



Solvent-free acetylation of cellulose nanofibers for improving compatibility and dispersion



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ABSTRACT

Cellulose nanofibers (CNFs), as bio-materials derived from wood or non-wood plants, have the advantages of being biodegradable, renewable, low cost, and having good mechanical properties compared to synthetic nanofibers. CNFs have been used as reinforcement in polymeric matrices, however, due to their polar surface, their dispersibility in non-polar solvents and compatibility with hydrophobic matrices are poor. In this work, the chemical modification of CNFs, using acetic anhydride in the presence of pyridine as a catalyst, was studied with the aim of changing the surface properties. Native and chemically modified CNFs were characterized in terms of dynamic absorption, thermal stability, surface chemistry, morphology, and crystal structure. The reaction of acetylation between the acetyl groups and the hydroxyl groups of the CNFs was examined using Fourier transform infrared (FT-IR) analysis, while its extent was assessed by titration. The ester content of CNFs was higher for the acetylated samples compared to the control samples. It was also shown that the crystallinity decreased moderately as a result of esterification. Thermal stability of the modified nanofibers was slightly increased. Unlike native CNFs, a stable aqueous suspension was obtained with the modified nanofibers in both ethanol and acetone. The contact angle measurements confirmed that the surface characteristics of acetylated CNFs were changed from hydrophilic to more hydrophobic. In addition, the obtained acetylated CNFs showed more hydrophobic surface, which is in favor of enhancing the hydrophobic non-polar mediums.

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1. Introduction

Over the last few years, the incorporation of lignocellulosic materials as reinforcing agents or as fillers in polymer composites has received an increased attention (Zahedi, Tabarsa, Ashori, Madhoushi, & Shakeri, 2013). The addition of fillers has a high impact upon economics for thermoplastics, while a general improvement in certain properties is also achieved. The renewability, sustainability and low abrasive nature of lignocellulosic reinforcements in comparison with glass or carbon fibers, further accelerate their use in regards of technical and material recycling (Abdul Khalil, Bhat, & Ireana Yusra, 2012; Tserki, Zafeiropoulos, Simon, & Panayiotou, 2005). Cellulose nanofibers (CNFs) are one class of natural fibers that have resulted in structures with remarkable mechanical properties (Masoodi, El-Hajjar, Pillai, & Sabo, 2012). Films or “nanopaper” of CNFs have also shown superior mechanical properties (Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008; Lee, Chun, Kang, & Park, 2009). Recently, CNFs have attracted considerable attention as reinforcement materials

because of reductions in the energy requirements for breaking down cellulose fibers in nanofibers (Jonoobi, Harun, Mathew, Hussein, & Oksman, 2010; Jonoobi, Harun, Mathew, & Oksman, 2010; Jonoobi, Mathew, Abdi, Makinejad, & Oksman, 2012; Saito et al., 2009; Teixeira et al., 2009). CNFs can be defined as the perfect stereoregular configurations of cellulose molecules in the primary cell wall of a plant (Siddiqui, Mills, Gardner, & Bousfield, 2011). The dimensions of these fibers may vary according to the origin of the cellulose. The isolated CNFs have a wide range of diameters, most are below 100 nm, depending on the type of method followed during their preparation (Gardner, Oporto, Mills, & Samir, 2008). The lateral dimensions of the nanofiber obtained from a wood pulp are about 5 nm and 20 nm (Hult, Larsson, & Iversen, 2002).

Although the CNFs have a great potential as mentioned above, the homogenous dispersion of CNFs in the non-polar polymeric matrix is difficult to attain due to their highly polar surface and hydrophilic nature (Eichhorn et al., 2010). The hydrophilic behavior of CNF is attributed to the hydroxyl groups that are located on the surface of the cellulose fibers (Hu, Chen, Xu, & Wang, 2011). Recently, several methods have been proposed to overcome this problem involving the chemical modification of the cellulose surface hydroxyl groups with various reagents (John & Anandjiwala, 2008; Siró & Plackett, 2010). Among the different modification

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Table 1
Chemical composition of the used CNFs.

Chemical	Value (%)
Cellulose	92.8 ± 0.5
Lignin	4.7 ± 0.7
Hemicellulose	0.5 ± 0.3
Extractive	0.4 ± 0.1
Ash	–

methods, acetylation is a kind of commonly used chemical modification, where the hydroxyl groups of cellulose are replaced by less hydrophilic acetyl groups (Nogi et al., 2006). The principle of the method is to react the hydroxyl groups (–OH) of the fiber constituents with acetyl groups (CH₃CO–) (Pandey, Nakagaito, & Takagi, 2013). The reaction is known to proceed full esterification of all the three hydroxyls of anhydro-D-glucose when it is carried out in a homogeneous phase (i.e. when cellulose is dissolved), but in the case of fibers and wood, where the reaction is heterogeneous, that is very rarely the case (Hu et al., 2009). The hydroxyl groups that react are those of the minor constituents of the fiber, i.e. lignin and hemicelluloses, and those of amorphous cellulose. This is because of the hydroxyl groups in crystalline regions with close packing and strong interchain bonding (Baiardo, Frisoni, Scandola, & Licciardello, 2002). After resolving the incompatibility issues between CNF and polymer to a satisfactory extent by adequate modification either in host or filler, it was assumed that dispersion of fiber may be enhanced with reduction in the size through introducing nano fillers for positive tailoring of different material properties (Nitz, Semke, Landers, & Mülhaupt, 2001).

