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A comparative study on properties of micro and nanopapers produced from cellulose and cellulose nanofibres

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ABSTRACT

Cellulose nanocrystals (CNCs) and cellulose nanofibres (CNFs) were successfully extracted from cellulose obtained from maize stalk residues. A variety of techniques, such as Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were used for characterization and the experimental results showed that lignin and hemicellulose were removed to a greater extent by following the chemical methods. Atomic force microscopy (AFM) results confirmed that the diameters of CNCs and CNFs were ranging from 3 to 7 nm and 4 to 10 nm, respectively, with their lengths in micro scale. CNCs suspension showed a flow of birefringence, however, the same was not observed in the case of suspension containing CNFs. XRD analysis confirmed that CNCs had high crystallinity index in comparison to cellulose and CNFs. Nanopapers were prepared from CNCs and CNFs by solvent evaporation method. Micropapers were also prepared from cellulose pulp by the same technique. Nanopapers made from CNFs showed less transparency as compared to nanopapers produced from CNCs whereas high transparency as compared to micropaper. Nanopapers produced from CNFs provided superior mechanical properties as compared to both micropaper and nanopapers produced from CNCs. Also, nanopapers produced from CNFs were thermally more stable as compared to nanopapers produced from CNCs but thermally less stable as compared to micropapers.

1. Introduction

The depletion of petroleum based resources and attendant environmental problems such as global warming, have shown a great interest in developing environmentally sustainable materials (Miao et al., 2014). Biobased materials could be used as suitable replacement to petroleum based materials to overcome environmental problems. These materials offer advantages, such as renewability, biodegradability and environmental friendliness. They are composed of cellulose, lignin, hemicelluloses and the extractives (Neto, Silvério, Oliveira, & Pasquini, 2013).

Cellulose is the most abundant natural homopolymer and renewable resource on earth. It is made up of bundles of fibrils called microfibrils. However, individual fibril consists of crystalline region and amorphous domains. CNCs are the rod shaped crystalline part remained after the removal of the amorphous domains (Rosa et al., 2010; Rosli, Ahmad, & Abdullah, 2013).

There are several methods available for extracting CNCs, which include enzyme or microbial hydrolysis (Satyamurthy & Vigneshwaran, 2013) and acid hydrolysis (Neto et al., 2013). However, sulphuric acid hydrolysis is one of the preferred methods for the extraction of CNCs from natural biobased materials due to the formation of sulphate charges on the surface of the material which helps in stabilizing the suspension (Fahma, Iwamoto, Hori, Iwata, & Takemura, 2011). On the other hand, CNFs are extracted by means of mechanical treatment such as high shear homogenization (Zhao et al., 2013), mechanical grinding (Yousefi et al., 2013), a combination of mechanical actions and enzyme hydrolysis (Qing et al., 2013), and a combination of mechanical actions and chemical method (Qing et al., 2013).

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The diameters of these CNCs and CNFs are in the nano scale (<100 nm) range with the lengths in micron size (Rosa et al., 2010; Satyamurthy & Vigneshwaran, 2013; Fahma et al., 2011; Zhao et al., 2013). Because of the improved properties of CNCs and CNFs, such as high aspect ratio, high surface area per unit volume, high strength and stiffness as compared to those of fibres, they are reported to provide improved properties of the composites when used as reinforcing elements (Chen, Liu, Chang, Cao, & Anderson, 2009).

Cellulose nanomaterials are usually extracted from natural fibres, such as flax (Cao, Dong, & Li, 2007), agave (Rosli et al., 2013), kenaf (Kargarzadeh et al., 2012) and sisal fibres (Siqueira, Tapin-Lingua, Bras, Perez, & Dufresne, 2010), etc. Very few studies have reported the extraction of cellulose nanomaterials from maize stalk residues. Maize is abundantly produced in South Africa and is planted all over the country annually in rainy seasons. Approximately 8 million tons of maize is produced yearly in South Africa in approximately 3.1 million hectares (ha) of land (Du Plessiss, 2003). In developing countries like South Africa and other African countries maize serves as a staple food in the majority of population. The agricultural sector produces maize for the purpose of economic growth and after harvesting, maize stalk residues remain in the field, because they do not have any direct use and therefore are underutilized (Du Plessiss, 2003). Maize stalk residues are used in low-value products, such as animal feed or disposed-off by incineration or dumped in waste sites due to the lack of space and little knowledge about possible value addition on such agricultural wastes (Brent, Rohwer, Friedrich, & Von Blottnitz, 2002). In this study, CNFs and CNCs are extracted from maize stalk residues by supermass colloider and acid hydrolysis, respectively.

