

Grafting of model primary amine compounds to cellulose nanowhiskers through periodate oxidation

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Abstract This study demonstrates regioselective oxidation of cellulose nanowhiskers using 2.80–10.02 mmols of sodium periodate per 5 g of whiskers followed by grafting with methyl and butyl amines through a Schiff base reaction to obtain their amine derivatives in 80–90 % yield. We found a corresponding increase in carbonyl content (0.06–0.14 mmols/g) of the dialdehyde cellulose nanowhiskers with the increase in oxidant as measured by titrimetric analysis and this was further evidenced by FT-IR spectroscopy. Grafting of amine compounds to the oxidized cellulose nanowhiskers resulted in their amine derivatives, which are found to be partially soluble in DMSO. Therefore, the reduction reaction between amines and carbonyl groups was confirmed through ^{13}C NMR spectra, which was also supported by copper titration, XPS, and FT-IR spectroscopy. Morphological integrity and crystallinity of the nanowhiskers was maintained after the chemical modification as studied by AFM and solid-state ^{13}C NMR, respectively.

Keywords Amine derivative · Cellulose nanowhiskers · Dialdehyde cellulose nanowhiskers · Periodate oxidation

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Introduction

Cellulose is the most abundant and sustainable polymeric raw material in nature, obtained from different vegetal, bacterial and animal sources. Formed by repeated units of glucose monomers, it has led to a global renaissance of interdisciplinary cellulose research because of its unique characteristics. For the past few decades, cellulose has attracted attention as one of the promising polysaccharides for accomplishing highly engineered nanoparticles, which can be significantly modified to tailor its properties for many potential applications (John and Thomas 2008; Klemm et al. 2011; Huang et al. 2006; Peng et al. 2011).

Controlled acid hydrolysis of cellulose fibers exploits the hierarchical structure of cellulose by selectively hydrolyzing the amorphous regions and leaving behind the less reactive crystalline regions called cellulose nanowhiskers (CNWs). These nanowhiskers are defined as elongated rod-like nanoparticles with typical dimension of 100–1,000 nm in length and 5–50 nm in width depending on their source as well as the hydrolysis conditions (Siqueira et al. 2009; Azizi Samir et al. 2005; Beck-Candanedo et al. 2005; Lima and Borsali 2004). Recently, cellulose nanowhiskers have attracted research attention as a green nanofiller in bionanocomposites because of their superior mechanical properties, high aspect ratio, low density, biocompatibility, high strength, and crystallinity (Habibi et al. 2010; Peresin et al. 2010; Dufresne 2008; Eichhorn 2011). To broaden their applications furthermore,

attempts were made to transform the polar hydroxyl groups into different polar and non-polar moieties, which have led to an increased interest in synthesis of functionalized nanowhiskers.

Due to the abundance of reactive hydroxyl groups at the surface of CNWs, esterification, and etherification are the most common approaches for chemical modification of cellulose whiskers although there are several reports on oxidation and nucleophilic substitution reaction. In fact, all these modifications are focused on the covalent functionalization of the surface hydroxyl groups. For example, Sassi et al. (Sassi and Chanzy 1995) acetylated valonia and tunicate whisker using acetic anhydride in acetic acid only affecting the cellulose chains localized at the surface. Acetylation of whiskers was also carried out in vinyl acetate, alkenyl succinic anhydride (ASA) to improve the dispersion of whiskers in organic solvents (Cetin et al. 2009; Nair et al. 2003; Angellier et al. 2005; Yuan et al. 2006).

Gousse et al. examined the silylation of the hydroxyl groups on tunicin whiskers using a series of alkyl dimethylchlorosilanes such as *n*-butyl, *n*-octyl and *n*-dodecyl silanes (Gousse et al. 2002). It was observed that silylated whiskers were readily dispersible in THF but their birefringence behavior and morphological integrity was lost at high degree of silylation ($DS > 1$). TEMPO mediated oxidation of CNWs, obtained from HCl hydrolysis of cellulose fibers was studied by various groups to impart a negative charge on the nanowhisiker surface (Araki et al. 2001; Montanari et al. 2005; Habibi et al. 2006). Araki et al. (Araki et al. 2001) further prepared novel sterically-stabilized aqueous whisker suspension combining TEMPO mediated carboxylation and grafting of amine terminated polyethylene glycol (PEG). Recently, Fujisawa et al. (Fujisawa et al. 2012) introduced primary aliphatic C_{12} -, C_{14} - or C_{16} -amines to TEMPO-oxidized nanowhisiker (TONc) surface via carboxyl/amine salt formation. The modified nanowhiskers were found to be nano-dispersible in isopropyl alcohol due to the conversion of hydrophilic TONc surface into hydrophobic by the long chain amines. TONc surfaces were also modified using octadecyl amine (ODA) through amidation and ionic complexation treatments by Johnson et al. (Johnson et al. 2011) to prepare their hydrophobic derivatives. Both treatments were found to be

effective in complete substitution of TONc carboxylic groups by ODA and the resulting TONc derivatives were readily dispersible in organic solvents of wide-ranging polarities.

