

SURFACE MODIFICATION OF TEMPO-MEDIATED CELLULOSE NANOFIBRIL WITH OCTADECYLAMINE

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ABSTRACT

SURFACE MODIFICATION OF TEMPO-MEDIATED CELLULOSE NANOFIBRIL WITH OCTADECYLAMINE. In this study, surface modification of 2,2,6,6-tetramethylpiperidine-1-oxyl radical TEMPO-cellulose nanofibrils (TCNF) was obtained by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS)-mediated system. The carboxylate groups on TCNF surface was replaced by conjugation of octadecylamine (ODA). The conversion of the carboxylate groups on CNF into amide I and II groups was confirmed by attenuated transform reflectance-infrared (ATR-FTIR) and elemental analysis study. Further, decarboxylation of TCNF at higher temperature was hindered by the presence of amide groups resulted in the higher thermal stability of TCNF as observed by thermogravimetry analysis (TGA). These results suggested the possibility of modifying surface negatively charged of TCNF with conjugated amine groups into thermally stable nanocellulose.

Keywords: Cellulose nanofibril, TEMPO, Octadecylamine, Conjugation, Thermal stability

ABSTRAK

MODIFIKASI NANOSELULOSA DARI PROSES OKSIDASI TEMPO DENGAN OCTADECYLAMINE. Penelitian ini membahas proses modifikasi permukaan dari nanoselulosa (TCNF) yang di peroleh dari pulp *hardwood* proses kraft yang terputihkan dengan proses oksidasi menggunakan 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO). Nanoselulosa yang dihasilkan memiliki muatan dengan terbentuknya gugus karboksil (-COO-Na⁺) sehingga membuat nanoselulosa semakin bersifat hidrofilik. Modifikasi ini ditujukan untuk mensubstitusi gugus karboksil dengan octadecylamine. Reaksi dijalankan dengan sistem 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) dan penambahan N-hydroxysuccinimide (NHS). Dari hasil analisa spektroskopi sinar infra (ATR-FTIR) diketahui bahwa gugus

nanoselulosa dapat dilakukan dengan substitusi gugus aktif sehingga meningkatkan kestabilan panas nanoselulosa dan diharapkan dapat memperluas aplikasi nanoselulosa dalam bidang nanokomposit.

Kata kunci: Nanoselulosa, TEMPO, Octadecylamine, Konjugasi, Stabilitas panas

INTRODUCTION

TEMPO-cellulose nanofibril (TCNF) obtained by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation has gained popularity in the field of bio-nanomaterials applications [1-7], due to the

regioselective surface modification of cellulose which promote large amounts of anionically charged sodium carboxylate that may cause the individualization of cellulose microfibrils by electrostatic repulsion and/or

osmotic effects in water, therefore reducing the energy consumption for nanocellulose isolation. Isogai et al. (2011) [8] reported the required energy was below 7 MJ.Kg⁻¹ of cellulose with yield above than 90%. In addition, the oxidation system can be conducted in environmentally-benign conditions (aqueous, pH 10-11, room temperature and atmospheric pressure). Thus suggested that TEMPO oxidation process is favorable for commercialization of nanocellulose production. Although TEMPO oxidant is expensive, however, co-oxidant reagents such as NaClO or NaClO₂ are inexpensive. Mao et al. (2010) [9] reported that the expensive TEMPO can be recycled and reused with reinforced addition back of sodium hypochlorite into the system and thus remained still effective in generating carboxylic acid groups.

The oxidation of cellulose occurred only on the surface of cellulose, keeping the inside crystal structure unoxidized [10,11] and maintaining the crystallinity, the modulus of elasticity of oxidized cellulose unchanged. However, the presence of carboxylated groups decreased the thermal stability of oxidized cellulose. Thus will limit the application of cellulose nanofibril especially for polymer nanocomposite. Fukuzumi et al. (2010)[12] modified the carboxylate cellulose by counter ion using several cation such as CaCl₂, Ca(OAc)₂, Ca(NO₃)₂ and CaI₂. Instead of ionic interaction, here we reported covalent bonded modification of TEMPO-oxidized cellulose with converted the carboxyl groups into octadecylamine. The aim of this study was to characterized the conjugation of octadecylamine groups onto cellulose nanofibrils by analyzing the functional groups, the elemental analysis and the crystal structure using X-ray diffraction and observed the thermal degradation of modified TCNF.

