect of silylation on MCC properties was, on the one hand, it decreased the CI and crystallite size, however, on the other hand, it increased the surface area and pore volume.

1. Introduction

Cellulose, a renewable and biodegradable polymer (Abraham et al., 2011; Eichhorn et al., 2010), is the most abundant polymer which widely available in nature composed of D-glucopyranose units linked by β-glycosidic bonds (Li et al., 2009). Since its intra- and intermolecular bonds involving hydroxyl group on each unit of cellulose macromolecules, cellulose has various ordered crystalline arrangements (Park, Baker, Himmel, Parilla, & Johnson, 2010). Isolation of cellulose can be done from various raw materials, such as rice husk (Rosa, Rehman, Miranda, Nachtigall, & Bica, 2012), *miscanthus sinensis* (Jin et al., 2017), oil palm empty fruit bunch (Xiang, Mohammed, & Baharuddin, 2016) and others forestry and agriculture waste product. Palm oil industry is one of the largest industries established in Indonesia. In 2015, the total land of oil palm plantation reported by Directorate of Processing and Marketing of Agricultural Products, Indonesian Ministry of Agriculture, reached 11.4 million Ha and each hectare produced approximately 20–24 tons of oil palm. Indonesian Directorate General of Plantation was also reported that the oil palm production is predicted to increase by 12.60% in the next year. The abundance of these agriculture products does not only have a great impact on Indonesia's foreign exchange, but they also influence to environmental. Especially, the most waste product derived from oil palm industry is oil palm empty fruit bunch (OPEFB) achieving 22–24% toward fresh oil palm fruit (Harsono, Mulyantara, Rizaluddin, Nakagawa-izumi, & Ohi, 2015). The negative impact of this waste product motivated us to conduct this research as one of the simple ways proposed to not only maintain this agriculture waste product numbers but also increase the economic values by transforming them into a useful material instead of burned in an incinerator or dumped.

In order to enhance the properties of waste OPEFB, one of strategy that can be performed is by transforming it to micro- or nano-scaled materials. Microcrystalline cellulose (MCC), integrated from bulk cellulose, is a micro-sized crystalline material, usually 10–50 μm with a degree of crystallinity (also referred as crystallinity index, CI) approximately 55–80% (Chuayjuljit, Su-uthai, & Charuchinda, 2010;

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https://doi.org/10.1016/j.carbpol.2017.12.060
Received 22 August 2017; Received in revised form 19 December 2017; Accepted 21 December 2017
Available online 23 December 2017
0144-8617/

Moon et al., 2011). It is extracted from cellulose through hydrolysis with a high acid concentration around 50–65% v/v to remove amorphous region leaving a high amount of crystalline phase (Ching & Ng, 2014; Lani, Ngadi, Johari, & Jusoh, 2014; Xiang et al., 2016). Microcrystalline cellulose could be extracted from a wide range of agriculture variety containing lignocellulose. Hussin et al. (2016) isolated MCC from leaf pulp of palm tree resulting high surface area by 5.64 $m^2 g^{-1}$ compared to native cellulose (2.04 $m^2 g^{-1}$). Utilization of OPEFB as starting material to extract MCC has been reported by previous research with different concentration of sulfuric acid. Xiang et al. (2016) employed 55% of sulfuric acid concentration to isolate MCC from palm tree stalk obtaining high crystallinity index by 82.2%. Ching and Ng (2014) hydrolyzed OPEFB with a high concentration of sulfuric acid by 64% resulting in MCC with 58% of CI. In a preliminary study, we applied Xiang et al. (2016) method to obtain MCC with high CI instead of Ching and Ng (2014) method. Unfortunately, the acid concentration was not suitable to isolate MCC from the Indonesian native OPEFB indicated by the black color of the product and low CI. Thus, we are motivated to conduct this research in order to determine the optimum concentration in OPEFB hydrolysis process to obtain high CI value of MCC by varying sulfuric acid concentration by 45%, 55%, and 65%.

Modifying the MCC surfaces by introducing functional compound is also promising approaches to enhance its properties for the wide application. Today, chemical modification of nano- or micro-crystalline structure materials is received much attention and to be a popular method in the literature (Eyley & Thielemans, 2014). Introducing a functional group to material surfaces is well-established by the previous researcher, pioneered by Ruiz-Hitzky and Fripiat (1976), to expand materials ability and applicability for such purposes, one of them is by silylation technique. The silylation is a technique to maintain material properties regarding their proposed application. The presence of multifunctional group on silane compound provides unique features, such as provide active functional group for further modification (He & Shi, 2011), offer good adhesion and physical properties (Frone, Berlioz, Chailan, & Panaitescu, 2013), as well as improve mechanical properties of materials (Zhang, Tingaut, Rentsch, & Zimmermann, 2015). Sèbe and coworkers (2015) has been successfully modified cellulose under controlled silylation by using methyltrimethoxysilane in water instead of alcoholic medium. Moreover, the investigation of tailoring properties of cellulose through silylation has been reported by previous researcher by using alkoxysilane compound, such as 3-methacryloxypropyltrimethoxysilane (Qu, Zhou, Zhang, Yao, & Zhang, 2012), 3-glycidoxypropyltrimethoxysilane (Lu, Askeland, & Drzal, 2008), and 3-aminopropyltriethoxysilane (Frone et al., 2013). However, it should be noted that Herrera, Letoffe, Reymond, and Bourgeat-Lami (2005) reported that the addition of a high amount of silane compound affected on decreasing of materials surface area. Thus, in this preliminary study, we optimized silylation condition in point of view on the employed alkoxysilane concentration. Based on our knowledge, there is no published paper reporting the use of alkoxysilane, synthesized by aminolysis of 3-glycidoxypropyltrimethoxysilane to form an aminosilane compound, as a surface modifier on isolated MCC from OPEFB.