Nucleophilic coupling of hydroxyl groups of cellulose nanowhiskers with epoxypropyltrimethyl ammonium chloride in presence of alkali was reported by Hasani et al. (Hasani et al. 2009), which introduced positive charges at the whisker surface. Several other examples of functionalization approach include grafting-onto and grafting-from whisker surfaces to demonstrate very good compatibility and high adhesion with synthetic polymers (Majoinen et al. 2011; Harrison et al. 2011). These grafting approaches frequently involve functionalization via surface hydroxyl groups to a presynthesized polymer through a coupling agent or to a polymer formed by in situ polymerization from immobilized initiators on the substrate surface.

Periodate oxidation approach offers a facile and important method for functionalization of hydroxyl groups in cellulose nanowhiskers. It is well known for its highly selective oxidative fragmentation of the C-2 and C-3 glycol bond of the glucose ring into C-2/C-3 dialdehyde product, which acts as a reactive intermediate for further derivatization (Kristiansen et al. 2010; Potthast et al. 2007; Zhang et al. 2008). Cellulose fibers containing active amine groups have been known for their antimicrobial properties and irreversible chemical modifications resulting from covalent attachment are highly effective and preferable method to introduce amine onto cellulose surfaces (Alonso et al. 2009; Cassano et al. 2009; El-Tahlawy et al. 2005; Ringot et al. 2011). The purpose of the present work is to utilize facile periodate oxidation approach in order to incorporate model primary amine compounds to cellulose nanowhisiker surfaces. In brief, cellulose nanowhiskers resulting from H_2SO_4 hydrolysis of bleached softwood pulp were oxidized in presence of sodium periodate to obtain the dialdehyde cellulose whisker product. These oxidized nanowhiskers were then grafted with methyl and butyl amine to obtain the corresponding amine derivatives employing a reductive-amination treatment. This article highlights our studies on the chemistry and the characterization of the modified nanowhiskers by copper titration, FT-IR, NMR and AFM.

Experimental

Materials

A fully bleached commercial softwood Kraft pulp was used as a source for cellulose nanowhiskers. All chemicals and solvents were purchased from VWR International and used as received unless otherwise specified.

Preparation of H₂SO₄-hydrolyzed cellulose nanowhiskers

The cellulose nanowhiskers were prepared by sulfuric acid hydrolysis of a bleached softwood pulp based on a literature procedure (Bondeson et al. 2006). In brief, 60.00 g (oven dried weight) of the pulp was mixed with H₂SO₄ solution (64 %, w/w, 1:10 g/mL) with continuous stirring at 45 °C for 45 min. The hydrolysis reaction was stopped by adding excess (10-fold) of distilled water followed by the removal of acidic solution by successive centrifugation at 12,000 rpm for 10 min until the supernatant became turbid. The sediment was collected and dialyzed (MWCO: 12–14,000) against tap water until the solution pH became neutral. After dialysis, the content was sonicated for 10 min and centrifuged for 5 min at 10,000 rpm. The cloudy supernatant, containing nanowhiskers, was collected and the remaining sediment was again mixed with water, sonicated and centrifuged to obtain additional nanowhisiker; this procedure was repeated till the supernatant was clear. Cellulose nanowhiskers were obtained in 20–30 % yield.

Sodium periodate oxidation of cellulose nanowhiskers

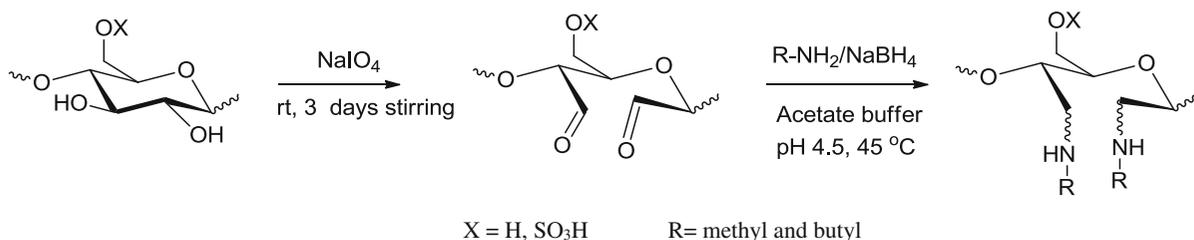
An aqueous mixture of cellulose nanowhiskers (250.00 mL, 2.00 wt%, w/v) and sodium periodate

