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# **Non-covalent polymer surface modification of cellulose nanocrystals using block copolymers**

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## **Abstract**

Cellulose nanocrystals (CNC) possess desirable mechanical and optical properties that make them a candidate in the development of next generation of polymer-based composites. However, CNC also have a critical issue associated with their use: their hydrophilicity and incompatibility with hydrophobic polymers. CNC surface properties must be modified for them to be successfully implemented by the industrial sector. Grafting (co)polymers chains on the CNC surface can provide compatibility to CNC with hydrophobic matrices and expand their potential range of applications. In this communication we report preliminary results of a simple method to functionalize CNC surface using block copolymers, where a cationic block anchors via complexation to the anionically charged CNC surface and the other block acts as a stabilizing block, providing dispersibility in various solvents. This is a much simpler and less expensive method than current routes based on covalent modification. The block copolymers poly(polyethylene glycol methacrylate)-*b*-poly(N-butyl-N'-vinyl imidazolium

bromide) (PPEGMA-*b*-PBUVIm) and poly(styrene)-*b*-PBUVIm (PS-*b*-PBUVIm) were first synthesized via nitroxide-mediated polymerization and then non-covalently adsorbed on the CNC surface. The functionalization was confirmed *via* FT-IR and TGA. The dispersion of polymer-modified CNC materials in organic solvents was evaluated *via* dynamic light scattering. Modified CNC yielded stable dispersions in organic solvents.

## **Introduction**

The acid hydrolysis of cellulose, usually with sulfuric acid and less commonly with hydrochloric acid, yields crystals of dimensions of ~100-200 nm by ~10 nm. Such crystals are known as crystalline nanocellulose or cellulose nanocrystals (CNC).<sup>[1-8]</sup> Due to their nanoscale dimension, CNC possess unique properties of interest to polymer and material scientists including high surface area, reinforcing ability, adhesion, and unique optical properties.<sup>[6-9]</sup> They can improve hardness, strength, thermal properties, and act as an effective gas barrier to reduce oxygen and water vapour transmission. CNC are also attractive as they are derived from renewable sources and are therefore recyclable and compostable.<sup>[1-10,13]</sup>

When sulfuric acid is used for the hydrolysis step, negatively charged sulfate half-esters are incorporated on the CNC surface, providing electrostatic stabilization in aqueous systems. Being highly polar and hydrophilic due to the hydroxyl functionalities in cellulose, CNC are also readily dispersible in polar solvents such as dimethyl sulfoxide (DMSO).<sup>[5,8,14]</sup> However, the hydrophilic, ionic nature of CNC presents a major challenge for the development of advanced materials due to their incompatibility with non-polar (hydrophobic) systems such as most polymeric matrices. In order to modify the surface properties of CNC, and make

them compatible with hydrophobic systems, CNC are commonly modified with different chemical functionalities or (co)polymer chains, which can potentially be done either covalently or non-covalently. In the non-covalent modification of CNC, usually the negatively charged sulfate half-esters are complexed with cationic moieties or cationic (co)polymers. In covalent modification, the OH groups on the CNC surface are modified using a variety of reactions to attach different functionalities or to graft polymer chains to the CNC surface.<sup>[6]</sup>

Efforts to improve the dispersion properties of CNC or their compatibility with non-polar systems (solvents or polymer matrices) by doing chemical modification have been reported in the literature. Hasani et al. reported the covalent functionalization of CNC with (2,3-epoxypropyl) trimethylammonium chloride (EPTMAC) yielding CNC with cationic hydroxypropyltrimethylammonium chloride substituents on the surface (HPTMAC-CNC) in order to obtain cationic surface-modified CNC under basic conditions.<sup>[13]</sup> The CNC exhibited  $\zeta$ -potential  $\approx +30$  mV for HPTMAC-CNC whereas for native CNC,  $\zeta$ -potential was  $\approx -39$  mV. It was reported that HPTMAC-CNC give aqueous suspensions that are electrostatically stabilized but show a tendency to gel above concentrations of 3.5% w/w. Zaman et al.<sup>[5]</sup> improved the methodology to functionalize CNC with HPTMAC through a semi-dry process or with the use of dimethyl sulfoxide (DMSO). It was confirmed that CNC-HPTMAC presented better colloidal stability due to higher concentration of cationic charges on the CNC surface, although this approach eventually led to the delayed onset of gelation.<sup>[5]</sup>

