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NON-COVALENT SURFACE MODIFICATION OF CELLULOSE NANOCRYSTALS BY POLYETHYLENEIMINE

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ABSTRACT

Cellulose nanocrystals (CNCs) are bio-derived, naturally occurring nanomaterials that disperse well in water according to their surface chemistry upon extraction. However, to be suspended in non-polar, hydrophobic media such as most polymers [1], the CNCs are chemically modified by reactions that are environmentally unfriendly and not cost-effective for the industry. The present work reports the preliminary findings of the non-covalent surface modification of CNCs using polyethyleneimine (PEI), a common additive used in the paper industry [2], through a low-cost process and without any use of organic solvents. The successful modification was confirmed through different techniques, including Fourier transform infrared (FTIR) spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Dynamic Light Scattering (DLS) and Zeta Potential (potential) measurements. The CNC agglomerates formed in aqueous suspensions as a result of the modification showed improved dispersion in toluene and were found to precipitate in deionized water. The turbidity measurements of the water suspensions of pristine and modified CNCs (mCNCs) were performed using UV-Visible (UV-Vis) transmission spectroscopy.

KEYWORDS

Cellulose Nanocrystals (CNCs), Polyethyleneimine (PEI), non-covalent surface modification, Dynamic-Light Scattering, Zeta Potential analysis

INTRODUCTION

Cellulose nanocrystals (CNCs) are renewable and abundantly derived nanomaterials that have received great attention in recent years due to their high mechanical strength, degradability, optical properties, low density and low cost [3, 4]. These unique characteristics illustrate the potential of CNCs to be used in various industries and applications, such as automobile and packaging industries [5].

The surface of commercial CNCs is hydrophilic and negatively charged due to the presence of hydroxyl and sulfate half-ester groups, respectively [6]. While the presence of negative surface charges allows increased polarity and better dispersion in aqueous media [7-10], it also restricts the CNCs in non-polar media [11, 12]. Therefore, surface modification is necessary to improve the compatibility between the CNCs and the non-polar suspending media [13].

The chemical modification of CNCs to introduce hydrophobic functionalities through covalent linkages is the most common approach utilized for surface modification of CNCs. The different methods that have been reported include silylation [15, 16], acetylation [17], esterification [18], etherification [19]. However, these methods involve the use of organic solvents, are tedious, and can increase production expenses. More recently, a gas phase, solvent-free approach known as photo-initiated chemical vapor deposition (PICVD) has been developed and shows promise for large-scale covalent modification [20].

The surface of CNCs can also be modified using a non-covalent approach of electrostatic attraction between the negatively charged (OSO₃⁻) groups and a cationic surface [21-25]. The CNC dispersion in organic solvents (toluene and cyclohexane) through the use of a phosphoric ester as surfactant has also been reported [26]. The CNCs were found to have enhanced dispersion in a low polarity solvent (tetrahydrofuran (THF)) after cationic surface modification with hexa-decyl-trimethylammonium bromide (HDTMA) [21].

Polyethyleneimine (PEI) is a cationic polymer, composed of amine groups and having a three-dimensional spherical stereo structure [27]. This polymer exists in both linear and branched molecular structures, the linear form having only

primary and secondary amine groups while the branched form has all three (primary, secondary, and tertiary amine groups) [28]. The protonation of PEI in water confers upon it a positive charge [29]. A study based on intrinsic viscosity and small-angle neutron scattering measurements of branched PEI in water showed that its conformation is quasi-unchanged over a pH range of 2 to 11 in the presence of salts [30]. The amine functionality of PEI has been grafted onto TEMPO-modified cellulose nanofibers; however, this method of modification may be undesirable as it can result in loss of crystal morphology and affect the structure of CNC particles [31]. Branched PEI has a higher density of amine groups that makes it an interesting polyelectrolyte that can interact with the negatively charged CNCs even at low concentrations.

In the present paper, we discuss preliminary findings on the non-covalent surface modification of CNCs by PEI through physical adsorption. The PEI modified CNCs (mCNCs) were studied for their particle size and net surface charge as functions of the amount of PEI. To understand the effect of surface modification of CNCs, the stability of the dispersion of CNCs and mCNCs in water was studied using DLS-Vis transmission spectroscopy along with a qualitative study of the miscibility of mCNC in organic solvents.

MATERIALS

Spray dried cellulose nanocrystals (CNCs), obtained through sulphuric acid hydrolysis of wood pulp, were supplied by CelluForce (Canada). Branched PEI (99% purity, 25,000 g mol⁻¹ polydispersity 2.5, density 1.03 g mL⁻¹ at 25 °C) was purchased from Sigma Aldrich Canada and used as received. Solutions of HCl 0.1 N and NaOH 12 N solutions were prepared using Milli-Q water. All other chemicals (ethanol, isopropanol, toluene and cyclohexane) used in this work were of analytical grade (purchased from Fisher Scientific) and used as received. Mineral oil PURETOL 7S (density 0.846 kg L⁻¹, kinematic viscosity 12.2 cSt) was supplied by Petro-Canada.