(0.60 g, 2.80 mmols) was stirred for 2 days in the absence of light at room temperature. The product was then placed into dialysis membranes (MWCO: 12–14,000) and dialyzed against tap water for 2 days to remove the spent oxidant, and then freeze-dried providing a gravimetric yield of 98 %. The same procedure was then repeated using 8.40 and 10.02 mmols of sodium periodate providing 95 and 97 % yield of the oxidized cellulose whiskers, correspondingly. These samples were named as DAC1, DAC2, and DAC3, where DAC = dialdehyde cellulose and 1, 2, 3 corresponds to 2.80, 8.40 and 10.02 mmols of sodium periodate employed, respectively.

Reaction of dialdehyde cellulose whiskers with amines

The dialdehyde cellulose whisker suspension (100 mL, 2.00 wt%) was acidified in acetate buffer (100 mL, pH 4.5, acetic acid/sodium acetate) and stirred for 15 min. Methyl and butyl amine was then slowly added to the suspension (5 eq. per glucose unit) in separate experiments and the mixture was continuously stirred at 45 °C for 6 h followed by the in situ reduction of the resulting imine intermediate at room temperature employing NaBH₄ (2.5 eq. per glucose unit) dissolved in 2 mL water. After stirring for 3 h, the product was dialyzed (MWCO: 12–14,000) against water until the pH was neutral and subsequently, the slurry was freeze dried to obtain the dry product with a yield of 80–90 %. A schematic pathway for oxidation and reductive-amination of cellulose nanowhiskers is shown in Scheme 1.

These samples were named as DACX-MA, DACX-BA, where DAC = dialdehyde cellulose, MA = methyl amine, BA = butyl amine and X = 1, 2, 3 corresponds to three levels of oxidation, respectively.



Scheme 1 Oxidation and reduction reaction of cellulose nanowhiskers

Determination of carbonyl groups by copper titration

The carbonyl group content of the starting and oxidized whiskers was determined following Tappi standard method T430 (Tappi Standard T430). Briefly, DAC nanowhiskers (1.00 g) were treated with an aqueous CuSO_4 solution (3.50 mL, 0.40 N) and a carbonate-bicarbonate solution (63.5 mL, 2.40 N, 1.04 N). The mixture was heated to 100 °C for 3 h, cooled, filtered, and washed with 5 % aqueous Na_2CO_3 solution (70 mL, w/v) and hot water (150 mL). The whiskers along with the filter paper were dispersed in 5 % phosphomolybdic acid (16.60 mL, w/v), stirred, filtered, and then washed thoroughly with water. The filtrate was diluted with deionized water (450 mL) followed by the titration with 0.05 N KMnO_4 to a faint pink end point. A blank test was also performed following the same procedure. For each sample, the experiment was repeated three times to obtain the copper number and the data were reported with an error of less than ± 4.0 %. The copper number and carbonyl group content was calculated by following the expressions (Rohrling et al. 2002).

$$\begin{aligned} \text{Copper number (Cu\#)} &= (6.36(V - B) N)/W \\ \text{Carbonyl Group Content (mmols/100 g)} \\ &= ((\text{Cu\#} - 0.07)/0.6) \end{aligned}$$

V = Volume of KMnO_4 solution to titrate the filtrate from the specimen, mL; B = Volume of KMnO_4 solution to titrate the blank filtrate, mL; N = Normality of KMnO_4 , 0.05 N, W = Weight of the CNWs, g.

FT-IR spectroscopy

The starting whisker and oxidized samples were dried at 105 °C for 6 h and then cooled to room temperature for FT-IR analysis. The oven dried CNWs, periodated oxidized CNWs and freeze dried amine derivatives were pressed into KBr pellets (1:200). Transmission mode FT-IR spectra were collected with a Nicolet Magna-IRTM 550 spectrometer. Spectra were obtained in 400–4,000 cm^{-1} range and for each sample 64 scans were taken at a resolution of 4 cm^{-1} .

NMR spectroscopy

^{13}C NMR spectra were obtained on a Bruker Avance-400 spectrometer operating at a frequency of

100.55 MHz at 45 °C. Freeze dried aminated samples (0.050 g) were dissolved in DMSO-d_6 (0.60 mL) with constant stirring at 45 °C for 3 h. An aliquot of this sample solution (0.50 mL) was transferred to an NMR tube and 30,000 scans were collected for each spectrum.

