Carbohydrate Polymers 89 (2012) 163–170

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Synthesis and characterization of cationically modified nanocrystalline cellulose

Masuduz Zaman[a,*], Huining Xiao[a], Felipe Chibante[b], Yonghao Ni[a,*]

[a] Limerick Pulp and Paper Research Center, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3
[b] Applied Nanotechnology Laboratory, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3

ARTICLE INFO

Article history:
Received 11 January 2012
Received in revised form 16 February 2012
Accepted 24 February 2012
Available online 13 March 2012

Keywords:
Nanocrystalline cellulose
Cationic modification
Charge density
Colloidal stability
Gelation

ABSTRACT

In this study, nanocrystalline cellulose (NCC) resulting from sulfuric acid hydrolysis of wood cellulose fiber, was rendered cationic by grafting with glycidyltrimethylammonium chloride (GTMAC). An optimization of the reaction parameters, such as water content, reactant mole ratio, and reaction media was performed. The presence of cationic GTMAC on the surface of NCC was confirmed by Fourier Transform Infrared Spectroscopy (FTIR). The cationically modified NCC was characterized by surface charge density, degree of substitution, ζ potential, and particle size. It was found that the cationic surface charge density of NCC can be increased by controlling the water content of the reaction system. Surface cationization of NCC led to an increase in the surface charge density over the un-modified NCC. The cationically modified NCC was well dispersed and stable in aqueous media due to enhanced cationic surface charge density. Transmission electron microscopy (TEM) images showed the improvement in state of dispersion of cationically modified NCC over the un-modified NCC. The optimum water content was found to be 36 wt% for aqueous based media and 0.5 water to DMSO volume ratio for aqueous–organic solvent reaction media. The increased surface charge density of NCC also delayed the onset of gelation in aqueous system.

1. Introduction

Recently, significant amount of research has been conducted for the development of renewable and biodegradable materials, which are also known as green products. Cellulose, which is the building block of all plants and constitutes a significant portion of the plant biomass, was the focus of these researches due to their renewable nature and abundance. It has been well known that the hydrolysis of cellulose from various sources with strong sulfuric acid or hydrochloric acid under controlled condition gives a suspension of rod-like cellulose crystals, whose length falls within the size range of 200–500 nm and width of 5–10 nm, and more commonly known as nanocrystalline cellulose (NCC) (Beck-Candanedo, Roman, & Gray, 2005). NCC exhibits many unique characteristics, including: (1) high strength, the Young's modulus and tensile strength of NCC can be up to 145 GPa and 7.5 GPa, respectively (Lahiji, Reifenberger, Raman, Rudie, & Moon, 2008); (2) high aspect ratio (up to 100) (Cranston & Gray, 2006); (3) high specific surface area (up to several hundred m^2/g) (Chazeau, Cavaille, Canova, Dendievel, & Boutherin, 1999); (4) polar groups (—OH) enriched surface (2–3 mmol/g), which provide excellent means of moisture adsorption and surface reactivity (Eyley & Thielemans, 2011); and (5) light weight, the hollow tubular or cellular nature of NCC reduces their density (1.59 g/cm^3) (OSullivan, 1997), making them light weight, especially when compared with the inorganic nanoparticles. The above unique characteristics give them improved material properties, therefore, a large variety of applications in various industries, such as pulp and paper, textile, biomedical, personal care products, plastics, and electronics.

Due to small size and very high specific surface area, NCC has a tendency to form aggregate in various systems. Sulfuric acid hydrolyzed cellulose nanocrystals have negatively charged sulfate ester groups on its surface that provide electrostatic stabilization (Dong, Kimura, Revol, & Gray, 1996; Revol, Bradford, Giasson, Marchessault, & Gray, 1992). NCC obtained from hydrochloric acid hydrolysis lacks surface charges and often form flocculate in various systems (Araki, Wada, Kuga, & Okano, 1998). Moreover, sulfate ester groups on NCC surface are rather labile and can be easily removed under mild alkaline condition (Habibi, Chanzy, & Vignon, 2006; Hasani, Cranston, Westman, & Gray, 2008; Kloser & Gray, 2010); therefore, the stabilization is not permanent. Over the past decade, many studies have been reported in the literature on surface modification of NCC in order to increase the dispersibility and compatibility of NCC in various systems, such as water, non-polar organic solvent, and polymer matrices. Several new methods have been developed including: TEMPO oxidation (Habibi et al., 2006; Montanari, Rountani, Heux, & Vignon, 2005),

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* Corresponding authors. Tel.: +1 506 4516857; fax: +1 506 4534767.
E-mail addresses: zaman.masuduz@gmail.com (M. Zaman), yonghao@unb.ca (Y. Ni).

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doi:10.1016/j.carbpol.2012.02.066

surfactant coating (Heux, Chauve, & Bonini, 2000), graft copolymerization (Araki, Wada, & Kuga, 2001), silane treatment (Gousse, Chanzy, Excoffier, Soubeyrand, & Fleury, 2002; Grunert & Winter, 2002), and surface acylation (Yuan, Nishiyama, Wada, & Kuga, 2006). These methods involved stabilization of NCC either by electrostatic repulsion of anionic groups or by steric hindrances by adsorbed or grafter polymers. While the anionically modified NCC stabilized by electrostatic repulsion showed good dispersion in polar solvents only, the steric stabilized NCC showed good dispersion in both polar and non-polar solvents (Araki et al., 2001). Surface silylation or acylation involves the selective replacement of hydrophilic hydroxyl group of NCC by hydrophobic silyl or acyl groups. The hydrophobic modification of NCC surface makes them more compatible with non-polar solvents and polymer matrices.