Later on, the obtained modified cellulose nanofibrils could be used as reinforcing agent as well as improving dispersibility of cellulose in biocomposite production for high toughness composite [13].

MATERIAL AND METHODS

Materials and Instruments

TCNF was isolated from dried hardwood bleached kraft pulp (HW-BKP) sheet (Moorim Paper Co. Ltd., Korea) which stored in a humidity chamber (JSR, LowTempIncubator, JSBL-250C, Korea) at 25 °C before used. The materials used were as follows: TEMPO (C₉H₁₈NO, 99%, Sigma-Aldrich), sodium bromide (NaBr, Sigma-Aldrich), sodium hypochlorite solution with chlorine content 12% (NaClO, Sigma-Aldrich), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC >98% purity, Sigma-Aldrich), octadecylamine (ODA 99.8%, Sigma-Aldrich), N-hydroxysuccinimide (NHS >98% purity, Sigma-Aldrich), dimethylformamide (DMF, ACS reagent grade

99.8%, Sigma-Aldrich). Water for this experiments was purified using *Ultras-pure* (ROtech, Korea) with conductivity around 6 µS/cm.

TCNF isolation

Isolation of TCNF was conducted following a previously published procedure[5]. In brief, 2 g of HWBKP was diluted in a water suspension containing 0.025 g TEMPO and 0.25 g NaBr. The mixture temperature was maintained at 23 °C. The oxidation reaction was started by adding NaClO as the oxidant reagent, 7.85 mmol/g, drop wise in order to keep the pH below 10 during the addition. Throughout the reaction process, the pH was adjusted at by adding 0.5 N NaOH at 10.5. When the pH reached constantly at 10.5, there was no NaOH was needed, indicating that the reaction finished. The excess NaClO was quenched by adding ethanol (ca. 5 mL). After that, the pH of the solution was neutralized by 0.5 N HCl. The TEMPO-oxidized pulp slurry was filtered, and washed several times. And then, 2% wt slurry of TEMPO-oxidized pulp was subjected to ultrasonication treatment (Sonomasher, power 30%, frequency 20,320 Hz). Finally, by centrifugation (12,000 g) (Labogene 1580, Centrifuge, Gyrozen Co., Ltd., Daejeon, Korea), the TCNF was obtained from the supernatant, where un-fibrillated fibers were separated in sediment.

Conductometric Titration

The carboxyl content of TCNF was measured by the conductometric titration method [6]. The 80 mL cellulose suspension with 0.05% solid content was stirred continually with addition of 5 mL 0.01 M NaCl while the pH of the suspension was adjusted to 2.5–3 by addition of 0.1 M HCl. The agglomeration of TCNF was hindered by making the suspension in very low solid content. The titration was started by adding 0.01 M NaOH was added at a rate of 0.1 mL/min up to pH 11 while the conductivity changes was recorded manually using a conductometer (SevenGo, METTLER TOLEDO,

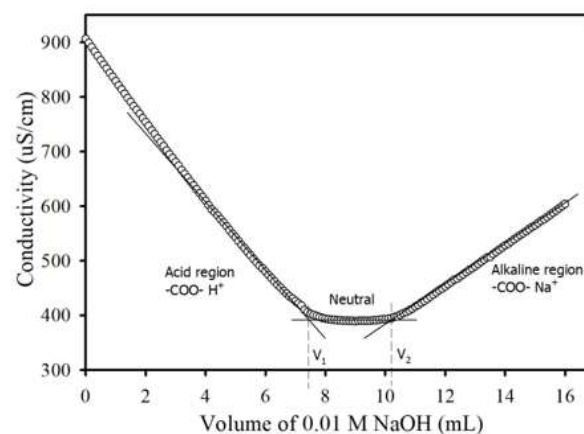


Figure 1. Typical graph for conductometric titration

China). A typical graph for the conductometric titration is shown in Figure 1. The conductivity decreased until the acid was neutralized by the addition of NaOH. At the end of neutralization (V_1), the conductivity remained unchanged to the end of step (V_2). Further addition of NaOH increased the conductivity.