For solid-state ^{13}C NMR experiments, the samples were added into 4-mm cylindrical ceramic MAS rotors. CP-MAS experiments utilized 10 kHz MAS probe head spinning speed, a 5 μs (90 deg) proton pulse, 1.5 ms contact pulse, 4 s recycle delay and 2 K scans. All spectra were recorded on pre-wet samples with 40–60 % water content and the data processing was performed offline using the NUTS software (Acorn NMR Inc.).

X-Ray photoelectron spectroscopy (XPS) analysis

Both unmodified and modified whisker samples were pressed into thin pellets and vacuum dried for 1 day to remove any moisture. X-ray photoelectron spectra of these samples were collected on a Thermo K-alpha XPS spectrometer with a monochromatic aluminum $\text{K}\alpha$ source operated at 12 kV and 6 mA under a pressure of 10^{-8} mbar. The binding energy scale was shifted to ensure that the main C–C/C–H contribution to the C1 s signal occurred at 285.0 eV.

AFM experiment

AFM experiments were conducted on a Veeco, NanoScope 3100 scanning probe microscope with a NanoScope IIIa controller. Amplitude images were obtained on air dried suspensions (0.001 wt.%) in tapping mode, using a 1–10 Ohm-cm phosphorus (n) doped Si tip, with a nominal frequency of 150 kHz.

Results and discussion

Cellulose nanowhiskers were oxidized in presence of sodium periodate to yield the corresponding C-2/C-3 dialdehyde product and the carbonyl content was determined by Cu^{2+} titration (Table 1). The results indicated a corresponding increase in carbonyl content with increasing sodium periodate equivalents, although a very low degree of oxidation (2.3 %) was observed, which was attributed to the non-uniform distribution of oxidation over fiber surfaces (Kim et al. 2000). Further evidence of carbonyl group was

Table 1 Carbonyl content of oxidized cellulose nanowhiskers

Samples	NaIO ₄ (mmols)	Carbonyl content (mmols g ⁻¹)
CNWs	0.00	0.006
DAC1	2.80	0.062
DAC2	8.40	0.114
DAC3	10.02	0.141

obtained from the transmission mode FT-IR spectra, as shown in Fig. 1. The characteristic C=O stretching vibration band of the dialdehyde cellulose nanowhis-ker appeared at 1,740 cm⁻¹ and this spectral data

confirms a gradual oxidation of nanowhiskers as the intensity of the carbonyl band increases with increased oxidant.

The dialdehyde cellulose nanowhiskers were then reacted with methyl amine and butyl amine to generate in situ the corresponding imines followed by sodium borohydride reduction to yield the amine derivatives. The presence of the amine functionality grafted to the cellulose whiskers was evidenced from FT-IR spectra (Figs. 2, 3) as indicated by the appearance of a new absorption band at 1,564 cm⁻¹ corresponding to N–H bending vibration. This result was further supported by ¹³C solution NMR spectra (Figs. 4, 5) as a result of their partial solubility in