Eyley et al. reported the functionalization of CNC with imidazolium cations via click chemistry.<sup>[15]</sup> The  $\zeta$ -potential of the imidazolium-grafted CNCs was +47 mV. Cationic

pyridinium-modified CNC, reported by the same group, showed  $\zeta$ -potential in the range of +54 to +59 mV.<sup>[16]</sup> The preparation of cationically functionalized CNC with different functionalities suitable for different environments have also been reported.<sup>[8,17]</sup> Miao and Hamad reported the CNC surface modification with (2-dodecen-1-yl) succinic anhydride.<sup>[18]</sup> The modified-CNC was dispersible in different low polarity organic solvents such as 1-methyl-2-pyrrolidinone (NMP), 2-butanone, chloroform, toluene, and styrene. The authors reported hydrodynamic diameters of 42 nm in NMP and 38 nm in styrene, suggesting that DDSA-CNC can disperse well in both polar (NMP) and nonpolar (styrene) organic media without apparent aggregation.<sup>[18]</sup> CNC has also been non-covalently modified with surfactants such as cetyltrimethylammonium bromide (CTAB) as reported by Abitbol et al.<sup>[19]</sup> In this report, the sulfate half ester groups on the CNC surface were functionalized with cetyltrimethylammonium (CTA<sup>+</sup>) from CTAB, yielding CNC-CTAB. The cation CTA<sup>+</sup> provided stabilization to form stable suspensions in ethanol only and a reduced stability in water attributed to the neutralization of negative charges on CNC surface with CTA<sup>+</sup>. The degree of functionalization of CNC with CTAB was dependent on the concentration of CTAB fed into the reaction, but too high ionic strength of the CTAB surfactant can hinder its adsorption on the CNC surface.<sup>[19]</sup> Hu, et al. used CNC-CTAB and CNC-didodecyldimethylammonium bromide (CNC-DMAB) to prepare Pickering emulsions, where the characteristics of the emulsifier (and of the emulsion) are determined by surfactant type and concentration on the CNC surface.<sup>[20]</sup> Kaboorani and Riedl reported CNC modification with hexadecyltrimethylammonium (HDTMA) bromide<sup>[4]</sup> which provided visually improved dispersibility in low-polarity solvents such as tetrahydrofuran (THF).<sup>[4]</sup> Brinati et al. reported a comprehensive study on the interactions between cationic surfactants of alkyltrimethylammonium C<sub>n</sub>TAB (n = 12, 14, and 16) with negatively charged

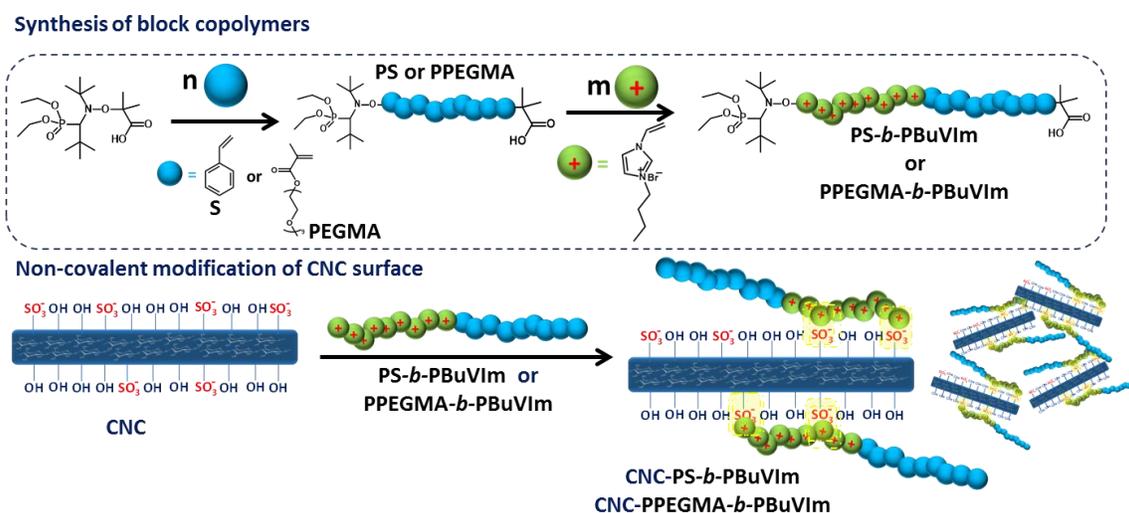
CNC.<sup>[21]</sup> They confirmed that interactions between the surfactants and the CNC surface are governed by the concentration of surfactant. At low surfactant concentration, a surfactant monolayer with the alkyl chains exposed to the water is formed whereas at high concentration, charge neutralization and association of the surfactant-decorated CNC aggregates led to flocculation.<sup>[21]</sup> Another example of interactions between surfactants and polymer (Jeffamine M600)-grafted CNC is the report from Peng and coworkers, where CNC-Jeffamine M600 interactions with anionic (SDS), cationic (DoTAB) and non-ionic (Brij 30) surfactants were investigated. DoTAB and M600-grafted CNC exhibited strong ionic interaction due to the neutralization of opposite charges.<sup>[22]</sup>