Octadecylamine Conjugation Onto TCNF (Amidated CNF)

TCNF suspension (1000 mL of 0.5 wt %, 1.6 mmol/g COONa content) was transferred into a three-neck round bottom flask with overhead stirring (400-500 rpm) and then the flask was equilibrated at 50 °C in water bath. EDC (7.76 g, 40.5 mmol) and NHS (5.59 g, 48.6 mmol) were dissolved in 20 mL water and added into the TCNF suspension. The pH of the reaction mixture was adjusted to 5.5 – 6.0 and maintained for 30 min to complete the activation of TCNF surface carboxylate groups. The solution of ODA (8.7 g, 32.4 mmol) in DMF (250 mL) was added to the TCNF suspension, which instantly changed the appearance from transparent to white. The pH of the mixture was subsequently adjusted and maintained at 7.5 – 8.0 using

unbound ODA. These steps were followed by multiple water washes until pH was neutral. The reaction scheme of this research is presented in Figure 2. The carboxylated groups on C6 was converted into octadecylamine by intermediate ester formation.

Characterizations

Morphology of TEMPO-oxidized Cellulose Nanofibrils

Morphology of cellulose nanofibrils was observed under TEM (H-7600, Hitachi) performed at an accelerating voltage of 100kV. Sample was prepared using following method; a very low concentration of TCNF suspension about 0.005% w/v was homogenized. A drop of the suspension was put on plastic film then copper grid was dipped in the suspension about 15 second, after that grid with nanocellulose on it was dipped in a drop uranyl acetate 2% aqueous on plastic film about 15 seconds. Excessed solution was blotted using filter paper. The grid was ready for examination after it was dry.

ATR-FTIR Analysis

Modified TCNF were freeze-dried (Ilshin BioBase Co. Ltd, FDA8508, Korea). Then, were grounded and analyzed using ALPHA-P model attenuated total reflectance-infrared (ATR-IR) equipment (Bruker Optics, Germany). Absorption in the range 4000–400 cm^{-1} was measured as the average value of 25 scans at 4 cm^{-1} resolution. The measurement was conducted in two replications.

Elemental Analysis

The C, H and N content on cellulose before and after treatment was determined by elemental analysis (Flash 2000; Thermo Fischer Scientific Inc., United States)

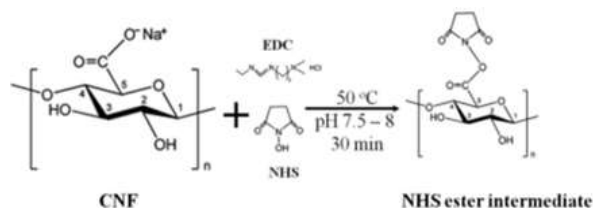
X-Ray Diffractometer

XRD measurements were carried out with an X-ray diffractometer (D/Max-2500, Rigaku, Japan) with $\text{CuK}\alpha$ -1 X-ray source with a wavelength of 1.541 Å from 10° to 40° in reflection mode, with steps of 0.02° and at a scanning rate of 6°/min.

Thermogravimetry Analysis (TGA)

Thermogravimetry (TG) and derivative thermogravimetry (DTG) analysis were carried out using a thermogravimetry instrument (TGA Q500 V20.13, Korea). About 10 mg of dried powder samples were heated up at a heating rate of 10 °C/min. from 25 to 600 °C under nitrogen atmosphere.