METHODS

Preparation of CNC-PEI Suspensions

The spray dried CNCs were added to deionized (DI) water and dispersed using an ultrasonic homogenizer (Cole-Parmer model CP505 500 W) operating at a power of 100 W, with a total energy dose of 2000 J/g applied by progressively lowering the concentration of CNCs: 1) 500 mg of CNC concentration of 2% (w/w); 2) diluting the suspension to 1.5% (w/w) of CNC and applying 500 J/g and 3) decreasing the concentration to 1% (w/w) and applying an additional 1000 J/g. Ultrasonication was carried out in an ice bath to avoid heating the suspension.

A solution of PEI was prepared in DI water at a concentration of 0.001 g/mL. To ensure complete dissolution, the solution was heated to 50 °C with mechanical magnetic stirring for 30 min at 300 rpm. Then, the PEI solution was diluted to concentrations of 0.0001, and 0.0002 g/mL and added dropwise to the CNC suspensions under mechanical stirring at 50 °C at 500 rpm for 4 h. The final amount of PEI added to the CNC suspension was 0.01 g and 0.02 g of PEI per g of CNC. No pH adjustment was done, and the recipe of the various systems is reported in Table 2.

FTIR Analysis

Fourier Transform Infrared spectroscopy (FTIR) was performed on CNCs before and after surface modification. The suspensions were frozen at -20 °C for 48 h and then dried (FreeZone 2.5 plus, Labconco, Kansas City, MO) for 72 h under vacuum (internal chamber temperature -87 °C) to dried pristine and mCNCs in the form of flakes. The samples were analyzed in attenuated total reflectance mode (ATR, Zn/Sr crystal) on a Perkin Elmer Spectrum 65 FTIR spectrometer. The spectra were recorded in the range of 6500–400 cm⁻¹ at 4000 scans at a resolution of 4 cm⁻¹.

XPS Analysis

X-Ray Photoelectron Spectroscopy (XPS) was used for the characterization of the mCNC surface. XPS survey spectra and C1s, O1s and N1s high-resolution spectra of pristine CNCs and mCNCs were obtained using a VG ESCALAB 3 MKII XPS. During the analysis, the chamber pressure was kept at 5 × 10⁻¹⁰ Torr. The take-off angle was fixed at 90° with respect to the sample surface. All spectra were obtained with a source at 300 W and the analyzed depth was less than 10 nm. In high-resolution, energy pass and energy step size were 20 eV and 0.05 eV, respectively. The Shirley method [33] was used to correct the background contribution.

Dynamic Light Scattering and Zeta Potential Analysis

Dynamic Light Scattering (DLS) and Zeta Potential (zeta potential) measurements were carried out on a Malvern Zetasizer Nano-S (ZS) and Malvern Zetasizer Nano-ZSP instruments, respectively, at 25 °C after diluting the suspensions to 0.05% (w/w) CNC. DLS analysis was done at 173° detection angle. The DLS Z-average polydispersity index (PDI) of the pristine and modified-CNC particles were calculated using calibration with polystyrene spherical particles. Measurements were repeated three times for each suspension to obtain average values.

For ζ -potential measurements, the electrophoretic mobility of particles was analyzed using the Smoluchowski equation, in the same diluted suspensions (0.05% (w/w) of CNCs) 3 and 7. The pH adjustment was done using 0.1 M HCl and 12 M NaOH solutions. Values reported are average of 15 measurements for each suspension.

UV-Visible Transmission Spectroscopy

UV-Visible spectroscopic analysis was performed as a function of time using a portable spectrometer (Ocean optics DH-2000). Transmittance measurements at a wavelength of 657 nm were recorded every 1 min for a total duration of 60 min, with integration and interval times of 10 ms and 1 min, respectively. The transmission measurements were repeated three times for each sample. The concentration of CNC or mCNC suspensions was kept at 1 wt % and all measurements were performed at room temperature. Ultrasound was applied at an amplitude of 20% for 15 s before starting the measurement. Analyses were conducted on 1 mL samples of each type at neutral pH, in a plastic disposable cuvette with 1 cm light path length.

