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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.

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 (CH_3CO—) (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:

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

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

atmosphere at 23 °C and 50% RH using a contact angle goniometer (Data physics OCA 15 plus). Contact angles were measured 1 and 30 seconds after the application of a 5-μL drop of water. In this investigation, the measurements were repeated 3 times at different locations on the surface of the networks and an arithmetic mean was calculated.

2.3.7. Morphological surface analysis

Scanning electron microscopy (SEM) images of CNFs networks were performed using a SEM Model WEGA-II TESCAN operating at 7 kV. The apparatus used a tungsten filament electron source and scanned at room temperature. All samples were sputter-coated with gold to avoid charging.

3. Results and discussion

3.1. Acetylation of the CNFs

The reaction involves the replacement of hydroxyl groups of the nanofibers with acetyl groups in the reagent. The chemical composition of the fibers showed that the fibers had 92% cellulose content, while the hemicelluloses and lignin contents were only 5%, and 0.5%, respectively (Table 1). The high cellulose content suggests that the acetylation of cellulose is more probable than the acetylation of lignin or hemicelluloses. However, dissolution of hemicelluloses could be occurring during the acetylation (Li, Mai, & Ye, 2000). Also under the acetylation, the nanofibers swell when treated with acetylating reagents, resulting in acetylation of hydroxyl groups on the surface. The used catalyst, pyridine, swells and opens the CNF cell walls, thus increasing the number of accessible reactive hydroxyl sites. The degree of substitution (DS) of acetylated nanofibers was calculated by titration as described by Kim et al. (2002) and the results showed that the DS was 0.2, which demonstrates that the nanofibers have been successfully acetylated.

3.2. FT-IR spectra

The FT-IR spectroscopy was used for the study of the chemical structures of the fibers after chemical modification. Fig. 1 shows the IR spectra of acetylated and non-acetylated CNF samples. The bands at 3395, 2902, 1643, 1162, and 612 cm^{-1} in Fig. 1(a) are associated with native CNF. The band at 3395 cm^{-1} corresponds to free OH groups on cellulose molecules. The absorption peaks around 2900 cm^{-1} for CNFs are due to stretching of C—H groups of cellulose. The peak at around 1640 cm^{-1} is probably associated with absorbed water in crystalline cellulose (Jonoobi, Harun, Mathew, & Oksman, 2010). In addition, no absorption was observed in the region between 2400 and 1730 cm^{-1} in the spectra. In comparison, the characteristic vibrations of the grafted acetyl groups were easily identified in the FT-IR spectra of modified nanofibers Fig. 1(b): namely the carbonyl C=O stretching vibration at 1737 cm^{-1} (C=O), the methyl in-plane bending in —O(C=O)—CH_3 at 1383 cm^{-1} (C—H), and the C—O stretching of acetyl group at 1244 cm^{-1} (C—O) (Çetin et al., 2009). Another important aspect observed in the cellulose acetate spectrum is the decreasing absorption intensity of the band located at around 3426 cm^{-1}, assigned to the stretching of the hydroxyl group when compared with CNF. This decreasing phenomenon occurs because the hydroxyl groups in CNFs are partially substituted by acetyl groups in the reaction. The absence of absorption at 1700 cm^{-1} attributed to carboxylic group indicated that the product was also free of any acetic acid byproduct (Adebajo & Frost, 2004).

3.3. Dispersion characteristics

The dispersions of acetylated and non-acetylated CNFs in ethanol and acetone are presented in Fig. 2. Fig. 2(b) and (d) shows that the acetylated nanofibers are stable and well-dispersed in both ethanol and acetone after 14 days, as expected while the phase separation observed in those cases of native (unmodified) ones Fig. 2(a) and (c). The non-acetylated nanofibers are not as stable and show a slow sedimentation in the used solvents. Çetin et al. (2009) have reported similar results for acetylated cellulose nanowhiskers. The stability of the nanofiber dispersions in the solvent is expected to depend on the size, surface characteristics, and concentration of nanofibers. The high stability of the modified nanofibers might be due to the replacement of OH groups in cellulose by acetyl groups, which are more hydrophobic, resulting in better dispersion. It is worth mentioning that a concentration lower than 1% might be less unstable because of the lower interaction between the fibers.

