



Surface functionalization of nanofibrillated cellulose extracted from wheat straw: Effect of process parameters



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ABSTRACT

Aggregates of microfibrillated cellulose isolated from wheat straw fibers were subjected to propionylation under different processing conditions of time, temperature and concentration. The treated fibers were then homogenized to obtain surface modified nanofibrillated cellulose. For varying parameters, progress of propionylation and its effects on various characteristics was investigated by FTIR, degree of substitution, elemental analysis, SEM, EDX, TEM, X-ray diffraction, static and dynamic contact angle measurements. Thermal stability of the nanofibrils was also investigated using thermogravimetric technique. FTIR analysis confirmed the propionylation of the hydroxyl groups of the cellulose fibers. The variations in reaction conditions such as time and temperature had shown considerable effect on degree of substitution (DS) and surface contact angle (CA). These characterization results represent the optimizing conditions under which cellulose nanofibrils with hydrophobic characteristics up to contact angle of 120° can be obtained.

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1. Introduction

Nanocellulose is one of most abundant and renewable natural material that has induced immense potential in global research for development of new green nanocomposites (Khalil, Bhat, & Yusra, 2012; Siró & Plackett, 2010). It is the main building constituent of wood and other lignocellulosic fibers and is responsible for providing them the required strength and stiffness. (Abe, Iwamoto, & Yano, 2007; Eichhorn et al., 2010; Habibi, Lucia, & Rojas, 2010; Siró & Plackett, 2010). In its native form, cellulose possesses crystalline fibrous structure, aligned parallel to each other, embedded in an amorphous matrix of lignin, pectin and hemicellulose. It is classified into (1) nanowhiskers and (2) nanofibrillated cellulose depending upon the morphology obtained after its isolation from the plant source (Belbekhouche et al., 2011; Khalil et al., 2014, 2012). Its super molecular structure along with strong and complex network of hydrogen bonds give it a crystalline structure which makes it insoluble in water and organic solvents under ambient temperatures.

The nanostructure of cellulosic fibers provides a large specific surface area along with numerous free hydroxyl groups on its surface rendering it hydrophilic, which makes its dispersion difficult

in hydrophobic polymers matrix (Gardner, Oporto, Mills, & Samir, 2008; Jackson et al., 2011; Volkert, Lehmann, & Hettrich, 2014). But the presence of free hydroxyl groups offer numerous opportunities for surface modifications of reactive sites (Gardner et al., 2008).

Esterification is one of the important chemical modification techniques that have been extensively used to modify microstructures of cellulose (Bledzki & Gassan, 1999; Volkert et al., 2014). The technique adjusts the hydrophobic/hydrophilic balance in cellulose thus improving its solubility in numerous organic solvents, augmenting dispersion and interfacial adhesion in different polymeric matrices (Goussé, Chanzy, Cerrada, & Fleury, 2004; Johansson, Tammelin, Campbell, Setälä, & Österberg, 2011; Jonoobi, Harun, Mathew, Hussein, & Oksman, 2010; Missoum, Belgacem, & Bras, 2013; Missoum, Bras, & Belgacem, 2012; Pahimanolis et al., 2011). The acetylation of surface hydroxyl groups of nanocellulose is comparatively a new area of research. Many authors have adopted separate strategies and reported effects of surface acetylation on properties of isolated nanofibrillated cellulose (NFCs) (Bulota, Kreitsmann, Hughes, & Paltakari, 2012; Jonoobi, Harun, Mathew, & Oksman, 2010; Jonoobi, Mathew, Abdi, Makinejad, & Oksman, 2012; Rodionova, Lenes, Eriksen, & Gregersen, 2011; Tingaut, Zimmermann, & Lopez-Suevos, 2009). Modification of nanofibrils using propionic anhydride is a less studied area but it has been found that use of propionic anhydride instead of acetic anhydride results in better dimensional stability of resultant fibers and their composites (Papadopoulos & Gkaraveli, 2003).

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This work involves the surface modification of nanofibrillated cellulose isolated from wheat straw fibers using an indirect esterification method using propionic anhydride (Belgacem & Gandini, 2009). The indirect method limits the reaction material on the exposed surface of nanofibrils without causing any destruction to the fiber's inner structure (Jonoobi, Harun, Mathew, Hussein et al., 2010). Microfibrillated aggregates of cellulose (MFCs) were treated under different processing conditions i.e. reaction time, temperature and concentration of reagent and were characterized using FTIR, SEM-EDX, CHNSO-elemental analysis and degree of substitution. Whereas, microfibrillar aggregates and their nanofibrils were characterized using powder WA-XRD and contact angle measurement techniques, TEM and TGA analysis was also conducted for NFC's to investigate the effect of modification on their morphology and thermal characteristics.

2. Experimental

2.1. Materials

Microfibrillated aggregates of cellulose (MFCs) isolated from wheat straw fibers using a physico-chemical method as described elsewhere (Kaushik & Singh, 2011) were subjected to surface modification. Propionic anhydride was procured from SRL Chem. India Pvt. Ltd. and was used as received. The other chemicals used were Pyridine, Toluene, H₂SO₄, ethanol were procured from Merck India Pvt. Ltd. and they were also used as received.