Dispersion in Organic Solvents

The dispersion of freeze-dried pristine CNCs and mCNCs was analyzed in organic solvents of different relative polarity indices (RPI, [34]): water (RPI = 1), ethanol (RPI = 0.654), isopropanol (RPI = 0.546), toluene (RPI = 0.099) and cyclohexane (RPI = 0.006). In addition, the mCNC particles were dispersed in mineral oil at two temperatures, 22 and 70 °C using magnetic stirring for 1 h at 200 rpm.

RESULTS AND DISCUSSION

Preparation of mCNCs

The addition of PEI onto CNCs resulted in the formation of aggregates and a consequent phase separation of the CNCs from the water dispersion. Despite the modification carried out in a low CNC concentration of 1% (w/w), the addition of PEI always led to formation of aggregates and a consequent decrease in the suspension stability of CNCs in water.

The modification of CNCs by PEI for this paper was done using the CNC suspensions prepared by applying ultrasonication energy of 2000 J/g of CNC. Given the preparation of CNC after addition of PEI, the analysis of mCNCs was carried out in triplicates and the measurements were averaged to allow as better representation of the suspension as would be possible. The mCNC suspensions were freeze-dried and used for analysis to carry out UV-Visible spectroscopy, FTIR and XPS analysis.

FTIR Analysis

The freeze-dried suspensions of pristine CNCs and mCNCs were analyzed by infrared spectroscopy (Fig. 1). The characteristic peaks of pristine -CNC at 1109 and 1162 cm^{-1} , between 1300 and 1440 cm^{-1} and between 3100 and 3600 cm^{-1} , attributed to O-H association, C-O-C stretching vibration, C-O stretching vibration, O-H bending vibration and O-H stretching vibration, respectively [19], were also observed in mCNCs indicating that the surface modification by PEI does not affect the chemical nature of CNCs. The presence of PEI in mCNCs was observed via two peaks at 2985 cm^{-1} and 1480 cm^{-1} (indicated by arrows in Fig. 1), which can be attributed to the amine groups. These were not observed in pristine CNCs. These peaks were also observed in chemically grafted PEI on cellulose nanofibers [31].

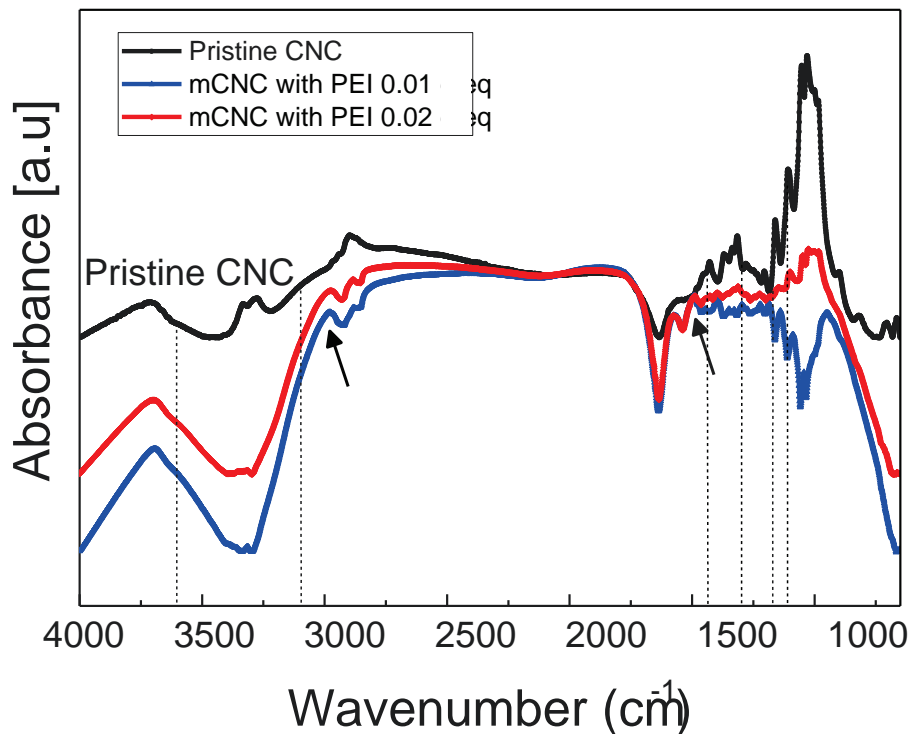


Fig. 1 FTIR spectra of pristine CNCs and mCNCs with different PEI (0.01 and 0.02 g per g CNC).

Dynamic Light Scattering (DLS) and Zeta Potential Analysis

DLS measurements are presented in Table 1 as the observed Z_w and PDI that are specific to the DLS technique. Since DLS is a technique meant for spherical particles, the reported Z_w are only being used for a comparison between pristine CNC and mCNC.