Step 1



Step 2

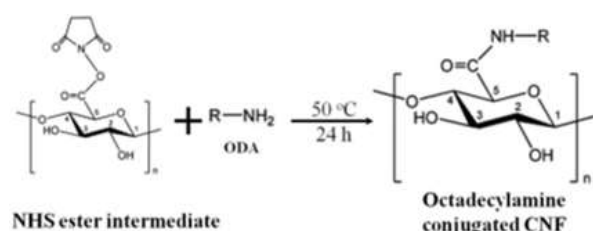


Figure 2. Reaction scheme of conjugating octadecylamine into TCNF

HCl (1 N) and NaOH (0.5 N). The stirring was continued for 24 h until the suspension turned into slightly yellow.

After the reaction finished, ODA-treated TCNF were recovered by dialysis and centrifugation. First, the suspensions were centrifuged to separate the nanocellulose (residue) from the mixture of solvents and dissolved reagents (supernatant). The residues were twice dispersed and centrifuged in water to remove traces of remaining reagents. Further, additional washes were performed with HCl (0.1 N) and ethanol respectively, to regenerate any residual carboxyl remaining after the treatments and to extract any remaining traces of

RESULT AND DISCUSSIONS

Carboxyl Content of TCNF

The carboxyl content of cellulose obtained for this study was about 1.4 mmol/g. In other words the degree of substitution of hydroxyl groups were 0.23 which indicated that in every 4.4 anhydroglucose unit (AGU, monomer) there was 1 carboxylate group. The higher co-oxidant level, the more carboxyl content on the cellulose surface [5]. However, it costs on the decrease of cellulose degree of polymerization [14].

The reaction with octadecylamine involved EDC/NHS process which made the surface of CNF became slightly hydrophobic by converting the carboxyl groups with amide (Amidation). Thus treatment was necessary since the high concentration of surface carboxyl group makes TEMPO-CNF strongly hydrophilic, i.e., water retention values of 400% and 200% for the salt form (-COO-Na⁺) and free acid (-COOH) forms, respectively [14]. Which further limit the application of the CNF in non polar solvent or hydrophobic polymer composite. Herewith the characterizations of CNF after amidation process:

Morphology of TEMPO-CNF

The morphology of cellulose nanofibrils is presented in Figure 3. Instead of cellulose nanocrystal

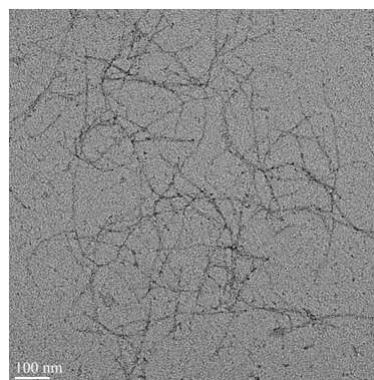


Figure 3. TEM image of CNF

that was obtained from harsh acid hydrolysis which remained only the crystal part region, cellulose nanofibrils are a combination of amorphous and crystalline region of cellulose fibrils [15]. Figure 3 shows that cellulose nanofibrils have long entangled fibrils up to micron in length while the diameter was below than 10 nm [16]. Unfortunately, we did not have the picture of modified amidated cellulose nanofibril. The color of freeze dried modified CNF changed from white into light yellow. After freeze dried processing, the modified TCNF agglomerated into powdered form, which indicated the formation of hydrogen bonding among hydroxyl groups from unreacted sites. We had tried to redisperse the dried modified TCNF into water solution, however due to the