Although many studies have been reported in the literature on the anionic and steric stabilization of NCC, very little research has been done on the cationic stabilization of NCC. To the best of our knowledge, the study reported by Hasani et al. (2008) is the first and only study on cationic modification of NCC (Hasani et al., 2008). However, it was reported in their study that surface cationization led to a decrease in surface charge density of the NCC. The poorly charged cationically modified NCC, which was prepared under the following conditions: more than 90% water content, 7%, w/v NaOH concentration, cationization agent to NCC molar ratio of 3 at a temperature of 65 °C for 4 h, showed lower electrostatic repulsion and formation of an isotropic gel at a relatively lower solid content (3.5 wt%).

In the literature there was a semi-dry method that was developed for the cationization of starch, which showed much improved results over the traditional wet method (Bendoraitiene, Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2006; Khalil, Beliakova, & Aly, 2001; Liu, Fatehi, Sadeghi, & Ni, 2011; Liu, Ni, Fatehi, & Saeed, 2011). In the present work, the authors studied the cationic surface modification of NCC using glycidyltrimethylammonium chloride (GTMAC) as a cationization agent, based on the semi-dry method. Effects of reaction parameters, such as water content, reaction media, and reactant mole ratio on the performance of the quaternization process have been systematically studied in order to obtain the optimum reaction condition.

2. Experimental

2.1. Materials

The H_2SO_4 hydrolyzed NCC was obtained from FPInnovations, Canada. Wood fiber was used as the NCC source. GTMAC was used as a cationization agent and obtained from Sigma–Aldrich, Canada. Potassium poly vinyl sulfate (PVSK) with a MW of 100,000–200,000, 97.7% esterified, was provided by Wako Pure Chem. Ltd. Japan. Polydiallyldimethylammonium chloride (PDADMAC) with a MW of 100,000–200,000 was purchased from Sigma–Aldrich Co. and applied without further purification. Cellulose dialysis membrane (MW cut-off 12,400) was obtained from Sigma–Aldrich. Ethanol, sodium hydroxide, and dimethyl sulfoxide were all analytical grade chemicals from Fisher Scientific Co., Canada and Alfa Aesar, USA.

2.2. Cationic surface modification of NCC

In previous studies, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHMAC) and GTMAC were widely used as cationization agents (Fatehi, Ates, Ward, Ni, & Xiao, 2009; Fatehi, Tutus, & Xiao, 2009; Fatehi & Xiao, 2008; Ren, Sun, Liu, Chao, & Luo, 2006) for functionalization of xylan, polyvinyl alcohol (PVA), etc. However, the cationization efficiency of CHMAC is found to be lower compared to GTMAC under similar conditions (Liu, Fatehi, et al., 2011). In this study, GTMAC was selected as the cationization agent due to its commercial availability and high cationization efficiency.

The modification of NCC has been carried out using two different methods: (1) wet process and (2) semi-dry process. In the wet process, the cationization reagent was added to an aqueous suspension of alkali activated NCC (Hasani et al., 2008). On the other hand, in the semi-dry process, the cationization agent has been added to a solid mixture of NCC and sodium hydroxide, which was partially wet (Khalil et al., 2001). Two different solvent systems: (1) water, and (2) mixture of water and dimethyl sulfoxide (DMSO), were used in the semi-dry process.

2.2.1. Cationic modification of NCC using wet process

In this process, 800 mg of water dispersible dried NCC was introduced into a polyethylene bag with the addition of 1 N $NaOH_{(aq)}$ solution and water, followed by intense hand kneading and ultrasonication to disperse the chemicals and disintegrate the solid NCC. GTMAC was added dropwise to this mixture and hand kneading was continued to obtain a homogeneous reaction system. Subsequently, the reaction mixture was kept in a thermostated ultrasonic water bath at 65 °C for temperature control. The reaction mixture was hand kneaded after every 15 min during the reaction. The molar ratio of GTMAC to anhydroglucose units in NCC was 3:1 and the catalyst (NaOH) dosage was 5% (by weight of NCC). After 4 h, the reaction was stopped by precipitating the reaction mixture in 95% ethanol. The unreacted reagents and by-products were removed by centrifugation. After centrifugation, the sediment was kept and the supernatant was removed and replaced by fresh 95% ethanol and recentrifuged. This procedure was continued twice. After that, the product was redispersed in deionized and distilled water and diluted 4 times. The suspension was then dialyzed (cellulose dialysis membrane, molecular weight cut-off 12,400 from Sigma–Aldrich) against deionized and distilled water for 3 days to remove the last residue of any unreacted reagents and by-products. The distilled and deionized water was replaced every 2 h in the first day and twice a day in the following 2 days. The product was concentrated by evaporation at a reduced pressure and temperature in a rotary evaporator.

