



Physico-chemical properties and thermal stability of microcrystalline cellulose isolated from Alfa fibres



Djalal Trache^{a,*}, André Donnot^b, Kamel Khimeche^a, Riad Benelmir^b, Nicolas Brosse^b

^a UER Chimie appliquée, Ecole Militaire Polytechnique, BP 17, Alger, Algeria

^b LERMAB, Faculté des Sciences et Technologies, Université de Lorraine, Vandœuvre-lès-Nancy, France

ARTICLE INFO

Article history:

Received 13 November 2013

Received in revised form 10 January 2014

Accepted 16 January 2014

Available online 27 January 2014

Keywords:

Microcrystalline cellulose

Alfa fibres

Chemical treatment

Characterization

Thermal properties

ABSTRACT

In this study, microcrystalline cellulose (Alfa-MCC) was extracted from Alfa fibres using acid hydrolysis method. The molecular weight of the cellulose samples was determined by gel permeation chromatography. The crystallinities were studied by means of X-ray diffraction and solid state cross polarization magic angle spinning ¹³C nuclear magnetic resonance spectroscopy, revealing that Alfa-MCC was more crystalline than the native cellulose isolated from Alfa fibres. The morphology of the celluloses was investigated using scanning electron microscopy, showing a compact structure and a rough surface. Furthermore, a good thermal stability was shown for Alfa-MCC. Based on these analyses, Alfa-MCC showed tremendous potential use as composites reinforcing agent, foods stabilizer and pharmaceutical additive.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Alfa grass or esparto grass (*Stipa tenacissima* L.) is a perennial tussock grass widely distributed in semi-arid ecosystems of the southern and western Mediterranean basin, mainly in the Maghreb (García-Fayos & Gasque, 2006). The main components of these fibres are cellulose, hemicellulose and lignin. These fibres have traditionally been used as animal feed and raw material for paper industry (Ahrens et al., 1998; Bessadok, Marais, Gouanvé, Colasse, & Zimmerlin, 2007). Utilization of Alfa fibres to produce biodegradable composites and thermoplastic materials has been recently published (Ben Brahim & Ben Cheikh, 2007; Maafi, Malek, Tighzert, & Dony, 2010; Nadji, Diouf, Benaboura, Bedard, & Riedl, 2009; Paiva, Ammar, Campos, Cheikh, & Cunha, 2007).

The isolation and characterization of microcrystalline cellulose particles (MCC) have been described from various cellulosic sources (Abdullah, 1991; Adel, Abd El-Wahab, Ibrahim, & Al-Shemy, 2011; Bocek, Shevchuk, & Lavrent'ev, 2003; Ejikeme, 2008; Ilindra & Dhake, 2008; Jahan, Saeed, He, & Ni, 2011; Keshk & Mohamed, 2011; Mohamad Haafiz, Eichhorn, & Jawaid, 2013a) and using several processes of extraction including mechanical treatments (Hanna et al., 2001; Laka & Chernyavskaya, 2007; Liimatainen, Sirviö, Haapala, Hormi, & Niinimäki, 2011), biological treatments (Adel, Abd El-Wahab, Ibrahim, & Al-Shemy, 2010; Janardhnan & Sain, 2006), and

chemical treatments, e.g., acid hydrolysis (see Adel et al., 2011; Ilindra & Dhake, 2008). All these methods lead to different types of MCC, depending on the cellulose raw materials, its pre-treatment, and more crucially on the disintegrating process itself. However, biological methods are desirable because glucose, a useful by-product, is generated; these methods are more expensive and lead to MCC products having a lower crystallinity. Thus, acid hydrolysis is the conventional method of choice for manufacturing MCC (Adel et al., 2011; Elanthikkal, Gopalakrishnanpanicker, Varghese, & Guthrie, 2010; Hanna et al., 2001; Ilindra & Dhake, 2008).