Fig. 1 FT-IR spectra. **a** nanowhiskers. **b** DAC1. **c** DAC2. **d** DAC3

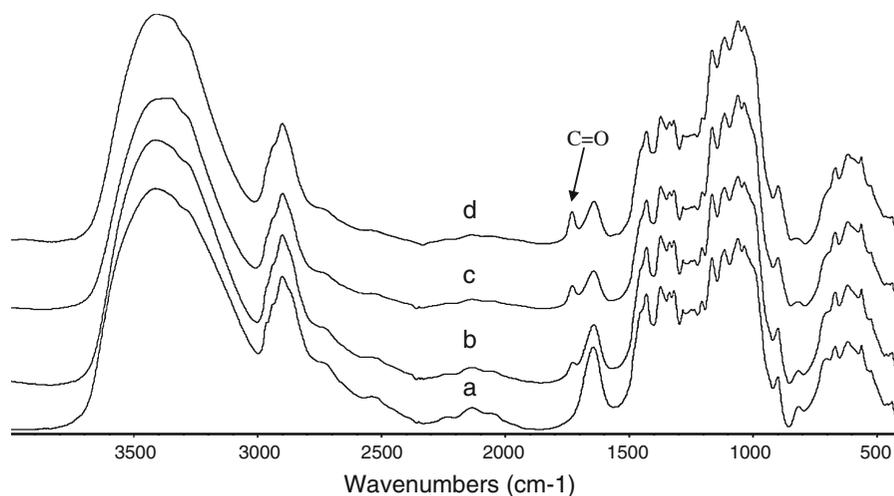


Fig. 2 FT-IR spectra. **a** DAC1-MA. **b** DAC2-MA. **c** DAC3-MA

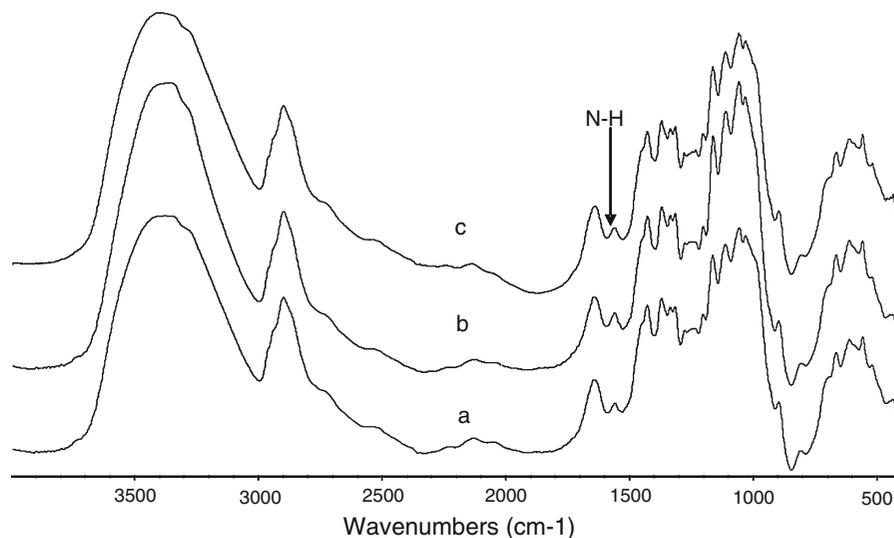


Fig. 3 FT-IR spectra.
a DAC1-BA. **b** DAC2-BA.
c DAC3-BA

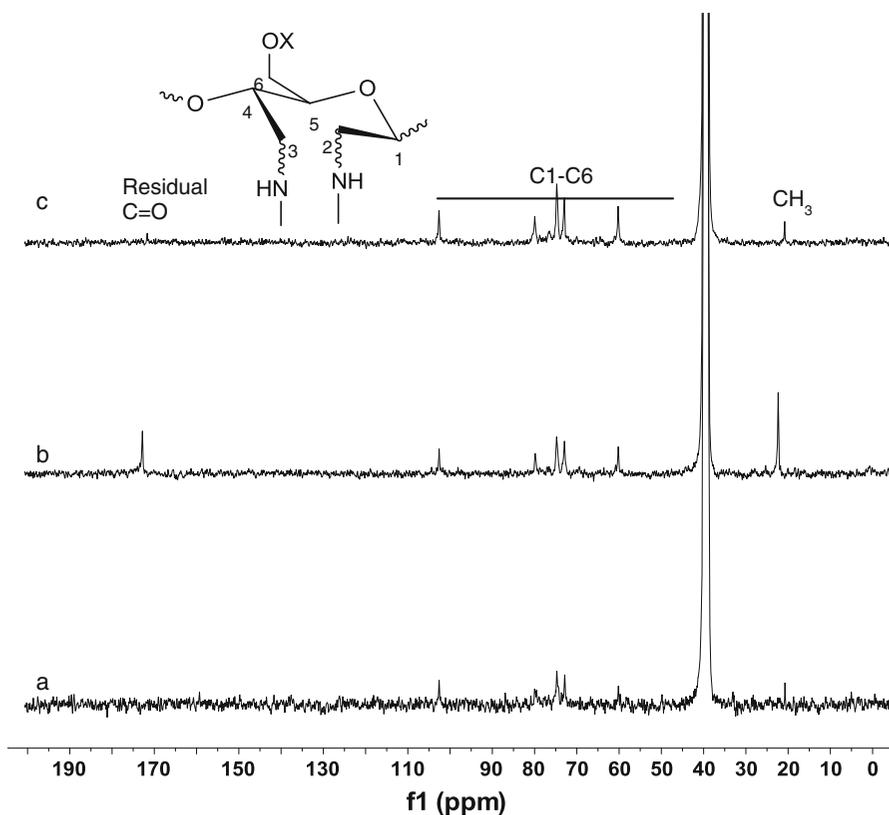
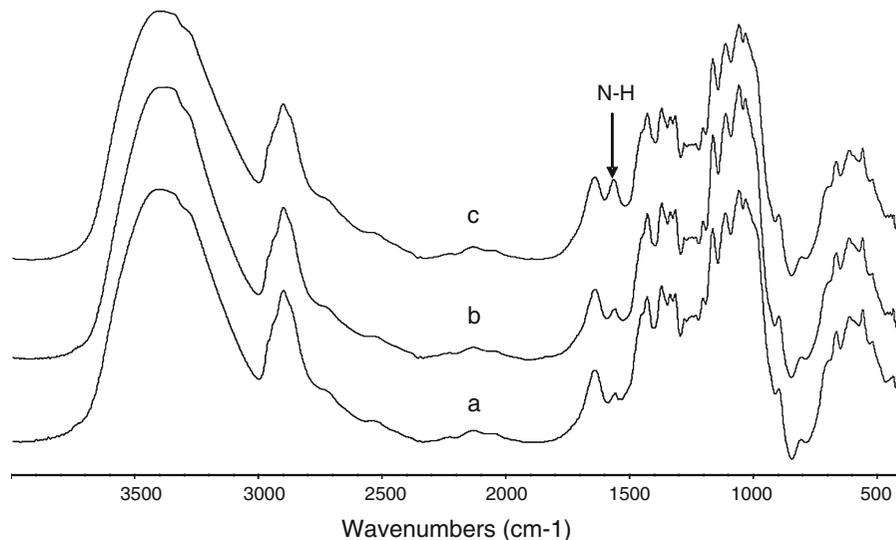