Grafting polymer chains to/from CNC surface via reversible-deactivation radical polymerization (RDRP), either atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain-transfer polymerization (RAFT) or more recently nitroxide-mediated polymerization (NMP) has recently been shown to provide new properties to CNC surfaces such as stimuli-responsiveness or compatibility with different systems.<sup>[6, 12, 23-26]</sup> However, these techniques typically require extensive and expensive modification processes to achieve the desired architectures which has prevented their adoption in commercial applications.

In this communication, we report preliminary results of a simple method to non-covalently modify CNC surface with block copolymers based on poly(polyethylene glycol methacrylate)-*b*-poly(butyl vinyl imidazolium bromide) (PPEGMA-*b*-PBuVIm) and poly(styrene)-*b*-PBuVIm (PS-*b*-PBuVIm). The cationic block (PBuVIm) interacts with the negative charges present on the CNC surface while either the PPEGMA or PS block acts as

a steric stabilizer (Scheme 1). The block copolymers were synthesized via nitroxide mediated polymerization (NMP). The functionalization of the CNC was confirmed via FT-IR and TGA. The dispersion and stabilization of polymer-modified CNC in several organic solvents was evaluated *via* dynamic light scattering (DLS), thereby providing a quantitative measure of stabilization effectiveness superior to visual observation.

These initial results of this research presented here focus on the development of an economically feasible, relatively simple, more efficient and environmentally-benign processes to modify CNC surface. The basic idea is to pre-synthesize different block copolymer chains. One block contains groups which can function as anchors groups, ionically attaching the polymer chains to CNC, and the second block provides compatibility with the polymer matrix in which the CNC are to be dispersed. Furthermore, the composition of the (co)polymer to be attached to CNC, its degree of polymerization (DP<sub>n</sub>) and any desired functionalities can be tailored to meet the specific demands of a given application.



**Scheme 1.** Synthesis of PPEGMA-*b*-PBuVIm and PS-*b*-PBuVIm and subsequent non-covalent functionalization of CNC.

## Experimental

The Materials and Instrumentation sections are detailed in the Supplementary Information.

### *Synthesis of N-butyl-N'-vinylimidazolium bromide (BuVIm)*

In a typical experiment, 20 g (0.2125 mol) of N-vinylimidazole were transferred to a 250 mL round bottom flask containing 1-bromobutane (58.23 g, 0.425 mol) and a magnetic stir bar. The flask was submerged in an oil bath at 40 °C and magnetically stirred for 20 h. After this, the reaction mixture was washed 3 times with ethyl acetate and finally a single wash with THF to yield a white solid which was then filtered and dried under vacuum.