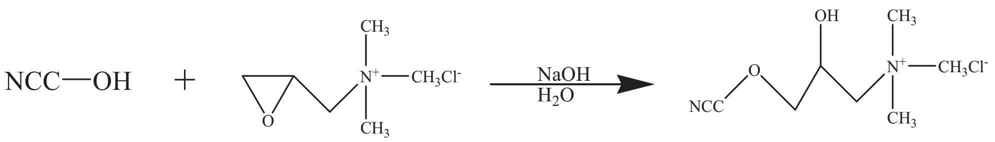
2.2.2. Cationic modification of NCC using semi-dry process

In this process, 1000 mg of water dispersible dried NCC and 50 mg of powdered sodium hydroxide were mixed thoroughly using a mortar and pestle for 5 min at room temperature and left to cool to room temperature. The solid mixture was then transferred to a polyethylene bag followed by addition of the solvent (water or water/DMSO mixture at various volume ratios). The cationization agent (GTMAC) was added dropwise to the previous mixture and mixed uniformly by hand kneading. Subsequently, the reaction mixture was kept in a thermostated ultrasonic water bath at 65 °C for 4 h while maintaining all other conditions as in the wet process. After 4 h, the product was precipitated in 95% ethanol, purified, and concentrated as for the wet process.

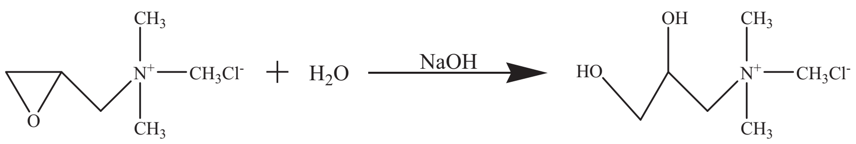
2.3. Characterization

2.3.1. Charge density measurements

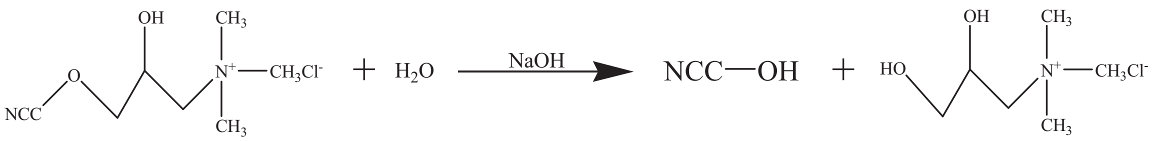
Charge densities of both un-modified and cationically modified NCC were measured using a colloidal titration method. In the colloidal titration, un-modified NCC and the cationically modified NCC were titrated with standard cationic polyelectrolyte [poly (diallyldimethyl ammonium chloride) (poly-DADMAC)] (concentration = 0.714 mN) and standard anionic polyelectrolyte [polyvinyl sulfate (PVSK)] (concentration = 1.0214 mN), respectively, which are widely used as the cationic and anionic reactants in colloidal titration (Ueno & Kina, 1985). The end point was determined using



(a) Scheme 1. Desired reaction: Cationization of NCC



(b) Scheme 2. Side reaction: Hydrolysis of GTMAC



(c) Scheme 3. Side reaction: Degradation of cationic NCC

Fig. 1. Competitive reactions during the cationic modification of NCC using GTMAC/H_2O/NaOH System.

Mütek PCD 03 Particle Charge Detector (Herrsching, Germany). Three repeated tests were conducted to obtain an average value for each sample.

2.3.2. Zeta potential and particle size measurements

The hydrodynamic particle sizes and ζ potentials of the un-modified and cationically modified NCC (prepared at various reaction conditions) in aqueous solutions (salt free) were measured at 25 °C using Brookhaven Zeta-Plus Microelectrophoresis Apparatus (Holtsville, NY, USA) and the software of 90 plus/BI-MASS. The scattering angle and operating wavelength were 90° and 658 nm, respectively. The analysis was conducted automatically to yield the mean diffusion coefficient. Then, from the Stokes–Einstein equation, the apparent hydrodynamic sizes of the NCC were assessed. This method has been widely used for the determination of the size of the polymers in aqueous solution (Buchhammer, Mende, & Oelmann, 2003; De Luca & Richards, 2003; Yusa, Kamachi, & Morishima, 2000). The ζ potential was calculated by measuring the electrophoretic mobility using the same instrument. The mobility value was converted to ζ potential using the Smoluchwski's approximation and the reported value is an average of 10 measurements.

2.3.3. Degree of substitution analysis

The degree of substitution of quaternary ammonium groups was calculated considering the nitrogen content of cationically modified NCC and using the formula given in the Appendix section. The nitrogen content of the cationically modified NCC was determined using a 9000 Series Nitrogen/Sulfur Analyzers, ANTEK Corp (USA). The analyzer was first calibrated using standard samples prepared from known concentrations of GTMAC in water. The sample was vaporized and combusted at a temperature in excess of 1000 °C.

2.3.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis of the un-modified and cationically modified NCC were performed using a Thermo Scientific Nicolet 6700 spectrometer in transmission mode. All the spectra were collected and processed using Thermo Scientific Nicolet's OMNIC®8 software. For transmission mode, a sample of KBr powder (IR grade, Aldrich) was used as the background. The sample was diluted by grinding with a mortar and pestle to approximately 2% by weight in KBr. The spectra were obtained using 100 scans at a nominal resolution of $4\,\mathrm{cm}^{-1}$.

2.3.5. Transmission electron microscopy (TEM) analysis

Aqueous suspension (0.4 wt%) of both the un-modified and cationically modified NCC was prepared and stored in a refrigerator (5 °C) for several weeks. The suspension was further diluted to 0.004 wt% for the TEM analysis. 20 μL of the solution was pipetted onto a carbon coated 200 mesh copper grid. The solution was dried overnight, and then examined using a JEOL 2010 STEM, operated at an accelerating voltage of 200 keV.