Due to its excellent properties, MCC has generated much attention and interest during these few last decades in both academic and industrial fields. In nanocomposite materials, MCC as reinforcing agent is attracting an increasing interest because of its potential advantages such as renewability, biodegradability and high surface area for bonding with resins. In addition, MCC exhibits a broad capacity to allow tailoring or grafting of chemical species to improve the morphology, thermal and mechanical properties of resulting composites (Azizi Samir, Alloin, & Dufresne, 2005; Hoyos, Cristia, & Vazquez, 2013; Mathew, Oskman, & Sain, 2005; Petersson, Kvien, & Oksman, 2007; Mohamad Haafiz, Hassan, Zakaria, Inuwa, & Islam, 2013b; Sun, Lu, Liu, Zhang, & Zhang, 2014a). Because of its chemical inactivity, absence of toxicity, high sorption and great hygroscopicity, MCC has received great interest (1) in pharmaceutical formulations, as a potential direct compression excipient especially in the design and development of tablets of poorly compressible and soluble drug (Chamsai & Sriamornsak, 2013; Kalita, Nath, Ochubiojo, & Buragohain, 2013; Levis & Deasy, 2001; Mallick,

* Corresponding author. Tel.: +213 661808275; fax: +213 21863204.

E-mail address: djalaltrache@gmail.com (D. Trache).

Pradhan, & Mahapatra, 2013; Oyeniyi & Itiola, 2012; Podczeck & Al-Muti, 2010), (2) in food industry, as stabilizer, emulsifier, thickener and gelling agents in several dairy compounds (Galal, Fatma, Ali, Jihan, & Sahar, 2010; Sanguansri & Augustin, 2006; Schuh, Allard, Herrmann, Gibis, & Kohlus, 2013). Therefore, additional information with regard to Alfa-MCC chemical structures and properties may certainly help the researchers to use Alfa fibres into beneficial above-mentioned applications.

To the best of our knowledge, the isolation and characterization of microcrystalline cellulose (Alfa-MCC) from Alfa fibres has never been described. In this work, MCC was extracted from Alfa fibres using acid hydrolysis method and was fully characterized through infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), ^{13}C nuclear magnetic resonance spectroscopy (NMR), Gel permeation chromatography (GPC) and thermal analysis. The comparison of Alfa-MCC and commercial microcrystalline cellulose (C-MCC) was also established.

2. Materials and methods

2.1. Raw materials

Alfa fibres were collected from the Saïda area, in Algeria. As received, these fibres were preconditioned before cellulose extraction took place. The fibres were washed with distilled water several times and dried in an oven at 80 °C for 24 h. Then they were shopped in an approximate length of 5–10 mm and kept in a vacuum desiccator. Cellulose microcrystalline (Avicel[®], MCC) was supplied by Merck. Hydrochloric acid (37%) and diethyl ether were purchased from VWR-Prolabo, sodium hypochlorite (NaClO) solution was provided from Alfa Aesar, ethanol and benzene were purchased from Sigma-Aldrich. All reagents are analysis grade and they were used without prior purification.

2.2. Characterization of the Alfa fibres

For the material under investigation, the moisture content was determined using a KERN MRS 120-3 Infra-red moisture analyser (drying at 105 °C to constant weight), the ash content was analyzed according to the standard method ASTM D-1102-84, hot water extracts were determined using the standard method ASTM D-1110-56, organic solvents extracts were analyzed using the standard method ASTM D-1107-56 modified by replacing benzene with toluene, the holocellulose content was determined according to ASTM D-1104-56, the lignin content was analyzed using ASTM D-1106-56 and, finally, the determination of α -cellulose was carried out according to ASTM D-1103-60. Consequently, Alfa fibres used are composed of 44.6% of pure cellulose, 67.3% of holocellulose, 21.5% of lignin, 3.9% of hot water extractives, 5.2% of organic solvents extractives, 2.2% of ash, and 4.8% of moisture content.

2.3. Pulping and bleaching

A cartridge containing 25 g of dried Alfa stems was placed in a Soxhlet equipped with 1000 mL round bottom flask. The sample was first subjected to extraction at 85 °C with 600 mL ethanol/toluene (2/1 (v/v)) mixture during 24 h (Nadji et al., 2009).