### *Synthesis of PPEGMA-*b*-PBuVIm via NMP*

In a three neck round bottom flask, BlocBuilder® (2.01 mmol, 0.769 g), styrene (0.20 mmol, 0.020 g, 42.2 µL), and PEGMA (10 g, 0.020 mol) were dissolved in ethanol (15 mL) and the flask immersed in an oil bath. The mixture was deoxygenated with N<sub>2</sub> for 30 min prior to raising the temperature to 80 °C under magnetic stirring. The flask was kept under these conditions for 0.5 h. PPEGMA [poly(PEGMA)] was precipitated in diethyl ether, filtered, and washed three times with diethyl ether before drying under vacuum. PPEGMA was analyzed by GPC and <sup>1</sup>H-NMR. For the chain extension, 3.0 g of PPEGMA (macroinitiator) was dissolved in DMF (18 mL) in a three neck round bottom flask, BuVIm (6.93 g, 0.030 mol) was transferred to the flask which was then immersed in an oil bath. The mixture was deoxygenated with N<sub>2</sub> for 30 min prior to raising the temperature to 125 °C under magnetic stirring and kept under these conditions for 24 h. Finally, the reaction mixture was dialyzed

for 3 days in deionized water. The solution recovered from the dialysis tube was then roto-evaporated to recover the final block copolymer.

#### *Synthesis of PS-*b*-PBuVIm via NMP*

PS macroinitiator was synthesized following previous reports. In a three neck round bottom flask, BlocBuilder® (3.67 mmol, 1.40 g) was dissolved in styrene (0.37 mol, 38.3 g, 42.2 mL) and immersed in an oil bath. The mixture was deoxygenated with N<sub>2</sub> for 30 min prior to raising the temperature to 115 °C under magnetic stirring. The flask was kept under these conditions for 2 h. PS was precipitated in methanol, filtered, and given three washes with methanol before drying under vacuum. PS was analyzed by GPC and <sup>1</sup>H-NMR. For chain extension to obtain the block copolymer, 1.0 g of PS (macroinitiator) was dissolved in DMF (10 mL) in a three neck round bottom flask. BuVIm (4.62 g, 0.02 mol) was added and the flask was immersed in an oil bath. The mixture was deoxygenated with N<sub>2</sub> for 30 min prior to raising the temperature to 125 °C under magnetic stirring and kept under these conditions for 24 h. The block copolymer PS-*b*-PBuVIm was precipitated in acetonitrile, filtered, and washed with fresh acetonitrile at least three times, and dried under vacuum.

#### *Synthesis of PBuVIm*

In a typical experiment, BuVIm (3.0 g, 0.013 mol) and AIBN (10.65 mg, 0.06 mmol) were dissolved in 8 mL of DMF in a 100 mL three neck round bottom flask and immersed in an oil bath. The mixture was deoxygenated with N<sub>2</sub> for 30 min prior to raising the temperature to 125 °C under magnetic stirring and kept under these conditions for 19 h. Finally the

reaction mixture was dialyzed for 3 days in deionized water. Solution recovered from the dialysis tube was roto-evaporated to recover the final homopolymer.

#### *Functionalization of CNC with PPEGMA-*b*-PBuVIm*

In a 100 mL three-neck round bottom flask 0.10 g of CNC were dispersed in 20 mL of DI water (under sonication for 15 min in an ice bath). Separately 0.80 g of PPEGMA-*b*-PBuVIm was dissolved in 35 mL of DI water, transferred to an addition funnel and fixed to the three-neck round bottom flask. The polymer solution was added drop-wise to the CNC dispersion (with sonication only during the addition step) under agitation. The mixture was magnetically stirred for 48 h at room temperature. To recover the CNC-PPEGMA-*b*-PBuVIm, the mixture was centrifuged and then washed four times by solvent exchange with methanol in order to remove the remaining free copolymer. Finally, a paste of CNC-PPEGMA-*b*-PBuVIm in methanol (~50% wt) was recovered. For the dispersion studies, 0.030 g of the paste was dispersed in 3.0 g of the chosen solvent.

#### *Functionalization of CNC with PS-*b*-PBuVIm*

In a 100 mL three-neck round bottom flask, 0.10 g of CNC were dispersed in 20 mL of DMSO (under sonication for 15 min in an ice bath). Separately 0.80 g of PS-*b*-PBuVIm was dissolved in 35 mL of DMSO, transferred to an addition funnel and fixed to the three-neck round bottom flask. Then the polymer solution was added drop-wise to the CNC dispersion (sonication only during the addition step) under agitation. The mixture was magnetically stirred for 48 h at room temperature. To recover the CNC-PS-*b*-PBuVIm the mixture was centrifuged and then washed four times by solvent exchange with DMSO-ethyl acetate and a final solvent exchange with ethyl acetate in order to remove the remaining free copolymer.