3.4. XRD spectra

The impact of chemical modification on the crystallinity and the structure of CNFs was further evaluated using XRD analysis. The diffraction profiles of acetylated and non-acetylated CNFs are presented in Fig. 3. The native sample peaks localize at around 18°, 22° and 25° were assigned to characterize the interplane distances of cellulose I_α and I_β phases (Hu et al., 2009; Maneerung, Tokura, & Rujiravanit, 2008). The position of this peak indicates the generation of a disorder when CNF was acetylated. The disorder is caused by the projection of the substituting groups (acetyl groups) along the axes and is associated with an increase in the interfibrillar distance and the breakdown of microfibrilllar structures (Barud et al., 2008).

The acetylated cellulose presents a less degree of crystallinity (62%) compared with that of the native CNF (67%) due to the substitution of the hydroxyl groups by acetyl groups with greater volume, which broke the inter- and intra-molecular hydrogen bonds of cellulose (Hu et al., 2011). On comparing the results, the modified nanofibers, which were obtained in this study, indicated similar transformation in crystallinity with those produced by acetylation technique as reported in previous studies (Ifuku et al., 2007; Jonoobi, Harun, Mathew, & Oksman, 2010).

3.5. Thermal analysis

The thermal properties of acetylated and native CNF samples are illustrated in Fig. 4. The TGA curves of both samples can be distinctly divided into three stages. During the initial stage from room temperature to 120 °C, the TGA thermogram of non-acetylated CNF displayed a minor weight loss, which is attributed to water desorption. However, this minor loss of weight is not obvious for the acetylated sample; that is to say, the acetylated samples are more hydrophobic than the native CNF. In the second stage, from 220 to 390 °C, the crystalline region started to be destructed and the polymer simultaneously decomposed, which evidently resulted in increase in amorphous structure and decrease in the degree of polymerization (Hu et al., 2011). During the third stage, from 390 to 600 °C, the crystalline region was completely destructed and the cellulose decomposed into monomer of D-glucopyranose, which could be further decomposed into free radicals (Yang, Xu, Ma, & Wang, 2008). The acetylated and non-acetylated nanofibers start to degrade at 300 and 290 °C, respectively, while the main degradation peaks for the acetylated and non-acetylated nanofibers were found to be 360 and 340 °C. In this case, the main degradation can