3. Results and discussion

3.1. Cationic modification of NCC in aqueous based reaction media

The cationic modification of NCC consists of a nucleophilic reaction between the alkali activated hydroxyl group of NCC and epoxy group of GTMAC (Fig. 1a). However, it has been reported in the literature that the main etherification reaction is also accompanied by the alkaline hydrolysis (Khalil et al., 2001; Liu, Ni, et al., 2011; Ren et al., 2006; Rena, Peng, Sun, & Kennedy, 2009), that is, during cationization, GTMAC is consumed in a competition between the two reactions: cationization of NCC (Fig. 1a), which is desirable, and the GTMAC hydrolysis reaction (Fig. 1b), which is undesirable (Ren et al., 2006; Rena et al., 2009). At a higher water content of the reaction system, more hydrolysis of GTMAC would occur (Fig. 1b). Thus, less GTMAC will be available for the cationization reaction. Moreover, it is also possible that, at a high water content, the hydrolysis of cationically modified NCC will occur (Fig. 1c), resulting in a further decrease in the cationization efficiency of the system (Khalil et al., 2001). Therefore, the water content of the reaction system may be critical for the cationization process.

Fig. 2 shows the effect of water content of the reaction system on the charge density of cationically modified NCC. The water content

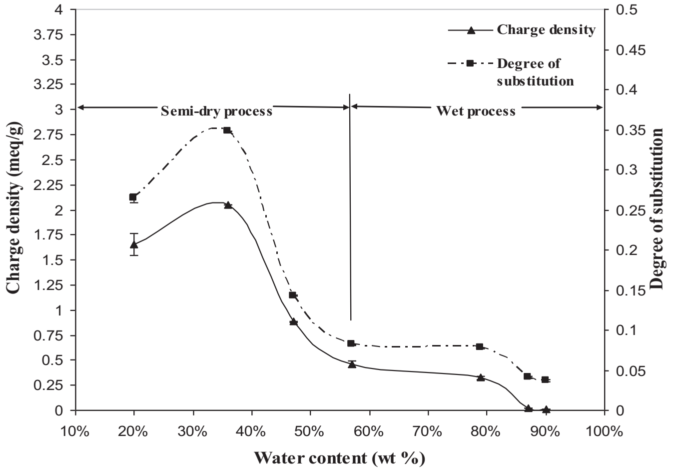


Fig. 2. Charge density and degree of substation of cationically modified NCC at various water contents of the cationization reaction system in the wet and semi-dry process.

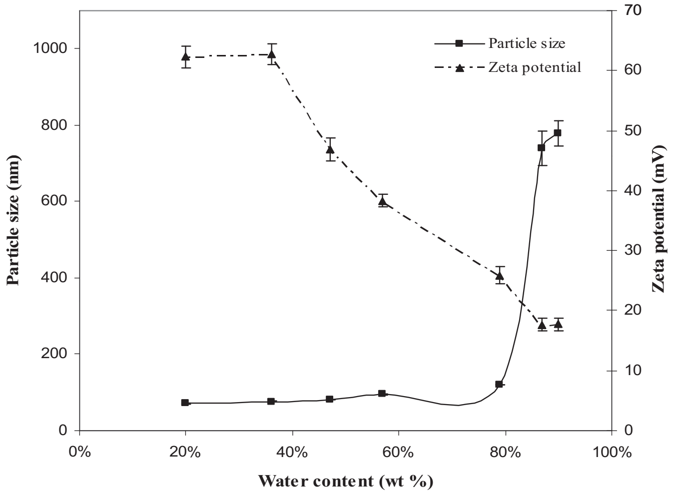


Fig. 3. ζ-Potential and hydrodynamic particle size of cationically modified NCC prepared at various water content of the cationization reaction system.

was varied between 20% and 90%, while the other reaction parameters were unchanged: molar ratio of GTMAC to anhydroglucose units in NCC of 3:1, the catalyst (NaOH) dosage of 5% (by weight of NCC), temperature of 65 °C, and reaction time of 4 h. From Fig. 2, it can be seen that the water content of the reaction system plays a critical role on the charge density of the cationically modified NCC for both the wet and semi-dry process. As shown in Fig. 2, at 87% water content, the charge density of the cationically modified NCC is +0.02 meq/g, which is 17 times lower than that of the un-modified NCC (−0.314 meq/g). However, in the wet process there was a significant increase in the charge density when the water content was reduced from 90% to 79%. The effect of reducing water content was also prominent in semi-dry process. The maximum charge density (+2.05 meq/g) was observed at 36% water content in the semi-dry process. This is due to the fact that in the semi-dry process, less water is available in the vicinity of GTMAC that would significantly reduce the hydrolysis reaction. Thus, more GTMAC would be available for the cationization reaction and the cationically modified NCC would have a higher charge density. Fig. 2 also shows that further decreasing the water content below 36% resulted in a small decrease in the charge density of cationically modified NCC. This can be attributed to the insufficient mixing of reagents under the conditions studied.