The pulping process was performed under atmospheric pressure. The dried Alfa stems were kept for 4 h at 85 °C in a 500 mL round bottom flask containing 300 mL of NaOH (1 mol/L), equipped with a reflux condenser and a magnetic stirrer. The obtained mixture was then immediately filtered. The residue was successively washed with 350 mL of NaClO solution (40 wt%) for 18 h at 30 °C, 250 mL of ethanol for 2 h at 30 °C and 250 mL of diethyl ether for 2 h at ordinary temperature (Maafi et al., 2010). After this treatment,

the cellulose pulp was washed with distilled water until pH of 7 was reached. At last, the residue obtained was dried for 24 h at 60 °C.

2.4. Microcrystalline cellulose preparation

Dry cellulose was suspended in an aqueous acid, heated under reflux conditions and gentle stirring and then cooled down to room temperature in a further 30 min. The degraded cellulose was filtered off in a coarse sintered-glass-filter crucible and washed with acid-free distilled water. For removing the last traces of acid, an aqueous suspension of degraded cellulose was neutralized to pH 7 with aqueous NaOH (1 mol/L), filtered off again, washed with distilled water and dried for 24 h at 50 °C. The resultant Alfa-MCC was transformed into fine powder by using a grinder. The product obtained after drying was snowy-white in appearance.

The hydrolysis experiments were performed using the same method described in the literature (Chauchan, Sapkal, Sapkal, & Zamre, 2009; Hanna et al., 2001) using 2.5 mol/L of hydrochloric acid at 85 °C for 120 min with constant agitation in the ratio of 1:10 pulp over liquor.

2.5. Characterization

2.5.1. Fourier transform infrared spectroscopy analysis (FTIR)

The dried samples were embedded in KBr pellets and analyzed by using a Shimadzu spectrometer 8400S. The spectra were recorded in transmittance band mode in the range of 4000–600 cm^{-1} . 32 scans were co-added in order to achieve an acceptable signal-to-noise ratio. In all cases, spectra resolution was maintained at 4 cm^{-1} .

2.5.2. Cellulose samples purity determination

The chemical compositions of the three carbohydrate polymers were determined by hydrolysis method (El Hage, Chrusciel, Desharnais, & Brosse, 2010; Hamed, Fouad, Hamed, & Al-Hajj, 2012; Obama, Ricochon, Muniglia, & Brosse, 2012). Samples were hydrolysed with 72% (w/w) sulphuric acid for 1 h at 30 °C. After that, it was diluted to 3% (w/w) sulphuric acid by adding water and then autoclaved at 121 °C. Monosaccharide contents in the filtrate were quantified using anion-exchange chromatography with pulsed amperometric detector (HPAEC-PAD: Dionex ICS-3000 system). The dried residues obtained were weighted to give klason lignin content. The acid-soluble lignin content was determined from absorbance at 205 nm according to Lin and Dence (Lin & Dence, 1992).

2.5.3. Gel permeation chromatography (GPC) measurements

2.5.3.1. Samples preparation. The three cellulose samples were derivatized using phenyl isocyanate to obtain cellulose tricarbanilate (CTC). The tricarbanilation process was done using the procedure described by Foston (Foston, Hubbell, & Ragauskas, 2011) in the following way: 15 mg of the dried cellulose sample, placed in 25 mL flask, was treated with 4 mL anhydrous pyridine and 0.5 mL phenyl isocyanate, sealed with Teflon-lined cap. The reaction mixture was then kept in oil bath at 70 °C and allowed to stir for 48 h. After the reaction completed, the solution was cooled and 1 mL methanol was added to quench any remaining phenyl isocyanate. Subsequently, the mixture was poured into 100 mL methanol–water (7:3). The precipitated CTC was purified through centrifuging by repeated washing with methanol–water for 3 times, and water for 2 times. The CTC was then lyophilized.

Prior to each GPC analysis, Cellulose derivatives were dissolved in tetrahydrofuran (THF), filtered through a 0.45 μm teflon membrane and placed in a 2 mL auto-sampler vial.

To minimize a rough random error, four analyses of each sample were performed: two CTC solutions were prepared and each

Download English Version:

<https://daneshyari.com/en/article/1375829>

Download Persian Version:

<https://daneshyari.com/article/1375829>

[Daneshyari.com](https://daneshyari.com)