Fig. 4 ^{13}C NMR spectra of nanowhiskers after adding (1:5 eq) of methyl amine. **a** DAC1-MA. **b** DAC2-MA. **c** DAC3-MA

DMSO, possibly due to the incorporation of non-polar small chains onto the surface of nanowhiskers. NMR spectra exhibited chemical shifts arising from the respective amine carbons as well as a peak at

172 ppm arising from aldehyde carbonyl carbon after adding 5 equivalent times of amines per glucose unit, suggesting the presence of residual carbonyl group in the sample. Additional evidence was obtained from

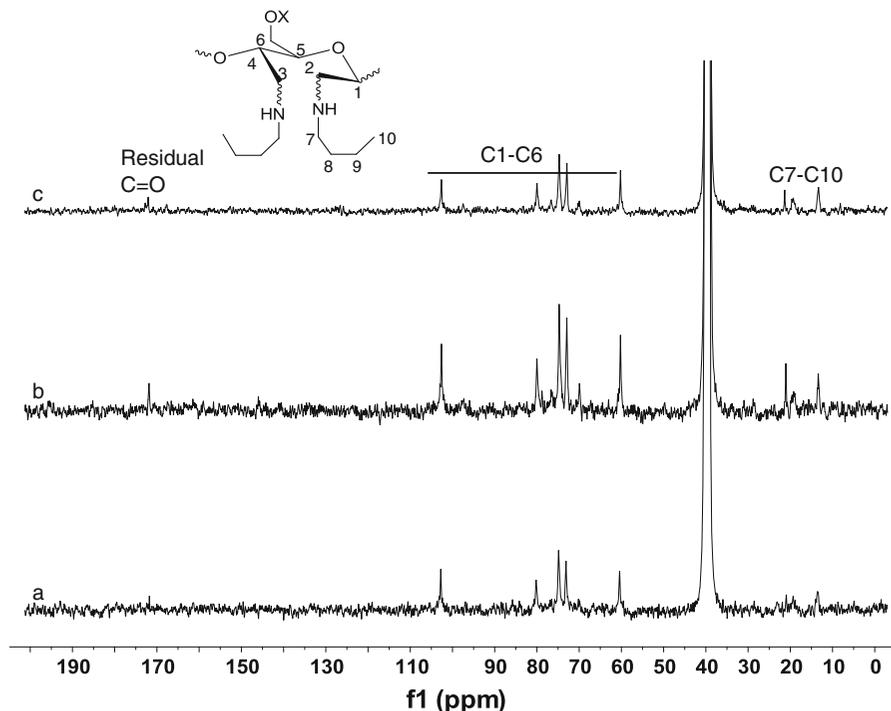


Fig. 5 ^{13}C NMR spectra of nanowhiskers after adding (1:5 eq) of butyl amine. **a** DAC1-BA. **b** DAC2-BA. **c** DAC3-BA

copper titration result of these amine grafted nanowhiskers (Table 2) showing the remaining unreacted carbonyls. However, with excess equivalent of amine (1:20) the carbonyl peak in NMR spectra disappears as shown in Fig. 6 and this was again supported from carbonyl content (Table 2) estimation through copper titration. The absence of carbonyl groups in amine grafted samples could be explained to their reduction into amine derivatives and to some extent the possible reduction by sodium borohydride. As a control experiment, cellulose nanowhiskers and the oxidized products were found insoluble in DMSO. The samples were further characterized by XPS in order to confirm the presence of amines on the surface of nanowhiskers.