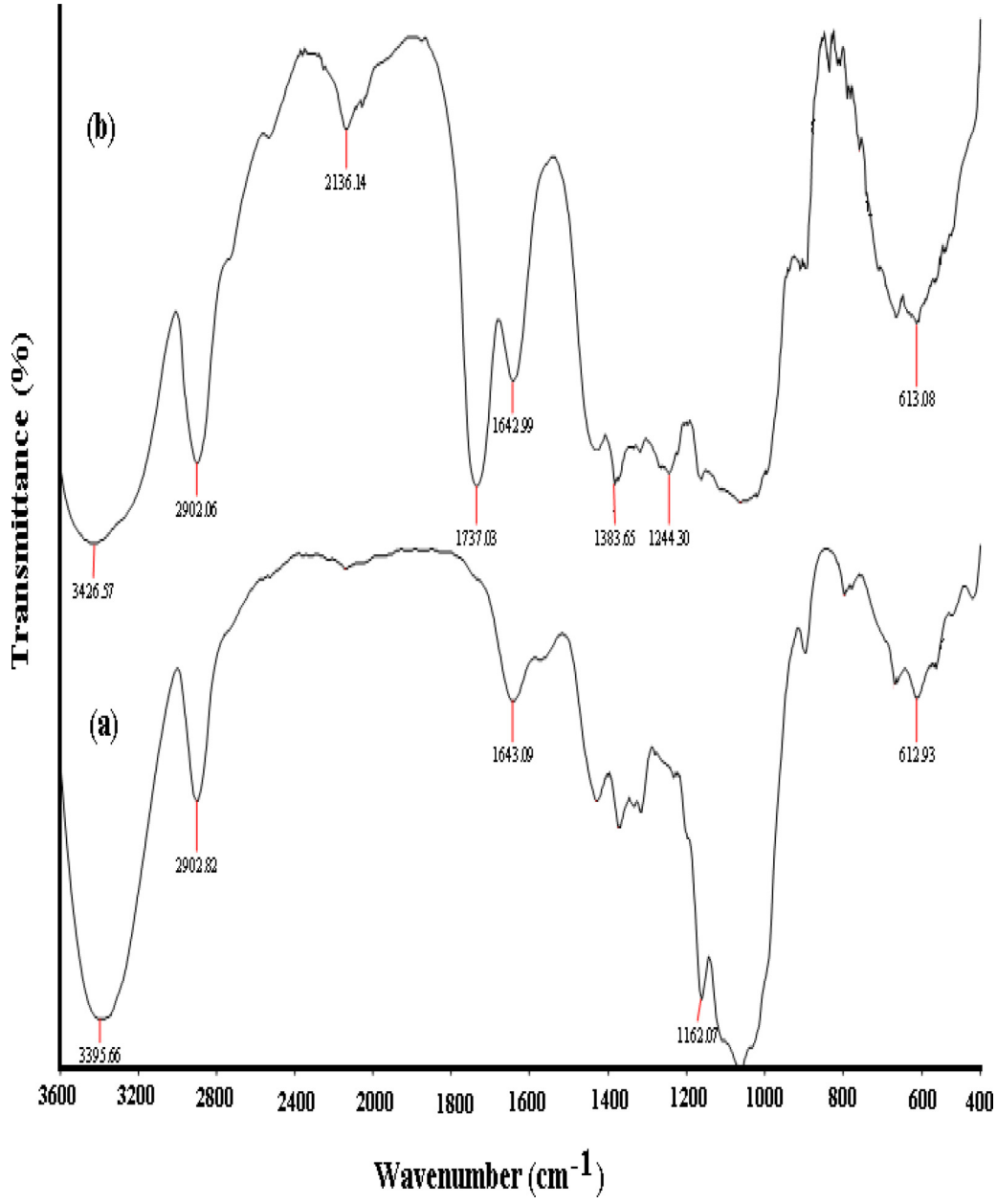

Fig. 1. FT-IR spectra of the (a) non-acetylated and (b) acetylated nanofibers.

be attributed to thermal decomposition of cellulose (Lin, Huang, Chang, Feng, & Yu, 2011). The TGA results in Fig. 4 illustrate an increase in thermal stability for the acetylated nanofibers as compared to the non-acetylated ones. The higher thermal stability of acetylated nanofibers can be attributed to the partial removal of hemicelluloses during acetylation. In addition, the higher thermal stability of modified nanofibers might be also due to the replacement of OH groups in cellulose by acetyl groups, which are more stable and thus result in better thermal stability (Lin et al., 2011). On the other hand, it is believed that the thermal stability of acetylated nanofibers depends on the degree of acetylation. During acetylation, thermal stability can be improved with the acetyl content (Ac), up to 10.5%, while a lower degradation temperature was observed for the highest Ac %. This phenomenon was probably due to the significant decrease in crystallinity (Tingaut, Zimmermann, & Lopez-Suevos, 2009).

3.6. Wettability

The contact angles were measured 1 and 30 s after the drop was applied to the sample surface. The contact angle for acetylated and non-acetylated nanofibers after 1 s was measured to be 75° and 54°, respectively. These values were reduced to 41° and 37° after 30 s for non-acetylated nanofibers (Fig. 5), while in both cases, the results illustrated no significant decrement in water droplet angle even after 30 s observation. The results show that the acetylation changed the surface characteristics of the nanofibers from highly hydrophilic to more hydrophobic. As expected, water wettability decreased drastically after acetylation, which further confirmed that the chemical modification had indeed occurred at the surface of CNF samples. These observations are in good agreement with Jonoobi et al. (2012), who reported the acetylation treatment using acetic anhydride.

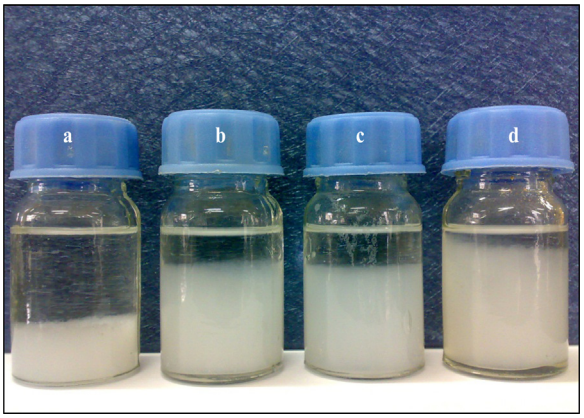

Fig. 2. Dispersion stability of the (a) native CNFs in acetone, (b) acetylated CNFs in acetone, (c) native CNFs in ethanol, and (d) acetylated CNFs in ethanol.