For the reinforcement to be effective, interaction between CNFs and matrices should be optimized. Understanding the surface properties of CNFs, therefore, is a necessary step in optimizing adhesion. The main objective of this work was to study the effect of chemical modification of CNFs using acetylation on the hydrophobicity and dispersibility. Furthermore, the properties of acetylated and non-acetylated CNFs in terms of thermal stability, surface morphology, and contact angle, chemical and structural characteristics were investigated.

2. Experimental

2.1. Materials

The used CNFs, isolated from the kenaf bast fibers (*Hibiscus cannabinus*), were provided by the Institute of Tropical Forestry and Forest Products (INTROP), Malaysia. The details of the pulping and bleaching treatments have been reported elsewhere (Jonoobi, Harun, Mathew, Hussein, et al., 2010). In short, the purification processes were soda-AQ pulping followed by three step bleaching (DEpD) process. The chemical analyses of the CNFs are presented in Table 1 (Jonoobi, Harun, Shakeri, Misra, & Oksmand, 2009). Acetic anhydride (95%) and pyridine were obtained from Merck Chemical Co., Germany. All these materials and solvents were used as received without further purification. Distilled water was used in all the experiments.

2.2. Chemical modification of the CNFs

The CNFs were acetylated using the method reported by Jonoobi, Harun, Mathew, Hussein et al. (2010) briefly as follows. Prior to acetylation, the aqueous suspension containing CNFs was extracted with acetone and methanol (2:1 by volume) in a Soxhlet for 6 h. Then, the solvent exchanged from methanol to glacial acetic acid by centrifugation (three times). The extracted CNFs, acetylated in

acetic anhydride (1:20 by weight) and 5 wt% pyridine as catalyst, were refluxed at 100 °C for 4 h. At the end of the reaction, the treated CNFs were extracted using distilled water (2:1 by volume) for 6 h in order to remove un-reacted acetic anhydride and acetic acid by-products. Finally, four cycles of solvent exchange was performed by centrifugation to obtain aqueous dispersions of acetylated CNFs.

2.3. Characterization

2.3.1. Degree of substitution

The degree of substitution (DS) was determined according to the method proposed by Kim, Nishiyama, and Kuga (2002). The acetylated and non-acetylated CNFs (100 mg, solid content of 2%) were placed in conical flasks. Consequently, 40 mL of 75% ethanol was added and the flasks were kept at 50 °C for 30 min. Finally, 40 mL of NaOH (0.5 N) solution was added to the mixture and heated to 50 °C for 15 min. The mixture was kept at room temperature for 48 h under constant stirring. The excess of NaOH was titrated with HCl (0.5 N) until a pH of 7 was obtained.

2.3.2. Spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was performed using a Perkin–Elmer Spectrum RXI (USA), in order to determine the changes in functional groups in the materials. The samples for FT-IR were mixed with KBr. The FT-IR analysis was carried out using 50 scans with a resolution of 4 cm^{–1}, in transmittance mode within the range of 3600–400 cm^{–1}.

2.3.3. Dispersibility

Stability of CNFs suspension was studied in a non-aqueous medium to determine the efficiency of acetylation of nanofibers. For this purpose, the aqueous (1 wt%) suspensions of acetylated and non-acetylated CNFs were prepared. Solvent exchange from water to acetone and ethanol was done using centrifugation. The suspensions were sonicated in order to disperse nanofibers thoroughly and then allowed to stand at room temperature for 2 weeks before photographing.

2.3.4. Crystallinity

The crystallinity of acetylated and non-acetylated nanofibers was recorded on an X-ray diffractometer, Hitachi S-4160 (Japan), with CuKα radiation (λ = 1.54 Å). The measurements were carried out in 2θ ranges between 5° and 50° with step size of 0.026° and time per step of 99.45 s. The crystalline index of cellulose, CrI, was calculated based on the empirical method proposed by Segal, Creely, Martin, and Conrad (1959) as follows:

$$\text{CrI} (\%) = \left[\frac{(I_{002} - I_{\text{am}})}{I_{002}} \right] \times 100 \quad (1)$$

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

2.3.5. Thermogravimetric analysis (TGA)

The thermal stability of treated and untreated nanofibers was studied using a TGA Q50 V6.3 Build 189 instrument. Approximately 4 mg of sample was weighed and heated from 30 to 600 °C at 20 °C/min under argon flow rate of 40 mL/min.

2.3.6. Dynamic absorption test (DAT)

In this test, a drop of liquid is applied to the sample and the image of the spreading droplet is recorded as a function of time using an automated digital camera. In order to measure the contact angle, both treated and untreated CNF networks were prepared by vacuum filtration using Whatman filter paper. The networks were dried at room temperature followed by hot plate at 60 °C for 48 h. The contact angle measurements were performed in laboratory

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