The degree of substitution of cationically modified NCC as a function of the water content for both the wet and semi-dry processes is also shown in Fig. 2. It can be seen that the degree of substitution of NCC follows the same trend for both the wet and semi-dry processes. Therefore, it can be stated that the increase in the charge density of the cationically modified NCC was due to increase in number of cationic substituents on the NCC surface.

The ζ-potential measurements confirmed the charge reversal of NCC after the cationic modification, i.e., from −57 ± 1.2 mV for the un-modified NCC to +63 ± 1.65 mV after the cationic modification at 36% water content of the reaction system. Fig. 3 shows the ζ-potential of the cationically modified NCC prepared at various water contents of the reactions system. It can be seen that the ζ-potential of cationically modified NCC increased with decreasing water content of the reaction system, which shows agreement with the results obtained from the charge density analysis. This is due to the fact that at lower water content less hydrolysis of GTMAC would occur, resulting in more substitution of hydroxyl group by the cationic group. The higher ζ-potential of cationically modified NCC indicates the increased colloidal stability in aqueous suspension.

Fig. 3 also shows the average hydrodynamic particle size of the cationically modified NCC as a function of water content of the cationization reaction system. Depending on the amount of surface charge, NCC may be in the form of nanofiber bundle or individual nanofiber in aqueous suspension. The size of the bundles depends on the degree of electrostatic repulsion or steric hindrance between the NCC particles. The higher the surface charge, the higher the electrostatic repulsion and the lower the bundle size. From Fig. 3, it can be seen that the particle size of cationically modified NCC prepared at 90% water content of the reaction system was 778 nm, which is significantly higher compared to that of the un-modified NCC (87 nm). This is due to the fact that cationically modified NCC prepared at a high water content of the reaction system has a very low surface charge. Therefore, due to the weak electrostatic repulsion, cationically modified NCC agglomerated and formed larger bundles. However, when the water content of the cationization reaction was reduced, the particle size decreased significantly due to stronger electrostatic repulsion between the highly charged cationically modified NCC.

3.2. Cationic modification of NCC in aqueous–organic based reaction media

Several studies have been reported in the literature on the use of aqueous–organic solvent mixture as a solvent for etherification reaction (Ayoub & Bliard, 2003; Ayouba, Berzin, Tighzert, & Bliard, 2004; Han & Sosulski, 1998; Heinze, Haack, & Rensing, 2004; Kweon, Sosulski, & Bhirud, 1997). In these studies, water has been partially replaced by an organic solvent, which has a strong miscibility with water. The presence of organic solvent reduces the availability of water molecule in the vicinity of cationization agent, thus reducing the hydrolysis reaction and increasing the cationization efficiency. Heinze et al. (2004) prepared various cationic derivatives of starch homogeneously with water–dimethyl sulfoxide (DMSO) and heterogeneously with water–ethanol system (Heinze et al., 2004). However, cationization efficiency of water–ethanol system was found to be worse compared to the water–DMSO system.

In this study, the cationization of NCC in water–DMSO system using semi-dry process was evaluated. The cationization was carried out at various water–DMSO volume ratios for a fixed amount of total solvent. Fig. 4 shows the effect of water to DMSO volume ratio on the charge density and degree of substitution of cationically modified NCC. As shown in Fig. 4, the charge density

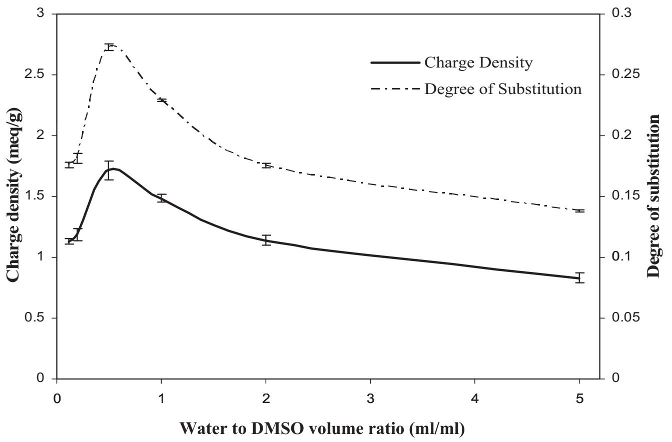


Fig. 4. Charge density and degree of substitution of cationically modified NCC as a function of aqueous–organic solvent volume ratio.

of the cationically modified NCC increased with increasing the amount of organic solvent in the reaction system up to an optimum point. This is mainly due to the fact that organic solvent favors the cationization reaction by decreasing the hydrolysis reaction. The degree of substitution also followed the same trend, which confirmed that the increase in the charge density was due to the substituted cationic groups. Fig. 4 also shows that decreasing the water to DMSO volume ratio below 0.5 resulted in a decrease in the charge density and the degree of substitution of cationically modified NCC. It was also observed that at a high organic content, the absorption of solvent/reagent system by the NCC/NaOH solid mixture was poor. This is due to the fact that certain amount of water is required in facilitating the diffusion and dispersion of GTMAC as well as enhancing the absorption of NCC/NaOH solid mixture during the cationization process (Wang et al., 2009). Moreover, it has been reported in the literature, that NaOH precipitates from the reaction mixture, if the system has a shortage of water (Bendoraitiene et al., 2006). Therefore, for solubilization of NaOH and alkaline activation of the hydroxyl group of NCC, certain critical amount of water is required. Below this critical water content, the cationization efficiency drops. Fig. 5 shows the ζ potential and particle size of cationically modified NCC prepared using the aqueous–organic solvent based semi-dry process. The ζ potential of cationically modified NCC increased with the decrease in the water to DMSO volume ratio up to 0.5, and then decreased. This is mainly due to the increase cationic substituent on NCC surface for the solvent volume ratio of up to 0.5, and then decreased as the surface charge decreased with increasing the organic solvent content. The particle size also showed similar trend while increasing the organic solvent content, and the results are in agreement with those of charge density and substitution degree.