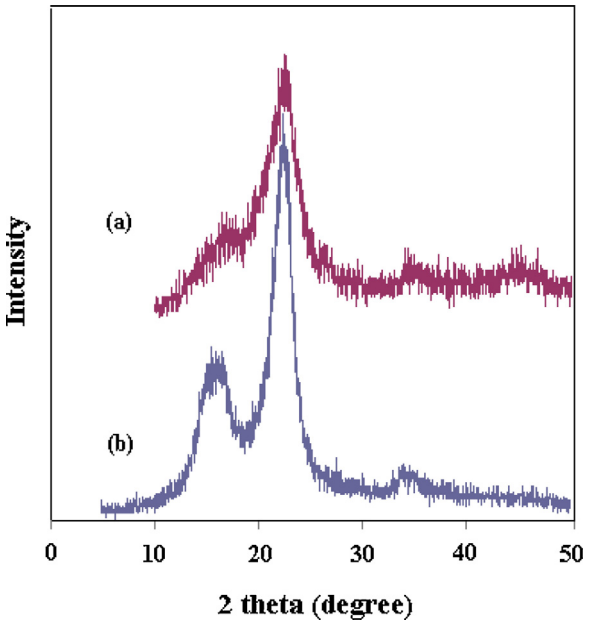

Fig. 3. XRD patterns of the (a) acetylated and (b) non-acetylated nanofibers.

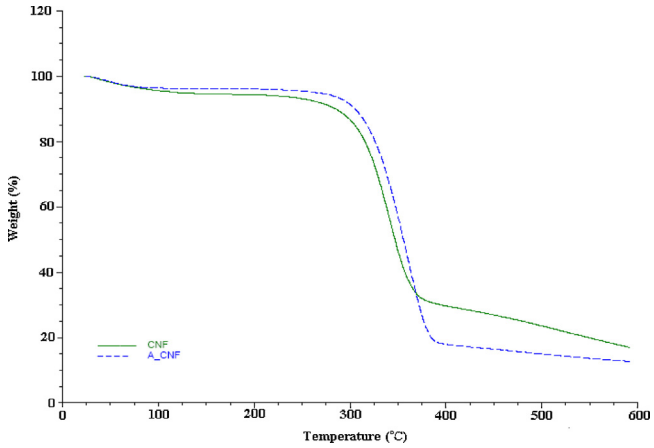

Fig. 4. TGA tracings of cellulose nanofibers before (CNF) and after (A-CNF) modification.

3.7. Surface morphology

The morphology of nanofibers before and after acetylation was studied using SEM (Fig. 6). As clearly seen, the surfaces of non-acetylated nanofibers are rather uniform, Fig. 6(a), while the acetylated ones are rougher, indicating that acetylation has affected the structure, Fig. 6(b). It might be dependent on the swelling effect of the pyridine, which is expected to favor the penetration of acetic anhydride and acetic acid into the swelled nanofibers, which rupture the cell wall structure (Hill, Khalil, & Hale, 1998). Moreover, it was observed that the nanofibers of native CNFs are densely coagulated, as shown in Fig. 6(a), with the imperceptible interstitial cavities due to the hydrophilicity of cellulose and the strong surface tension of water. In contrast to this, the acetylated CNFs are separated from each other with more holes. This change is considered to be the result of increased hydrophobicity of the acetylated surfaces (Ifuku et al., 2007).