Finally, a paste of CNC-PS-*b*-PBuVIm in ethyl acetate (~50% wt) was recovered. For the dispersion studies, 0.030 g of the paste was dispersed in 3.0 g of the chosen solvent.

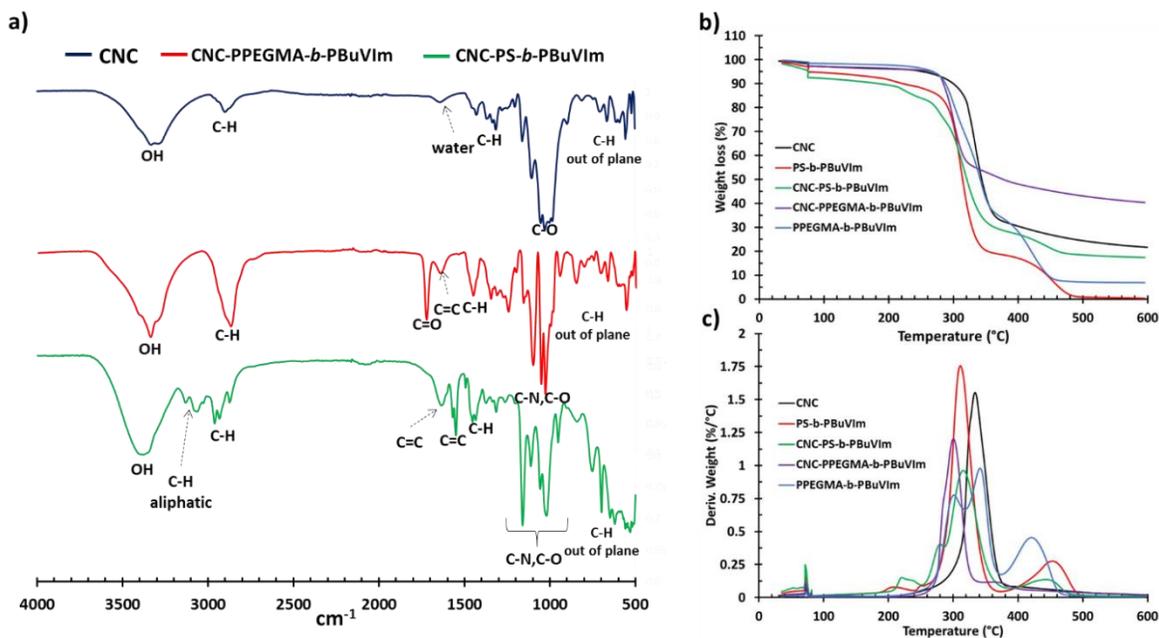
## Results and discussion

The non-covalent modification of CNC with two different block copolymers, PPEGMA-*b*-PBuVIm and PS-*b*-PBuVIm, was studied. The first copolymer is a double hydrophilic block copolymer (DHBC)<sup>[27,28]</sup> since both blocks are water-soluble. The PBuVIm (cationic) block interacts with CNC (anchoring block) ionically while the PPEGMA stabilizing block is chosen to act as a compatibilizer with the external environment (i.e. non-polar systems), thereby stabilizing the CNC dispersion. PPEGMA is miscible with a wide variety of low to high polarity solvents.<sup>[29,30]</sup> PS-*b*-PBuVIm is an amphiphilic block copolymer comprised of a hydrophobic PS block and a hydrophilic ionic PBuVIm block. Such block copolymers are well-known as stabilizers in colloidal systems where one block acts as a compatibilizer with the environment and the other block interacts with the particle or substrate.<sup>[31-33]</sup>