As is evidenced from Table 1, the particle size of CNCs is in presence of PEI indicating some adsorption of the polymer onto the CNC particles in the suspension. Also, the increase in the PDI of the mCNC suspension points to the non-uniformity in particle size for the mCNC suspension. This is coherent with the aggregate formation observed upon addition of PEI to the CNC suspension.

Table. 1 Z_w and PDI from DLS measurements carried out on the pristine CNC and mCNC suspensions made using PEI 0.01 g eq and 0.02 g eq per g of CNC. No pH adjustment was done for either sample (natural pH is reported in Table 2)

| Sample | Z_w (nm) | PDI |
|--------------------------------|-------------|------|
| Pristine CNC | 121 ± 1 | 0.29 |
| mCNC (PEI 0.01 g eq per g CNC) | 189 ± 5 | 0.38 |
| mCNC (PEI 0.02 g eq per g CNC) | 319 ± 6 | 0.51 |

The size of the aggregates was not uniform and getting reproducibility in the DLS measurements was an issue. The lack of reproducibility in the DLS measurements arises from the fact that the mCNC suspension is highly heterogeneous with regard to the aggregate and particle size. The addition of PEI resulted in phase separation of CNC in the form of aggregates regardless of the sonication energy level. The dilution of a heterogeneous sample such as the mCNC suspension is difficult as the volume of the suspension used for the dilution may not always be the best representation of the entire population of particle/aggregates in the mCNC suspension.

The ζ -potential values are an indication of the surface charge of the particles in the suspension. As would be expected, the pristine CNC sample gave a negative ζ -potential at pH 3 and 7, indicative of the presence of COO^- groups on the surface of CNC (Table 2). The ζ -potential value increased from -54 ± 5 mV at pH 7 to -33 ± 0.1 mV at pH 3. The reason for this observed increase is unclear and a more thorough analysis on CNCs is the focus of on-going work in our group. For now, we shall only confine ourselves to a comparative change in ζ -potential between the CNC and mCNC.

Table. 2 The ζ -potential values in mV for pristine CNC and mCNC made using PEI 0.01 g eq and 0.02 g eq per g of CNC at pH 3, 7, and pH adjustment are given below

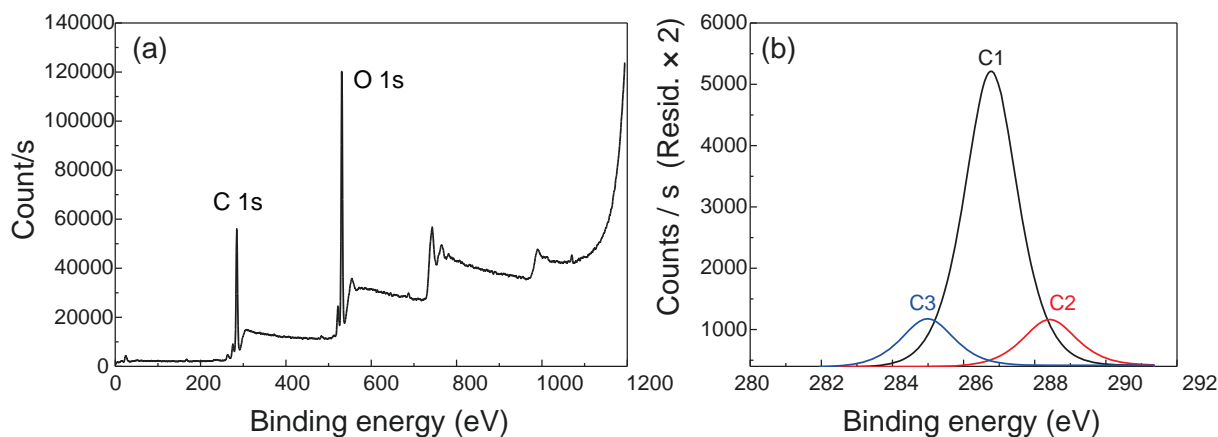
| Sample | - potential without pH adjustment | - potential at pH=3 | - potential at pH=7 |
|--------------------------------|-----------------------------------|---------------------|---------------------|
| Pristine CNC | -52 ± 2 mV (pH= 6.7) | -33 ± 0.1 mV | -54 ± 5 mV |
| mCNC (PEI 0.01 g eq per g CNC) | -23 ± 1 mV (pH= 7.1) | -2 ± 2 mV | -24 ± 0.2 mV |
| mCNC (PEI 0.02 g eq per g CNC) | -20 ± 3 mV (pH= 7.3) | 18 ± 1 mV | -20 ± 4 mV |

The surface charge of CNC also becomes less negative in the presence of PEI, indicating charge neutralization of CNC negative charge by the positively charged protonated amine groups of PEI. More is the PEI, greater is the decrease in negative surface charge and for mCNC made using 0.02 g eq of CNC, it is found to even become positive at pH 3 of the suspension.