Surface elemental composition of unmodified and modified cellulose nanowhiskers determined from XPS analysis is summarized in Table 3, which only investigates the sample surface (~ 10 nm deep) (Morandi et al. 2009). As expected, pure nanowhiskers consist of mainly carbon and oxygen. After grafting with methyl and butyl amines the nanowhisker surface shows the presence of nitrogen along with carbon and oxygen. The treatment of cellulose nanowhiskers with

Table 2 Carbonyl content of amine grafted nanowhiskers determined by copper number titration

Samples	Initial carbonyl content (mmols g^{-1})	Carbonyl content (1:5 eq amines) (mmols g^{-1})	Carbonyl content (1:20 eq amines) (mmols g^{-1})
DAC1	0.062	0.021	0.001
DAC2	0.114	0.060	0.002
DAC3	0.141	0.103	0.002

methyl and butyl amines caused an increase in the concentration of carbon and nitrogen, which is a clear indication of the attachment of the primary amines to the whisker surface. We observed a maximum of 1.3 and 2.1 % of nitrogen in DAC3-MA and DAC3-BA samples respectively. However, DAC1-MA and DAC1-BA samples did not exhibit any nitrogen content on the surface possibly due to its low degree of substitution.

Investigation of surface morphology of cellulose nanowhisker and its derivatives was carried out by AFM as shown in Fig. 7. AFM images show that the

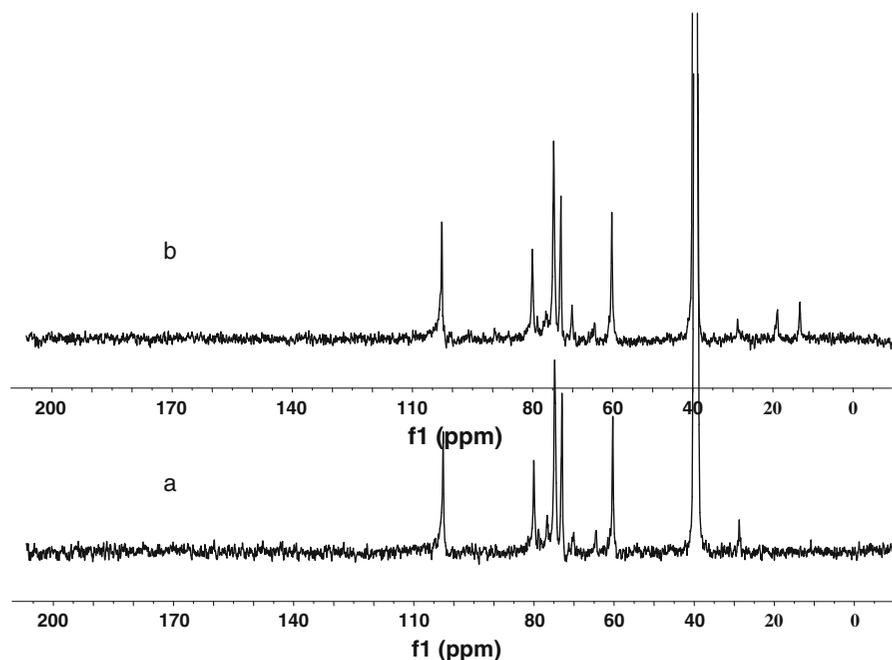


Fig. 6 Typical ^{13}C NMR spectra of nanowhiskers after adding excess (1:20 eq) of amine. **a** DAC-MA. **b** DAC-BA

Table 3 Surface elemental composition of cellulose nanowhiskers before and after chemical modification

Sample	Elemental composition (%)			Sample	Elemental composition (%)		
	O	C	N		O	C	N
Nanowhiskers	38.6	53.25	0				
DAC1-MA	37.9	55.1		DAC1-BA	37.4	54.5	
DAC2-MA	37.2	55.2	0.5	DAC2-BA	37.5	54.5	0.6
DAC3-MA	33.4	58.0	0.9	DAC3-BA	34.0	56.3	1.2
DAC3-MA (1:20)	32.6	58.6	1.3	DAC3-BA (1:20)	33.6	57.2	2.1

nanowhiskers maintained their characteristic morphology even after grafting with amines. Nanowhiskers seem to be agglomerated before chemical modifications but they were found to be separated from each other after chemical modification due to the incorporation of relatively hydrophobic groups on the surface.

Determination of crystallinity using different techniques has been extensively studied in literature and it has been concluded that the crystallinity index (CrI) varies substantially depending on the choice of instrument and data analysis technique implemented. The two most commonly used techniques for determining the crystallinity index are NMR and XRD. However, XRD method always shows significantly

higher crystallinity values than NMR although the trend of CrI is consistent in each measurement (Park et al. 2010).