PPEGMA-*b*-PBuVIm and PS-*b*-PBuVIm were synthesized via NMP and their structure confirmed by <sup>1</sup>H-NMR. Figure S1 shows the <sup>1</sup>H-NMR spectra of both block copolymers. The molecular weight distributions of the PPEGMA and PS macroinitiators were obtained by GPC (as detailed in the experimental section). The final  $M_n$  of the block copolymers and molar composition were determined by <sup>1</sup>H-NMR. We were not able to obtain reliable GPC data for the block copolymers, due to the widely differing solubilities of the blocks in any GPC solvent. The PPEGMA and PS blocks were synthesized first and then used as macroinitiators for the polymerization with BuVIm to make the second block of each

respective block copolymer. The PPEGMA macroinitiator had  $M_n = 20,700$  g/mol (~40 units),  $\mathcal{D} = 1.47$ , (by GPC, based on PMMA standards), and  $M_n = 22,500$  g/mol determined by  $^1\text{H-NMR}$ . Styrene (10 mol%) was used as comonomer in the PEGMA polymerization to enhance the control over the polymerization.<sup>[34]</sup> After chain extension with BuVIm, the block copolymer PPEGMA-*b*-PBuVIm, was obtained. The  $M_n$  of the PBuVIm block was estimated by  $^1\text{H-NMR}$  to be  $M_n = 7800$  g/mol (~34 units). Using the  $M_n$  of the first and second blocks determined by  $^1\text{H-NMR}$ , the  $M_n$  of the block copolymer was 30300 g/mol, with a molar composition of 54% PPEGMA and 46% PBuVIm, yielding PPEGMA<sub>(40)</sub>-*b*-PBuVIm<sub>(34)</sub>.

The PS macroinitiator had a  $M_n = 2900$  g/mol ( $\mathcal{D} = 1.18$ ) as determined by GPC (based on PS standards). The  $M_n$  of the macroinitiator by  $^1\text{H-NMR}$  was 3100 g/mol (~28 units). After chain extension with BuVIm, the  $M_n$  of the PBuVIm block was estimated by  $^1\text{H-NMR}$  to be  $M_n = 900$  g/mol (~4 units). Using  $^1\text{H-NMR}$   $M_n$  values of each block, the overall block  $M_n$  was calculated as  $M_n = 37000$  g/mol with molar composition 89% PS and 11% PBuVIm (PS<sub>(28)</sub>-*b*-PBuVIm<sub>(4)</sub>).



**Figure 1.** a) FTIR analysis of CNC, CNC-PPEGMA-*b*-PBuVIm and CNC-PS-*b*-PBuVIm; b) weight loss versus temperature; (c) derivative weight loss versus temperature of CNC, CNC-PPEGMA-*b*-PBuVIm, CNC-PS-*b*-PBuVIm, PPEGMA-*b*-PBuVIm and PS-*b*-PBuVIm respectively.