To summarize the DLS and ζ -potential measurements done so far, the particle size is found to increase and the surface negative charge is found to decrease for the mCNC as a function of PEI used for the modification. However, a critical analytical view of the data makes it apparent that mCNC samples are difficult to analyze under the current method of preparation and result in large degree of heterogeneity in particles/aggregates, thus preventing reproducibility in the measured values. A detailed analysis of the mCNC suspensions is currently being pursued to improve the method of modification and gain better control over suspension stability as well as an understanding of this system.

XPS Analysis

The XPS spectra and atomic surface composition of pristine and mCNC are presented in Fig. 2 and Table 3.



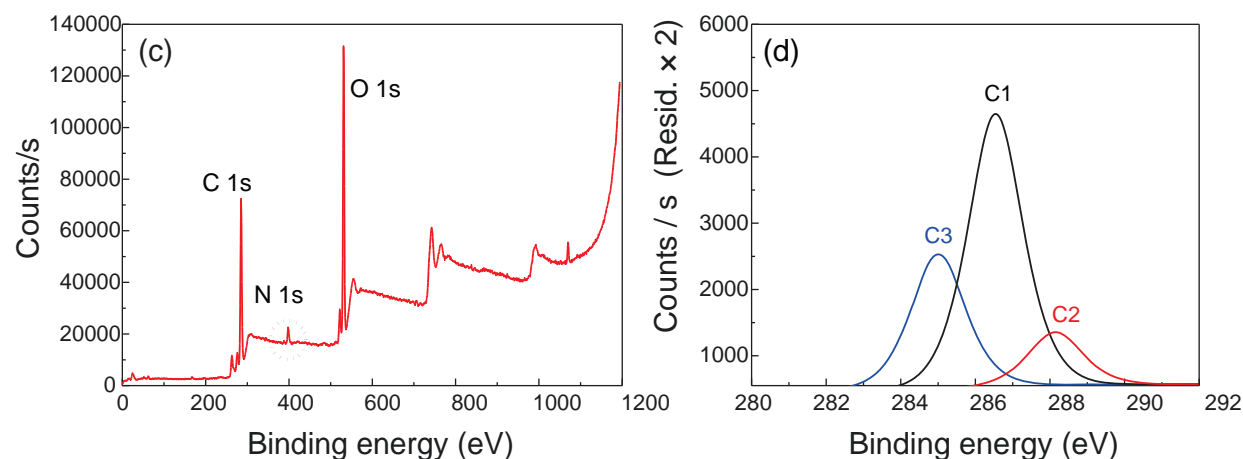


Fig. 2 XPS survey spectra and deconvolution of C1s signal into its constituent contributions for (a,d) pristine CNC and (c,d) mCNC with PEI/CNC 2 wt %.

No nitrogen signal was detected for the pristine CNC within the investigated range in the survey scan (Fig. 2a). After surface modification with PEI, a nitrogen peak was observed at 400 eV (Fig. 2c), indicative of PEI presence on the CNC surface. The high-resolution C1s peaks for pristine mCNC were resolved into three Gaussian component peaks to gain further information about the structure of bonded carbon before and after surface modification (Fig. 2b and 2d): C-C or C-H at 285.0 eV (C3), C-O at 286.6 eV (C1) and O-C-O at 288.1 eV (C2) [35, 36]. The ratio peak areas representing C-O (C1) and O-C-O (C2) bonds of cellulose chains, remained approximately constant before (1.04) and after (0.97) surface modification. This indicates that the modification did not change the nature of underlying cellulose. However, a substantial increase in the percentage of C-H (C3) was observed and can be resulting from the contribution of the C-C and C-H bonds in PEI. The relative atomic percent mass of both, C and N, is higher for mCNC than pristine CNC while the O/C ratio decreases for the mCNC (Table 3). The contribution of the carbon peak from the PEI chains and the masking of the cellulose oxygen by the presence of PEI on the surface of CNC can explain this observation.