2. Experimental

2.1. Materials

The raw OPEFB was used as received from Indonesian Institute of Science with chopped form (fiber length 2–5 mm, approximately). The chemicals were purchased from Merck and Sigma Aldrich, such as sodium hydroxide (Merck), sulfuric acid (Merck), ethanol (Merck), and acetic acid glacial (Merck). Technical grade sodium hypochlorite was purchased from Bratachem Corp. Distilled water was received from Integrated MIPA Laboratory, Universitas Sebelas Maret. Aminosilane compound was synthesized via aminolysis (3-glycidoxypropyl) trimethoxysilane (GPTMS, Aldrich) with ethylenediamine (EDA, Merck).

2.2. Optimization of microcrystalline cellulose isolation from raw OPEFB

The key parameter of optimization on isolation of MCC is the crystallinity index measured from XRD data. In this research, the optimized variable was sulfuric acid concentration on hydrolysis process, i.e. 45%, 55% and 65% v/v. There were three main steps conducted to isolate MCC, specifically bleaching, alkaline treatment and acid hydrolysis. The cleaned raw OPEFB was bleached using 15% v/v of acidified sodium hypochlorite solution. The ratio between raw OPEFB and sodium hypochlorite solution was arranged by 1:25 (g/mL). The bleaching process was carried out for 2 h at 80 °C and repeated three times. The bleached OPEFB was then cleaned using distilled water and dried overnight at 60 °C. Afterward, the bleached OPEFB was alkaline treated to remove lignin content using 17.5% w/v sodium hydroxide solution. The alkaline treatment was performed at room temperature for 2 h with ratio 1:12.5 (g/mL). This process was repeated for twice and after that, the alkaline treated OPEFB was neutralized using distilled water and dried for 12 h at 60 °C. The hydrolysis of OPEFB was conducted in the final stage after bleaching and alkaline treatment. In this stage, the sulfuric acid employed in hydrolysis process was varied by 45%, 55% and 65% v/v. The hydrolysis was performed at 45 °C for 45 min with OPEFB ratio toward sulfuric acid by 1:20 (g/mL). Then, the amount of cooled distilled water was added to terminate hydrolysis process. The final product on hydrolysis process was noted as MCC-X, where X is the sulfuric acid concentration, for example, MCC-45, MCC-55 and MCC-65 assigned for MCC obtained by hydrolyzing cellulose with 45, 55 and 65% of sulfuric acid. The raw OPEFB, bleached OPEFB, alkalinized OPEFB and hydrolysis products were characterized using FTIR (model IR-Prestige 21 Shimadzhu). Moreover, to determine the optimum condition on hydrolysis process, each product resulted from hydrolysis at 45%, 55%, and 65% sulfuric acid concentration were analyzed their crystallinity toward XRD data.

2.3. Silylation of microcrystalline cellulose

The silylation of MCC was done via introducing synthesized aminosilane into MCC-45 obtained from a hydrolyzed product with 45% sulfuric acid. The aminosilane was synthesized through aminolysis of 1 mmol GPTMS (0.236 g) with excess 3 mmol EDA (0.180 g) at room temperature in distilled water (2 mL) medium. The reaction was monitored for 1 h. The product was then characterized using FTIR and ^{1}H NMR. FTIR characterization was done using IR-Prestige 21 model 8201 PC Shimadzhu. IR GPTMS (KBr, cm^{-1}): 2943 (s, C—H), 2874 (w, C—H), 2841 (s, C—H), 1465 (m), 1193 (s, O—CH_3), 1087 (b, Si—O), 910 (s, epoxy ring). IR EDA (KBr, cm^{-1}): 3361 (b, N—H), 2934 (s, C—H), 2861 (s, C—H), 1599 (s, ν_{bend} N—H), 923 (b). IR aminosilane product (KBr, cm^{-1}): 3490 ((s, C—H), 2876 (s, C—H), 1642 (b, ν_{bend}N—H), 1101 (b, Si—O), there is no epoxy ring vibration peak observed. ^{1}H NMR aminosilane product (Agilent 400 MHz, CD_3OD, δ in ppm): 0.64 (broad s, 2H), 1.27 (s, $-NH_2$), 1.69 (broad s, 2H), 1.88 (s, −NH-), 2.71–2.87 (m, an overlapping of $-C(H_2)-NH-$, $-NH-C(H_2)-$ and $-C(H_2)-NH_2$), 3.30 (t, 2H), 3.45 (d, 2H), 3.88 (m, 1H).

The silylation of MCC-45 was performed in water medium according to Zhang et al. (2015). After obtaining the aminosilane product, it was added into dispersed MCC in distilled water. The reaction was occurred for 24 h at 70 °C with the aminosilane compound ratio to MCC-45 by 1:1; 3:1; and 5:1 (mmol g^{-1}). Afterward, the suspension was collected by centrifugation at 1000 rpm for 10 min. The product was then cleaned using distilled water and centrifuged for three times. The silylated MCC was then called as s-MCC.

2.4. X-ray diffraction measurement

The XRD data were collected using XRD model Shimadzhu XRD Lab-X 6000 with Cu Kα radiation source. The measurement was conducted at 2θ between 2 and 80° and compressed to 5–50° in this report. The