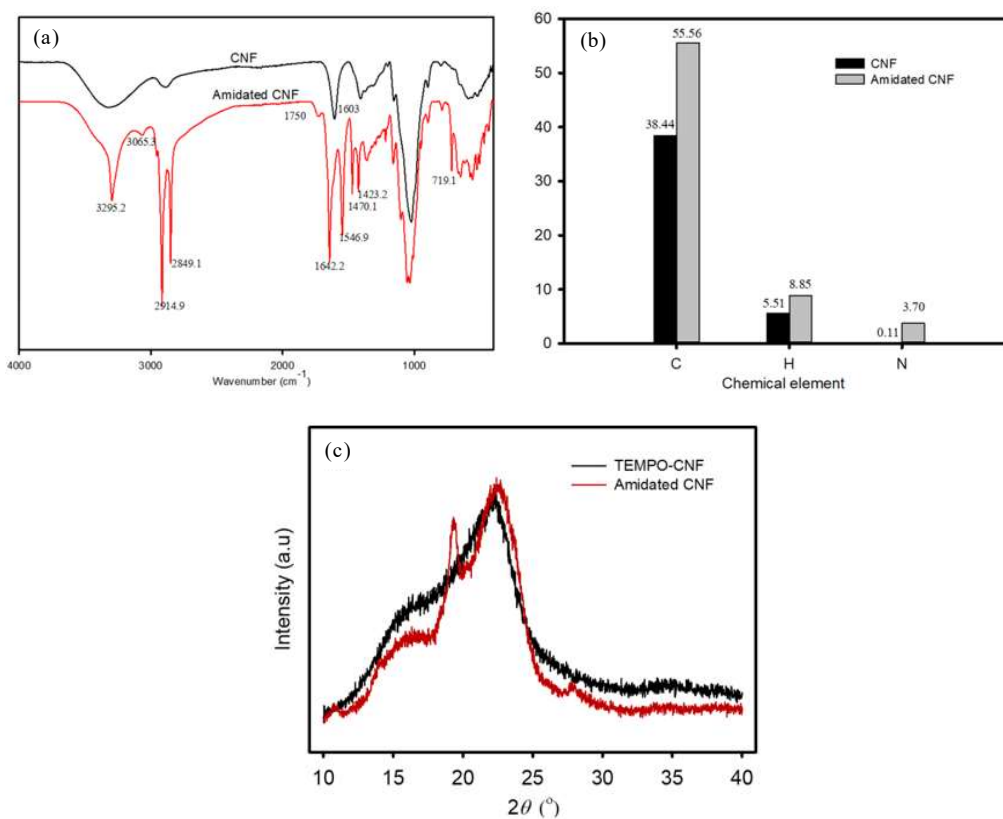


Figure 4. (a). ATR-FTIR spectra, (b). elemental analysis and c. XRD diffractogram of CNF and amidated CNF

conjugated of octadecylamine, TCNF were not diluted well, suggesting that the modified TCNF improved its hydrophobicity.

ATR-FTIR Analysis

ATR-FTIR spectra (Figure 4a) confirms the presence of amide I (C=O stretching, 1642 cm^{-1}) and amide II (combined N-H deformation and C-N stretching, 1546 cm^{-1}) bands on the TCNF after amidation process. Whereas the peak at 1603 cm^{-1} (asymmetric C=O stretching vibration of the COO- groups) from TCNF was reduced indicates complete consumption of available -COONa groups during the amidation. Peak at 3295 cm^{-1} represents N-H stretching vibration of secondary amides, peak 2849 – 2915 cm^{-1} corresponds to -CH methyl and methylene stretching and deformation at (1470 cm^{-1} / 719 cm^{-1}) bands showed the octadecyl tail were observed in the spectrum of amidated TCNF [17]. Another interesting finding is the observation of elemental component of modified TCNF.

Figure 4b shows nitrogen content increased after amidation process as well as C and H content, as evident of octadecylamine presented on the surface of TCNF. The XRD diffraction profiles of amidated TCNF, together with those of oxidized CNF reference are presented in Figure 4c. After the crystallinity analysis, the crystallinity of CNF before and after amidation process was not changed significantly, with the exception of strong and narrow peak after amidation at 19 ° that correspond to crystalline impurity presented in our sample. These patterns is also reported in the literature [18]. Thus result suggested that the amidation process did not modify the morphology and the core of cellulose nanofibrils since the substitution took place only on the surface of cellulose.