Table. 3 XPS analysis of CNC before and after surface modification with PEI

| Name | Binding Energy (eV) | Identification | Relative atomic % | | |
|------|---------------------|-------------------------|-------------------|----------------------|----------------------|
| | | | Pristine CNC | mCNC | |
| | | | | PEI/CNC 0.01 g eq | PEI/CNC 0.02 g eq |
| C1s | 285.0 | C-C or C-H (C3) | 6.4 | 17.3 | 17.2 |
| | 286.6 | C-O in cellulose (C1) | 40.2 | 35.0 | 36.7 |
| | 288.1 | O-C-O in cellulose (C2) | 6.3 | 6.8 | 7.2 |
| | TOTAL | | 53.0 | 59.1 | 61.1 |
| N1s | 399.2 | Amine | - | 2.4 | 2.1 |
| | 400.1 | Amide | - | 1.1 | 0.9 |
| | 401.7 | Protonated N | - | 0.3 | 0.3 |
| | TOTAL | | 0 | 3.8 | 3.4 |

| | | | | | |
|-----|-------|-------------------|------|------|------|
| O1s | 531.4 | O=C-N | - | 3.5 | 2.1 |
| | 532.6 | C-OH in cellulose | 28.2 | 20.2 | 20.6 |
| | 533.2 | C-O-C | 18.8 | 13.5 | 13.1 |
| | TOTAL | | 47.0 | 37.2 | 35.8 |

UV-Visible transmission Spectroscopic Analysis

Fig. 3 presents UV-Vis transmittance spectra. The pristine CNC suspension was stable over at least 60 min based on UV-Vis recordings, while the mCNC precipitated from water, which is indicated by an increase in the transmission signal. This is in accordance with the previously mentioned observations of CNC aggregation upon addition of PEI and the increase in potential values that would indicate decreased electrostatic repulsion between the mCNC particles and hence, reduced suspension stability.

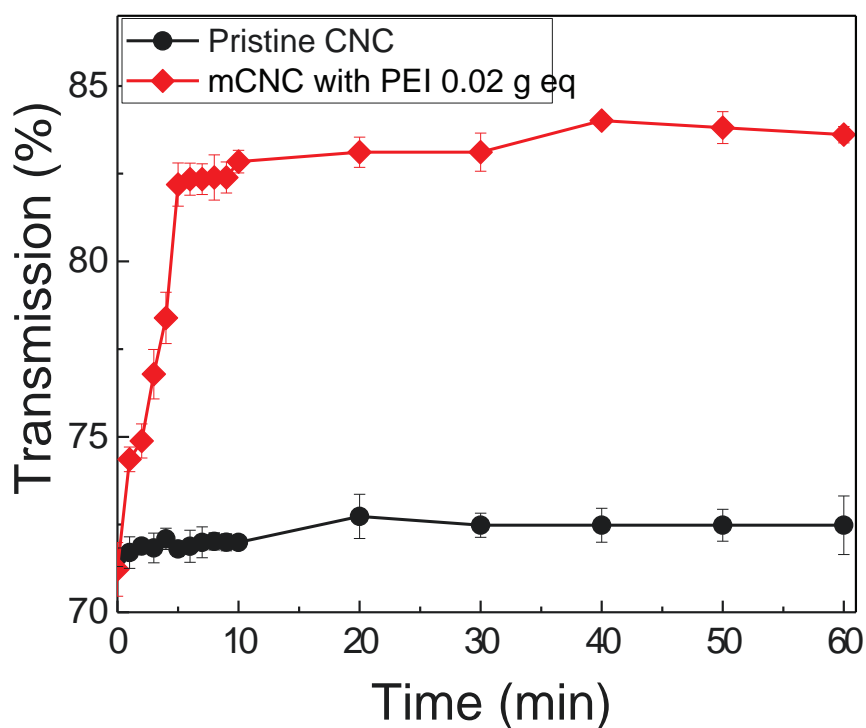


Fig. 3 UV-Vis transmittance spectra at 657 nm for pristine CNC and mCNC (0.02 g eq of PEI per g of CNC) dispersed in deionized water.

Dispersion of mCNC in Solvents

The degree of dispersion in various solvents was assessed visually (Fig 4).

Fig. 4 Dispersion state of (a) pristine CNC (b) mCNC (0.02 g eq per g of CNC) (1) deionized water (2) ethanol (3) isopropanol (4) toluene (5) cyclohexane

The pristine CNC showed good dispersion in deionized water, however, mCNC precipitated. An ultrasonication of 5000 J/g CNC was applied to aid the dispersion of mCNC in water, however, no improvement in degree of dispersion was observed. The pristine CNC can be seen to have reduced dispersion in ethanol and isopropanol but comparatively better than mCNC. A notable observation was the improved dispersion of mCNC in intermediate polarity solvents opposed to the pristine CNC that showed almost no dispersion. While dispersion in toluene cannot be qualified as good, agglomerates were still noticeable. The reduction of surface charge on CNC due to adsorption of PEI can explain the improvement with respect to pristine CNC. Non-polar cyclohexane had low affinity for both CNC and pristine CNC. The mCNC particles were also dispersed in mineral oil at 22 and 70°C to see the stability of CNC when subjected to a strongly hydrophobic environment. The particles were collected after the dispersion in mineral oil and could not be re-dispersed in water, indicating that PEI maintains its affinity for CNC over treatment with mineral oil, irrespective of the temperature of the oil.