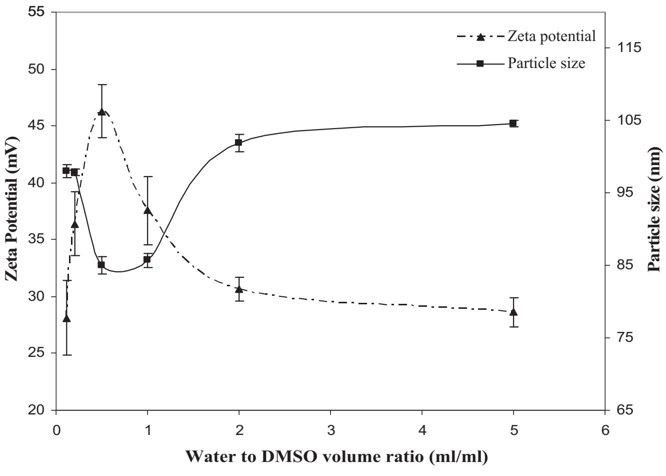


Fig. 5. ζ-Potential and hydrodynamic particle size of cationically modified NCC as a function of aqueous–organic solvent volume ratio.

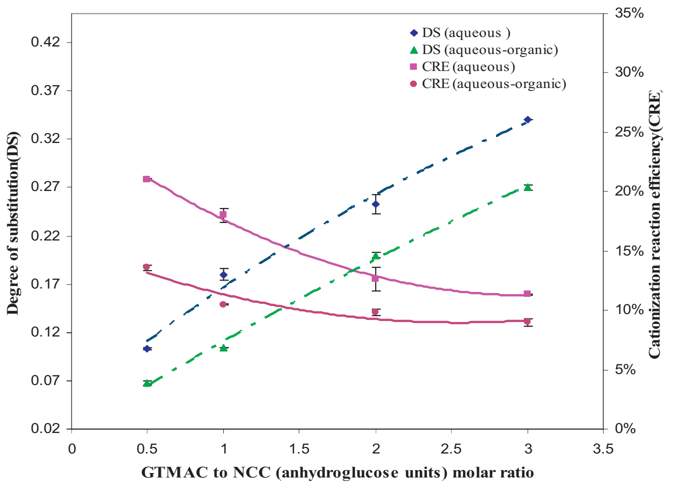


Fig. 6. Effect of GTMAC to AGU molar ratio on the degree of substitution and cationization reaction efficiency in aqueous based and aqueous–organic solvent based semi-dry process.

3.3. *Effect of GTMAC to NCC molar ratio on the cationization reaction efficiency and degree of substitution*

Using the semi-dry process, cationic modification of NCC was carried out at various GTMAC to anhydroglucose unit (AGU) molar ratios (0.5–3) for both the aqueous and aqueous–organic solvent based reaction media, while other conditions were kept at their optimum: 36 wt% water content (aqueous based media), 0.5 water to DMSO volume ratio (aqueous–organic solvent reaction media), 5 wt% NaOH, temperature of 65 °C, and 4 h of reaction time. From Fig. 6, it can be seen that the degree of substitution increased while the cationization reaction efficiency decreased with increasing the GTMAC to AGU molar ratio. This can be explained as follows (Khalil et al., 2001): at a lower molar ratio, the limited availability of GTMAC in the vicinity of the glucose molecule provides poor substitution of hydroxyl groups by the GTMAC, thus giving a low degree of substitution. However, at lower molar ratio there is an excess of hydroxyl groups per GTMAC molecule which favors the etherification reaction over hydrolysis reaction and increases the cationization reaction efficiency. At higher molar ratio greater availability of GTMAC increases the degree of substitution. However, at a higher GTMAC content, more GTMAC was consumed in the hydrolysis reactions, resulting in decreased cationization efficiency.

It can be also noticed from Fig. 6 that at the equal GTMAC to NCC molar ratio, both the degree of substitution and cationization reaction efficiency are higher for aqueous based semi-dry process compared to the aqueous–organic solvent based semi-dry process. This can be due to the poor absorption of reagent by NCC/NaOH solid mixture in the aqueous–organic solvent based system. The above results support the conclusion that the absorption effect is a critical parameter for the performance of the cationic modification in the semi-dry process.

Table 1
Gelling behavior of un-modified and cationically modified NCC.

Water content of the cationization reaction system	Charge density (meq/g)	Onset of gelation (wt% NCC)
Un-modified NCC	−0.314	8.5
>90% (Hasani et al., 2008)	+0.12	3.5
90%	+0.02	2.99
47%	+0.89	8.90
36%	+2.05	12

3.4. *Effect of charge density on the characteristic gelation of cationically modified NCC*

Hasani et al. (2008) reported that cationically modified NCC showed a tendency to form thixotropic gel in concentrated aqueous suspensions of cationically modified NCC. A lower electrostatic repulsion was mainly responsible for the observed gelation (Hasani et al., 2008). In this research, the gelation behavior of cationically modified NCC as a function of its surface charge density was evaluated. It was observed that highly charged cationically modified NCC showed significantly different gelling behavior compared to the poorly charged cationically modified NCC. The gelling characteristics of both the un-modified and cationically modified NCC at various surface charge densities are illustrated in Table 1.