Thermogravimetry analysis

Figure 5 depicts the profile of weight loss (Figure 5a) and derivative weight loss (Figure 5b) of amidated CNF. Thermal degradation of cellulose involves a groups of endothermic reactions that can occur in the form of dehydration, hydrolysis, oxidation, decarboxylation especially for oxidated cellulose and transglycosylation process [19].

From figure 5a, it shows clearly that the dehydration process was higher in unmodified CNF, suggested that water affinity of amidated CNF decreases (the amidated CNF was more hydrophobic). Further, in case of TEMPO-mediated CNF, the formation of sodium carboxylate groups leads to a significant decrease in thermal degradation point due to decarboxylation mechanism. The first step of mass loss is a fast degradation starts at 220 -274 °C and followed by slow degradation at 450 °C (Figure 5b). It is generally accepted that the first step in the cellulose pyrolysis is mainly due

to the depolymerization of solid cellulose to form levoglucosan, while the second step of mass loss of TEMPO-CNF is due to the lower thermal stability of uronic acids such as glucuronic and galacturonic acid [12]. In case of amidated CNF, decarboxylation of TEMPO-CNF was hindered by the presence of amide groups resulted in higher thermal stability. Fukuzumi et al. 2010 [12] studied to improve thermal stability of TEMPO-CNF by modification of carboxyl groups with counter ion-exchanged and methyl esterification (trimethylsilyl diazomethane). These metylated increased the degradation temperature from 273 to 313 °C. In this study, maximum degradation showed at 309.2 and 383.1 °C, while the char residue at 600 °C, the amidated TCNF resulted in lower residue. This result are in conjunction with the thermal stability study of oxidized bacterial cellulose compared to unmodified counterpart [20].

CONCLUSION

A method to improved thermal stability of cellulose nanofibril by covalent bonding has been obtained by conjugation of octadecylamine onto TEMPO-mediated cellulose nanofibrils. The hydrophobicity of cellulose also improved due to the

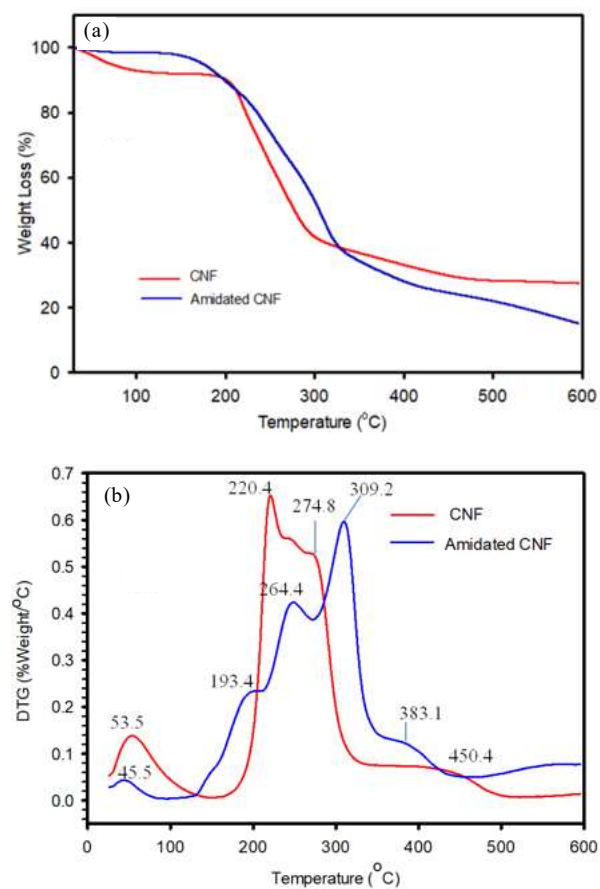


Figure 5. (a). Thermogravimetry weight loss and (b). derivative thermogravimetry weight loss of CNF and amidated CNF plots as a function of temperature.

converted of carboxyl groups into amide groups. The dispersion of modified cellulose in non polar solvent will be studied further.

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