The density of water and toluene are quite similar but as seen in Fig 3 and 4, the mCNC immediately separates out of water while it has an improved affinity for toluene. The CNCs have been shown to behave as amphiphilic particles with varying degree of suspension stability in different solvents based on their polarity, hydrophobicity, viscosity, and density [37]. Since, the dispersion of particles in a solvent is governed by various parameters such as the particle size, surface charge, polarity of the particle, and particle interactions, further work needs to be carried out in preventing agglomerate formation during modification and having a better uniformity in particle size in the case of mCNC, while we have demonstrated promising results in this preliminary study, additional work is required to control particle size and dispersion stability of mCNC. We do not understand differences in dispersion in various solvents. Also, the phase separation and heterogeneity of the CNC prevented a systematic rheological characterization of the system. The challenges are being addressed as part of ongoing research.

CONCLUSION

The surface modification of CNC by a simple phenomenon of physical adsorption of PEI has been presented. The change in apparent size of the CNC and its surface potential indicate the degradation of CNC as a function of the amount of PEI. The addition of PEI to the CNC suspension results in almost an instantaneous formation of aggregates and a resulting phase separation of the CNC particles. This preliminary study is promising in the fact that surface modification of CNC does not always require a chemical modification of the particles and can be carried out in an industrially friendly way. However, it would be important to address certain challenges encountered in this study such as, the lack of control over the suspension stability after introducing the PEI-CNC suspension, the limitation of heterogeneity in preventing reliable characterization of rheological properties and DLS and zeta potential analysis, and the dispersion behavior of mCNC in different solvents, to gain better understanding of this system and its possible applications in various fields.

REFERENCES

- [1] Ljungberg N, Cavailh  JY, Heux N. Nanocomposites of isotactic polypropylene reinforced with cellulose whiskers. *Polymer* 47:6285-6292 (2006)