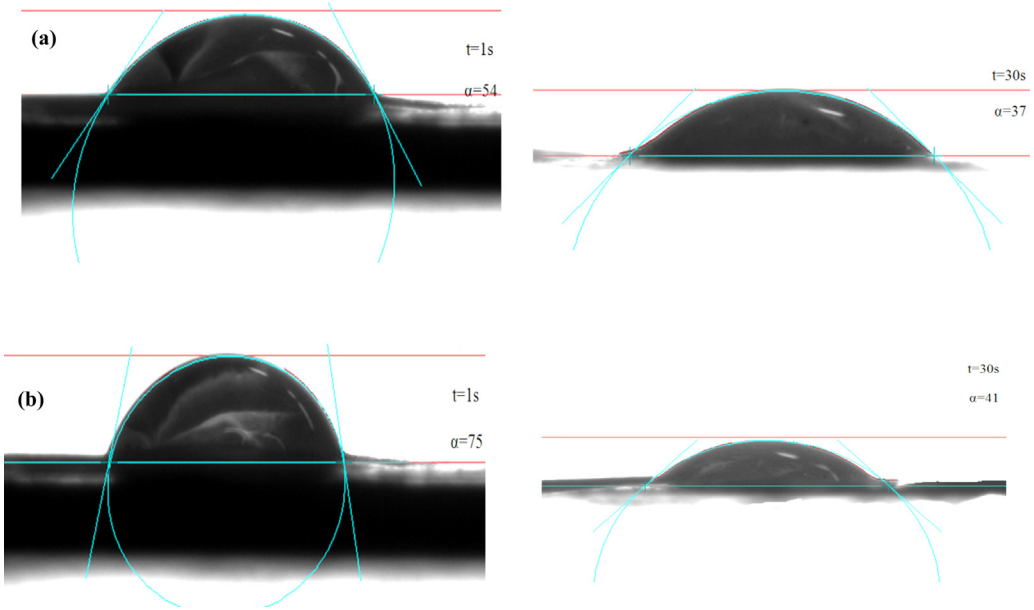

Fig. 5. Images of water drops used to determine contact angles of native (a) and acetylated (b) CNFs after 1 s (left) and 30 s (right).

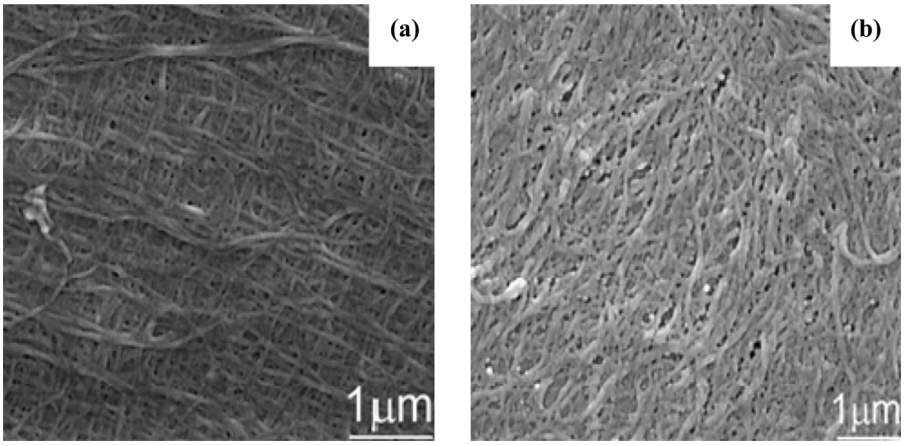

Fig. 6. SEM micrographs of (a) native CNFs and (b) acetylated CNFs.

4. Conclusions

The main purpose of this study was to reduce CNFs' hydrophilic character and thus improve their compatibility with common non-polar polymeric matrices. Some conclusions of chemical modification of CNFs are as follows:

(a) FT-IR results displayed a successful acetylation of CNFs.
(b) The dispersion of CNFs in non-aqueous mediums (acetone and ethanol) showed that the hydrophobicity of the acetylated CNFs significantly increased compared to the non-acetylated nanofibers.
(c) X-ray analysis revealed that the acetylation process reduced the crystallinity of the cellulose chains.
(d) TGA results revealed that the thermal stability of modified CNFs was moderately increased.
(e) The contact angle measurements indicated that the acetylation treatment changed the surface characteristics of the CNFs from hydrophilic to more hydrophobic.
(f) The SEM study showed that the surfaces of the acetylated nanofibers were slightly rough, while the non-acetylated nanofibers had smooth and uniform surfaces.
(g) Finally, it is concluded that the esterification reaction using pyridine as catalyst was efficient and could be considered as a facile method to modify the surface of nanofibers, which opens up a new opportunity for using CNFs as reinforcement in non-polar polymer matrices.

Acknowledgments

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