From Table 1, it can be seen that the cationically modified NCC that was prepared at 90% water content of the reaction system, having a charge density of 0.02 meq/g, gelled at 2.99 wt%, while the cationically modified NCC having a charge density of 0.89 meq/g and 2.05 meq/g showed the onset of gelation at 8.90 wt% and 12 wt%, respectively. The delayed gelation can be attributed to the strong electrostatic repulsion of the highly charged NCC that resists gelation upon concentration of the cationically modified NCC.

3.5. *State of dispersion of cationically modified NCC*

Transmission electron micrograph of the un-modified NCC and cationically modified NCC is presented in Fig. 7. In the case of the un-modified NCC, instead of individual nanocrystals, they remained as a bundle of several nanocrystals (Fig. 7a and b). This can be due to the relatively lower surface charge density (−0.314 meq/g) of the un-modified NCC. Moreover, some localized aggregation was also observed for the un-modified NCC (Fig. 7c).

The cationically modified NCC prepared by the wet process (79% water content) also showed poor state of dispersion due to the lower cationic surface charge density (+0.325 meq/g). However, the cationically modified NCC prepared in the semi-dry process (36% water content) showed much better state of dispersion (Fig. 7e and f). The rod-like appearance of individual nanocrystals was evident. The increased charge density (+2.05 meq/g) of cationically modified NCC from the semi-dry process resulted in stronger electrostatic repulsion of the positively charged cationic groups located at the surface of the nanocrystals, thus improving the dispersion of the NCC.

3.6. *FTIR analysis*

Fig. 8 shows the FTIR spectra of the un-modified and cationically modified NCC. A strong band due to hydroxyl (—OH) stretching appeared at 3413 cm^{-1} (Jahan, Saeed, He, & Ni, 2011; Peng et al., 2009; Sun, Sun, Liu, Fowler, & Tomkinson, 2002). The absorbance at 2902 cm^{-1} was due to symmetric C—H vibrations (Jahan et al., 2011; Sun et al., 2002). An intense band at 1644 cm^{-1} originated from

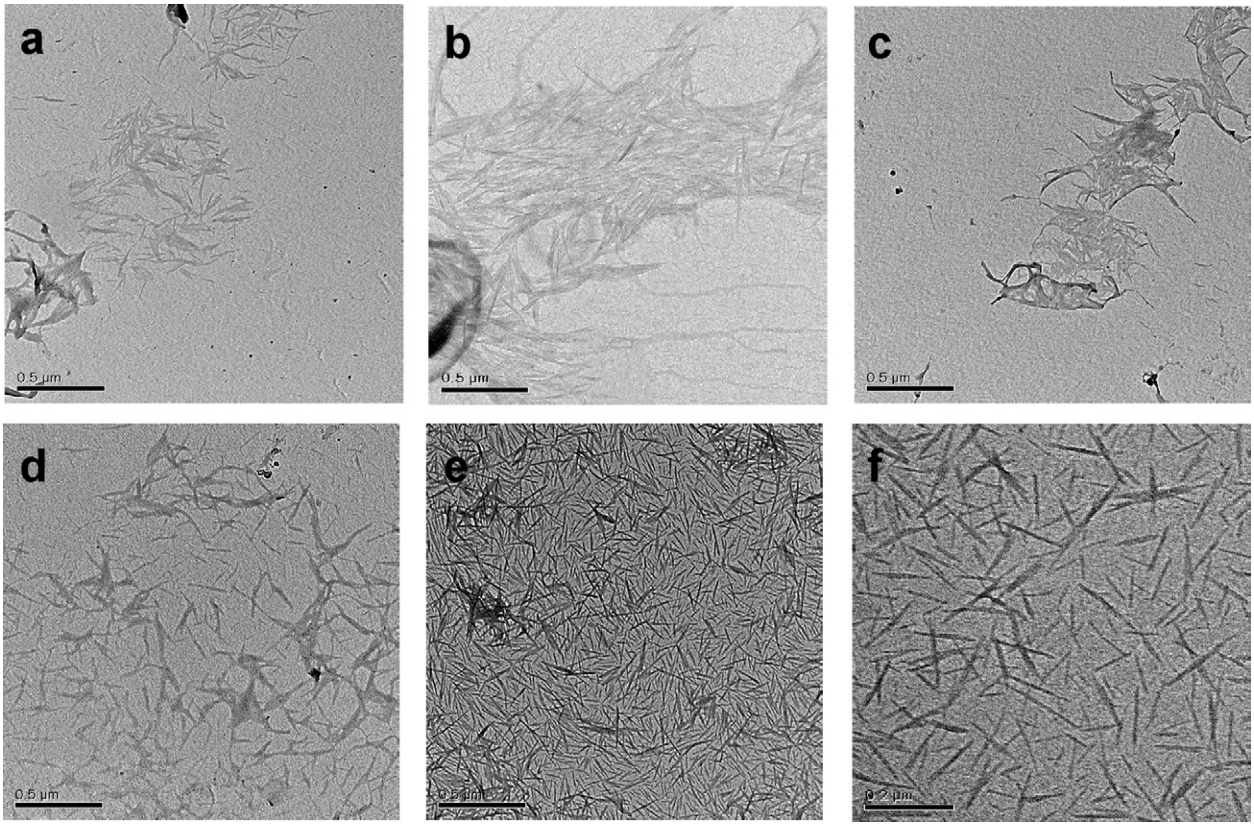


Fig. 7. TEM image of cationically modified and un-modified NCC obtained from H_2SO_4 hydrolysis of wood cellulose: (a–c) un-modified NCC, (d) cationically modified NCC prepared from the wet process, and (e and f) cationically modified NCC prepared from the semi-dry process.