We have used solid-state ^{13}C NMR method to measure the crystallinity index, where spectra of all the samples were analyzed using line shape analysis based on the method outlined by (Larsson et al. 1999). Crystallinity index was calculated from the ratio of the peak areas in crystalline region to the peak areas in non-crystalline regions with an error of approximately 3 %. It was observed that CrI of nanowhiskers was preserved even after the oxidation–reduction reaction (Table 4), which could be due to the grafting of small molecules onto the whiskers. Similar observation was made in the literature, where morphology and

Fig. 7 AFM image of 0.001 wt% suspensions. **a** nanowhiskers. **b** DAC3. **c** DAC3-MA. **d** DAC3-BA

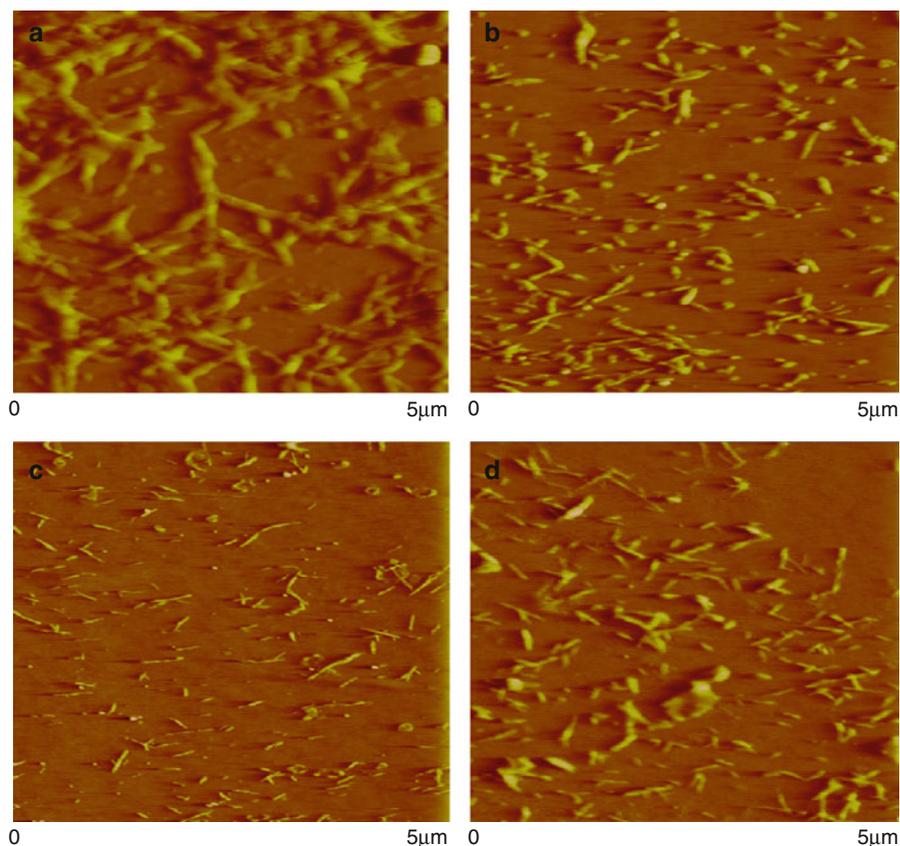


Table 4 Crystallinity index of cellulose nanowhiskers before and after chemical modification

Samples	Crystallinity index (CrI)
CNWs	56.5
DAC1	55.5
DAC2	57.2
DAC3	57.0
DAC3-MA	55.9
DAC3-BA	57.7

crystallinity of nanowhiskers is retained after chemical modification (Yuan et al. 2006).

Conclusions

Cellulose nanowhiskers prepared by sulfuric acid hydrolysis of bleached softwood pulp were successfully grafted with model methyl and butyl amines through the combination of periodate oxidation and reductive-amination reaction in aqueous media and this

modification was confirmed using FT-IR, NMR, Cu^{2+} titration, XPS as well as AFM. Interestingly, the modified whiskers were found to be soluble in DMSO even at a low content of amine groups. Occurrence of partial non polar moieties on nanowhisker surfaces by introducing alkyl chains is the most likely reason. As a consequence, the effective grafting of amines to whiskers was demonstrated by ^{13}C NMR with additional evidence from FT-IR, XPS, and copper titration experiments. The grafting procedure modifies cellulose nanowhiskers without any major change in morphology and crystallinity. This oxidation and reduction methodology was further utilized to synthesize cellulose nanowhisker carrier molecules for drugs and biomolecules (Dash and Ragauskas 2012). In conclusion, periodate oxidation and reductive-amination could be a promising path to attach various amine containing compounds such as enzymes, antibiotics to the nanowhisker surfaces for potential biomedical applications.

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