2.2. Propionylation of microfibrillated cellulose fibers (MFCs)

A mixture of toluene (~50 ml) and pyridine (~2.5 ml) with H₂SO₄ (0.1 ml) catalyst was taken as a medium for esterification. Toluene restricts the swelling of fibers and do not allow the reactants to enter into the bulk sites of fibers. A small amount of pyridine was used for increasing the number of accessible reactive hydroxyl sites and enhancing the rate of acetylation (Jonoobi, Harun, Mathew, Hussein et al., 2010). For the surface treatment, microfibrillated aggregates of cellulose (MFCs) extracted from wheat straw were oven dried at 38 ± 2 °C overnight. A fixed weight i.e. 1 g (±0.01) of dried MFCs were then soaked in the prepared reaction medium. The mixture was taken in the stoppers glass tube and a fixed concentration of propionic anhydride in fiber to reagent ratio (w/v) was poured and shaken vigorously for 5–10 min. Finally, the glass tube was put in the oil bath under different temperatures and reaction time. After completion of treatment, samples were immediately cooled and centrifuged with toluene for 15–20 min to terminate the reaction. The treated fibers were then vacuum filtered with ethanol (50% aq.) and de-ionized water and finally dried at 50–60 °C for 24 h.

In order to optimize the results, two different fibers to anhydride concentration ratio (w/v) of 1:2 and 1:4 were taken and temperature was varied from 60, 80 and 100 °C for 0.45, 1.30, 3 and 5 h of reaction time. Sample designation based processing conditions are given in the Table 1.

2.3. Isolation of unmodified & modified nanofibrillated cellulose (NFCs)

The unmodified and modified MFCs were subjected to high shear action of IKA T-18 digital homogenizer (8500 ± 200 RPM) to obtain nanofibrillated cellulose. In this process, different samples were taken in distilled water and subjected to high shear homogenization for mechanical separation of nanofibers from MFCs. Each sample was homogenized for 20 min to obtain uniform nanosized

fibers with entangled network after disintegrating the MFCs. The final suspension of NFCs was then dried overnight at 50 ± 0.5 °C.

2.4. Measurements

Perkin Elmer RX-FTIR spectrophotometer was used to identify variations in the functional groups as result of surface treatment. Fiber samples were prepared using KBr disk methods and spectra were recorded in a spectral range of 4000–450 cm⁻¹ with a resolution of 2 cm⁻¹.

Degree of substitution (DS) of propionyl groups on the fiber surface was estimated using a titration method as described in literature (Kim, Nishiyama, & Kuga, 2002; Rodionova et al., 2011). The percentage of ester content and DS values for each sample were calculated by Eqs. (1) and (2) given below. Each test was performed thrice to ensure reproducibility.

Ester Content (%)

$$= \frac{[(\text{Blank (ml)} - \text{Sample (ml)}) \times \text{Molarity of HCl}]}{\text{Sample Weight (g)}} \times 100 \quad (1)$$

$$DS = \frac{[162 \times \text{Ester Content (\%)}]}{[4300 - (42 - \text{Ester Content (\%)})]} \quad (2)$$

A Perkin-Elmer 240C CHNSO-Elemental Analytical Instrument (USA) was used to conduct elemental analysis of unmodified and modified MFCs.

Surface elemental analysis was also conducted using low energy dispersive X-ray cartography (EDX) of INCAX-Act, Oxford Instruments coupled with Scanning Electron Microscope (SEM).

The surface morphology of unmodified and modified MFC samples was also observed by using a separate scanning electron microscope model JSM JEOL-6490.

The network and surface topography of unmodified and modified nanofibrillated cellulose was observed using Transmission Electron Microscope (TEM) model Hitachi-2100. All the images were taken at 80 kV accelerating voltage.

The samples of unmodified and modified NFCs were analyzed in powdered form using a Philips X'Pert Pro X-ray diffractometer. Crystallinity index (CrI) of the nanofibrils was calculated using Eq. (3) derived from the Segal empirical method (Krassig, 1985; Segal, Creely, Martin, & Conrad, 1959).

$$\text{Crystallinity Index (CrI)} = 100 \times \frac{I_{\text{Total}} - I_{\text{Am}}}{I_{\text{Total}}} \quad (3)$$

where, I_{Total} is the maximum intensity of the (002) lattice diffraction and I_{Am} is the intensity diffraction at 18° 2θ diffraction angle. The crystallite size was also estimated using Scherrer's equation (Eq. (4)) (Bodor, 1991).

$$t_{hkl} = \frac{\kappa \lambda}{\beta_{hkl} \cos \theta} \quad (4)$$

where, t_{hkl} is the thickness of crystallites at the (hkl) plane of diffraction, λ is X-ray wavelength ($\lambda = 0.1542$ nm for CuK α), θ is the Bragg angle of the reflection, β_{hkl} is the pure integral of width of the reflection at half maximum height, and K is the Scherrer constant.

The surface properties of different modified MFCs and its NFCs were estimated for static & dynamic contact angles (DCA) measurements for a check time of 0.2 s. These measurements were done with a Dynamic Absorption Tester DAT 1100 at 23 °C and 50% RH.

Thermal characteristics of untreated and surface treated NFCs were determined using Perkin Elmer STA-6000 Thermal gravimetric Analyzer (TGA). Each test was performed in nitrogen atmosphere at a heating rate of 10 °C/min⁻¹ from room temperature to 500 °C.

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