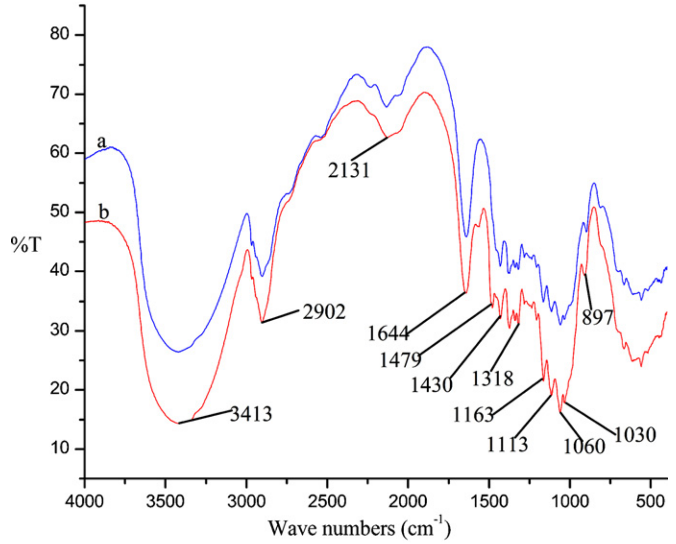


Fig. 8. FTIR spectra of un-modified NCC (Spectrum a) and cationically modified NCC (Spectrum b).

the absorbed moisture of the un-modified NCC (Ren et al., 2006). The absorbance at 897 cm^{-1} can be assigned to the C—H deformation mode of the glycosidic linkage between the glucose units (Kacurakova, Ebringerova, Hirsch, & Hromadkova, 1994; Liu, Fatehi, et al., 2011). The absorbance between 1030 cm^{-1} and 1163 cm^{-1} is attributed to the C—O stretching in major ether bands in NCC (Liu, Fatehi, et al., 2011).

Compared to Spectrum a, Spectrum b of the cationically modified NCC (prepared under the conditions of GTMAC to NCC molar ratio of 3, NaOH 5% by weight of NCC, water content of 36 wt%, temperature of 65 °C, time of 4 h) gives clear evidence of quaternization in NCC. An increase in intensity of the major ether bands in the region between 1030 cm^{-1} and 1163 cm^{-1} provides evidence of grafting of GTMAC onto the NCC surface (Ren et al., 2006). In addition, a prominent band at 1479 cm^{-1} was observed, which can be attributed to CH_2 bending mode and methyl groups of the cationic substituent (Kacurakova et al., 1994; Ren et al., 2006).

4. Conclusions

Nanocrystalline cellulose was successfully rendered cationic by grafting GTMAC onto the NCC surface. It was found that the water content of the reaction system plays a critical role on the efficiency of the cationization process. In the semi-dry process, the water content of the reaction system was significantly reduced, resulting in improved cationization efficiency. Introducing organic solvent, dimethyl sulfoxide (DMSO) in the reaction system also improved the cationization performance. However, the aqueous–organic solvent semi-dry process was not as effective as the aqueous semi-dry process. This can be due to the fact that in the semi-dry process, absorption of solvent/reagent system by the NCC/NaOH solid mixture was a dominant factor for the cationization reactions. The ζ potential measurements confirmed the increase in the colloidal stability of cationically modified NCC due to an increase in the surface charge. The stronger electrostatic repulsion of the highly charged cationically modified NCC led to the delayed onset of gelation. The TEM results showed the good dispersion of cationically modified NCC and rod-like geometry of NCC.

Acknowledgments

The authors wish to thank NSERC for funding this research, and FPInnovations for providing the NCC sample.

Appendix A. Appendix

1. *Estimation of Degree of Substitution (DS)*

The Nitrogen content of cationically modified NCC was estimated by elemental analysis (9000 Series Nitrogen/Sulfur Analyzers, ANTEK Corp, USA). Degree of substitution was calculated according to the nitrogen content (%N) using the following equation:

$$\mathrm{DS} = \frac{162 \times N\%}{1400 - 151.5 \times N\%}$$

Where, $N\%$ is the amount of nitrogen in cationic NCC in weight percentage, 162 is the molecular weight of anhydroglucose unit, and 151.5 is the molecular weight of glycidyltrimethylammonium chloride (GTMAC).

2. *Estimation of Cationization Reaction Efficiency (CRE)*

The cationization reaction efficiency refers to the percentage of added cationic reagent that has potentially reacted with the NCC, i.e. the amount of cationizing agent that has been grafted with the glucose molecules. Cationization reaction efficiency was calculated from the following equation:

$$\%\mathrm{CRE} = \frac{\text{Degree of substitution (DS)}}{\text{GTMAC to AGU molar ratio}} \times 100$$

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