- [2] Bilitewski B., Darbra R. M., Barcelo D., Chapra G., Global Risk-Based Management of Chemical Additives I: Production, Usage and Environmental Occurrence, Springer Heidelberg Dordrecht London New York (2012).
- [3] Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J, Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem Soc Rev* 40:3941 (2011).
- [4] Klemm D, Kramer F, Moritz S, Lindstrom T, Ankerfors M., Gray D., Dorris A., Nanocelluloses: A New Family of Nature-Based Materials, *Angew Chemie Int Ed* 50:5438...5466 (2011).
- [5] Tang J, Sisler J, Grishkewich N, Tam KC Functionalization of cellulose nanocrystals for advanced applications. *J Colloid Interface Sci* 494:397...409 (2017).
- [6] Dong XM, Kimura T, Revol J-F, Gray D, Effects of Ionic Strength on the Isotropic Chiral Nematic Phase Transition of Suspensions of Cellulose Crystallites. *Langmuir* 12:2076...2082 (1996).
- [7] Simonsen J, Habibi Y Cellulose Nanocrystals in Polymer. *Cellulose* 273...292 (2008).
- [8] Rodriguez NLG, Thielemans W, Dufresne A, Sissabouwhiskers reinforced polyvinyl acetate nanocomposites, *Cellulose* 13:261...270 (2006).
- [9] Roohani M, Habibi Y, Belgacem NM, Abraham G, K.A. N., Dufresne A., Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites, *Eur Polym J* 44:2489...2498 (2008).
- [10] George J, Sabapathi SN, Siddaramaiah Water Soluble Polymer-Based Nanocomposites Containing Cellulose Nanocrystals, 75: 259...293 (2015).
- [11] Habibi Y, Lucia LA, Rojas OJ, Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications, *Chem Rev* 110:3479...3500 (2010).
- [12] Sojoudiasli H, Heuzey MC, Carreau PJ, Mechanical and rheological properties of cellulose nanocrystal (CNC)-polypropylene composites, *Polym Compos* 1...9 (2016).
- [13] Eichhorn SJ, Cellulose nanowhiskers: promising materials for advanced applications, *Soft Matter* 7:303 (2011).
- [14] Habibi Y, Key advances in the chemical modification of nanocelluloses. *Chem Soc Rev* 43:1519...1542 (2014).
- [15] Goussé C, Chanzy H, Excoffier G, Soubeyrand L, Fleury E, Stable suspensions of partially silylated cellulose whiskers dispersed in organic solvents. *Polymer* 43:2645...2651 (2002).
- [16] Kargarzadeh H, M. Sheltami R, Ahmad I, Abdullatif A, Dufresne A, Cellulose nanocrystal: A promising toughening agent for unsaturated polyester nanocomposite. *Polymer* 56:346...357 (2015).
- [17] Ashori A, Babaee M, Jonoobi M, Hamzeh Y, Solvent-free acetylation of cellulose nanofibers for improving compatibility and dispersion. *Carbohydr Polym* 102:369...375 (2014).
- [18] Lin N, Dufresne A, Nanocellulose in biomedicine: Current status and future prospect. *Eur Polym J* 59:302...325 (2014).
- [19] Akhlaghi SP, Zaman M, Mohammed N, Brinatti C, Berry R, Loh W, Tam K C, Synthesis of amine functionalized cellulose nanocrystals: optimization and characterization. *Carbohydr Res* 409:48...55 (2015).
- [20] Javanbakht T, Raphael W, Tavares JR, Physicochemical properties of cellulose nanocrystals treated by photo-initiated chemical vapour deposition (PICVD). *Can J Chem Eng* 94:1135...1139 (2016).
- [21] Kaboorani A and Reidl B, Surface modification of cellulose nanocrystals (CNC) by a cationic surfactant, *Industrial Crops and Products* 65:45...55 (2015).
- [22] Kedzior S.A., Marway H.S., Cranston E.D., Tailoring Cellulose Nanocrystal and Surfactant Behavior in Miniemulsion Polymerization, *Macromolecules* 50:2685 (2017).
- [23] Huang L., Ye Z., Berry R., Modification of Cellulose Nanocrystals with Quaternary Ammonium-Containing Hyperbranched Polyethylene Ionomers by Ionic Assembly, *ACS Sustainable Chem. Eng* 5:4950 (2017).
- [24] Li M-C, Mei C., Xu X., Lee S., Wu Q., Cationic surface modification of cellulose nanocrystals: Toward tailoring dispersion and interface in carboxymethyl cellulose films, *Polymer* 107, 200-210 (2016).
- [25] Hu Z., Ballinger S., Pelton R., Cranston E.D., Surfactant-enhanced cellulose nanocrystal Pickering emulsions, *Journal of Colloid and Interface Science* 439:139...148 (2015).
- [26] Heux L., Chauve G., Bonini D, Nonflocculating and chiral-nematic self-ordering of cellulose microcrystals suspensions in nonpolar solvents. *Langmuir* 16:8210...8212 (2000).
- [27] Liu B, Huang Y., Polyethyleneimine modified eggshell membrane as a novel biosorbent for adsorption and detoxification of Cr(VI) from water. *J Mater Chem* 21:17413 (2011).
- [28] Lungu CN, Diudea M V., Putz M V., Grudzinski L, Linear and branched PEIs (Polyethylenimines) and their property space. *Int J Mol Sci* 17:555 (2016).
- [29] Jun B-MM, Nguyen TPN, Ahn S-H, Kin I-C, Kwon Y-M, Application of polyethyleneimine draw solution in a combined forward osmosis/nanofiltration system. *J Appl Polym Sci* 132:1...9 (2015).
- [30] Kobayashi S, Hiroishi K, Tokunoh M, Saegusa T, Characteristic properties of linear and branched poly(ethylenimines), *Macromolecules* 20:1496...1500 (1987).
- [31] Zhao J, Li Q, Zhang X, Xiao M, Zhang W, Li G, Grafting of polyethyleneimine onto cellulose nanofibers for interfacial enhancement in their epoxy nanocomposites, *Carbohydr Polym* 157:1419...1425 (2017).

- [32] Holycross DR, Chai M, Comprehensive NMR Studies of the Structures and Properties of PEI Polymers, *Macromolecules* 46:6891...6897 (2013).
- [33] Shirley DA, High-Resolution X-Ray Photoemission Spectroscopy of the Valence Bands of Gold, *Phys Rev B* 5:4709...4714 (1972).
- [34] Reichardt C, *Solvents and Solvent Effects in Organic Chemistry*, Third Edit. Wiley-VCH Verlag GmbH & Co. KGaA (2003).
- [35] Cao X, Habibi Y, Lucia L, One-pot polymerization-in-situ grafting, and processing of waterborne polyurethane-cellulose nanocrystal nanocomposites, *J Mater Chem* 19:7137-7145 (2009).
- [36] Li M. C., Mei C., Xu X., Lee S, Wu Q., Cationic surface modification of cellulose nanocrystals: Toward tailoring dispersion and interface in carboxymethyl cellulose films, *Polymers* 107: 200-210 (2016).
- [37] Bruel C., Beuguel Q., Tavares J.R., Carreau P.J., Houzelle M., On the apparent structural hydrophobicity of cellulose nanocrystals, *J-FOR The Journal of Science and Technology for Forest Products and Processes* 7(4) ISSN 1927-632X (2018)