CNFs are usually utilized to prepare nanopapers or they are used for the development of composite materials in most cases (Sehaqui, Liu, Zhou, & Berglund, 2010). The process of preparing nanopapers is analogous to the traditional papermaking process; the only difference is that nanopapers are made up of high aspect ratio nanomaterials in comparison to conventional paper (Sehaqui et al., 2010; Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008). The common processes of preparing nanopapers are: solvent evaporation method (Wu et al., 2013; Fukuzumi, Saito, & Isogai, 2013) and filtration accompanied with hot pressing method (Missoum, Martoïa, Belgacem, & Bras, 2013; Wang, Li, & Zhang, 2013). CNFs in wet state are in gel-like form and the fibres are normally in an entangled state. During water evaporation process the individual fibres attract each other by means of capillary action and create hydrogen bonding amongst them. Nanopapers have been reported to exhibit high strength and stiffness, excellent optical transparency, and low thermal expansion (Sehaqui et al., 2010).

Various studies have shown that nanopapers prepared from CNFs (from various sources) using mechanical grinding technique have high tensile strength and high tensile modulus (Yousefi et al., 2013; Qing et al., 2013; Wang et al., 2013). Qing et al. (2013) reported that the tensile strength and tensile modulus of nanopapers prepared from bleached eucalyptus Kraft pulp was about 123 MPa and 7 GPa, respectively. The findings obtained by Yousefi et al. (2013) showed that nanopapers prepared from bacterial cellulose and canola straw had tensile strength and tensile modulus of 185 and 114 MPa and 17.3 and 13.6 GPa, respectively. Also, Wang et al. (2013) prepared nanopapers from waste corrugated paper pulp by oven drying and hot pressing method. They found that the tensile strength and tensile modulus of nanopapers prepared by oven drying and hot pressing nanopapers were about 140 and 152 MPa and 6.5 and 9.26 GPa.

The main objective of this study was to extract cellulose from maize stalk residues and to characterize it by FTIR, ESEM, TGA and XRD techniques. Another objective of this study was to produce high quality CNFs and CNCs from cellulose obtained maize stalk residues using supermass colloider and acid hydrolysis. The morphological features of the CNFs and CNCs will be determined by AFM. Also, their dispersion in suspensions will be determined by light polarized microscopy. The obtained CNFs and CNCs were used to develop nanopapers and their mechanical, thermal properties and optical transparency were investigated. Micropaper was prepared from extracted cellulose pulp and used as a control for comparison.

2. Materials and methods

2.1. Materials

The post harvested maize stalks residues were supplied by a farm in Cofimvaba in Eastern Cape, South Africa. They were grounded into a coarse powder by Hamermeul. Sodium hydroxide (NaOH) pellets, potassium hydroxide (KOH) and sulphuric acid (H_2SO_4) of 99.9%, 85% and 98% purity, respectively, were obtained from Minema Chemicals, South Africa. Sodium chlorite ($NaClO_2$) of 80% purity was purchased from Sigma Aldrich, South Africa.

2.2. Experimental methods

2.2.1. Extraction of cellulose

The post-harvested maize stalks were grounded into a coarse powder by Hamermeul. The maize stalk powder was then weighed and dried in an oven at 50 °C overnight and treated with 1.5% NaOH, 1.5% $NaClO_2$, and 1.5% KOH, respectively, for 1 h. Each treatment was repeated four times with repeated washes using deionized water to remove excess chemicals and to achieve a neutral pH. The schematic diagram of the extraction of cellulose from maize stalk residues and extraction of cellulose nanocrystals and nanofibres is shown in Fig. 1.

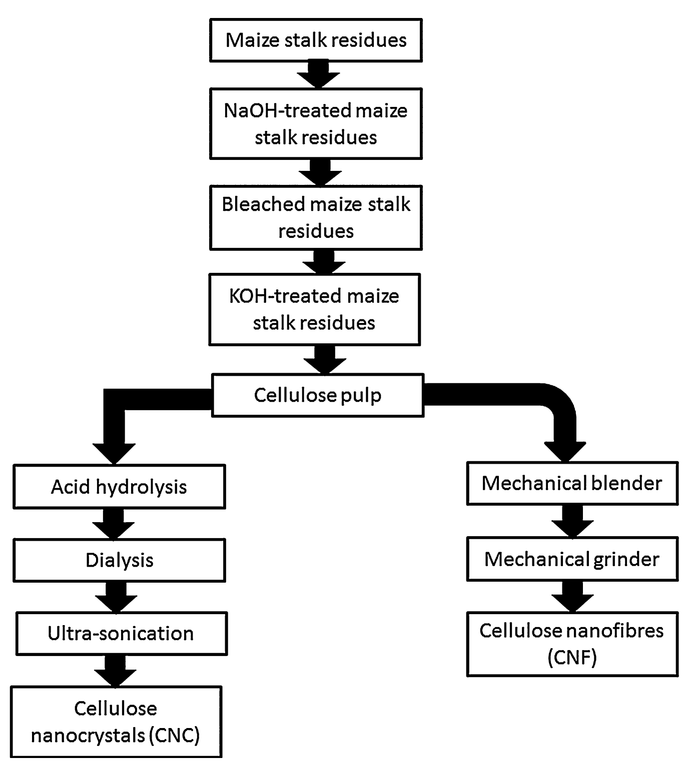

Fig. 1. Extraction of cellulose nanocrystals and nanofibres from cellulose obtained from maize stalk residues.