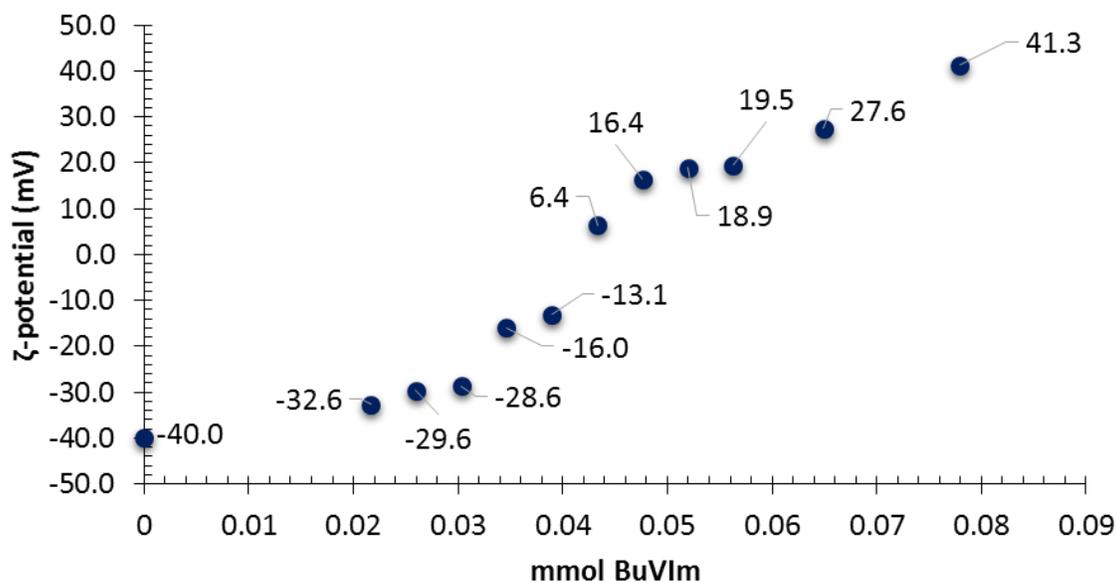
FTIR analysis verified the non-covalent modification of CNC with both block copolymers. Figure 1a shows the FTIR spectra of CNC, CNC-PPEGMA-*b*-PBuVIm and CNC-PS-*b*-PBuVIm. The FTIR spectra corresponding to CNC shows at  $1088\text{ cm}^{-1}$  the signal from the C-O-C ( $\nu$ , C-O-C) bonds, at  $1160$  and  $1150\text{ cm}^{-1}$  the stretching vibrations of the C-O bonds, at  $1414\text{ cm}^{-1}$  and  $1315\text{ cm}^{-1}$  the bending vibrations of  $-\text{CH}_2-$  and  $-\text{CH}-$ , at  $2875\text{ cm}^{-1}$  the stretching vibrations from C-H, and at  $3448\text{ cm}^{-1}$  a band from the stretching vibration of the O-H bonds. The FTIR spectra of both CNC-PPEGMA-*b*-PBuVIm and CNC-PS-*b*-PBuVIm show the characteristic signals of the PBuVIm block at  $1649\text{ cm}^{-1}$  of the C=C

stretching vibration of the imidazole ring. This could be mistaken with water adsorbed by CNC at  $1630\text{ cm}^{-1}$ , however it is more intense and shifted approximately  $20\text{ cm}^{-1}$ . The peak at  $1490\text{-}1500\text{ cm}^{-1}$  is attributed to C-H bending vibrations of the backbone chain (in coupling with the C-C and C=N ring stretching vibrations) as previously reported by Talu et al.<sup>[35]</sup> In the spectra of CNC-PPEGMA-*b*-PBuVIm, the presence of PPEGMA is confirmed by the stretching vibration of the carbonyl group from the methacrylic unit. The spectra of CNC-PS-*b*-PBuVIm also shows the signals of the PS block; the aromatic vibrations from the C-H are observed at  $3000\text{-}3100\text{ cm}^{-1}$  and the stretching vibrations of C=C bonds from the benzene ring at  $1543\text{ cm}^{-1}$ .

TGA also confirmed the functionalization of CNC with both block copolymers. Figures 1b and 2c show weight losses and the derivative weights ( $\%/^{\circ}\text{C}$ ) of CNC, CNC-PS-*b*-PBuVIm, CNC-PPEGMA-*b*-PBuVIm, PS-*b*-PBuVIm and PPEGMA-*b*-PBuVIm. The thermogram of native CNC shows the single-step onset degradation temperature around  $275\text{ }^{\circ}\text{C}$ . For PPEGMA-*b*-PBuVIm, two decomposition stages are observed, at  $250\text{-}380\text{ }^{\circ}\text{C}$  and at  $370\text{-}480\text{ }^{\circ}\text{C}$ . For PS-*b*-PBuVIm a first decomposition is observed at  $250\text{-}380\text{ }^{\circ}\text{C}$  and a second at  $390\text{-}490\text{ }^{\circ}\text{C}$ . Thermograms of both CNC-PS-*b*-PBuVIm and CNC-PPEGMA-*b*-PBuVIm show a first decomposition attributed to CNC and polymer chains and a second at higher temperature attributed to the final decomposition of the polymeric chains, which is similar to the decomposition exhibited by the corresponding block copolymers.

Prior to functionalizing the CNC surface with the block copolymer, a study to determine how the CNC  $\zeta$ -potential changes with varying amounts of added PBuVIm homopolymer was conducted. Batches of  $0.10\text{ g}$  of CNC were non-covalently functionalized with PBuVIm ( $M_n$

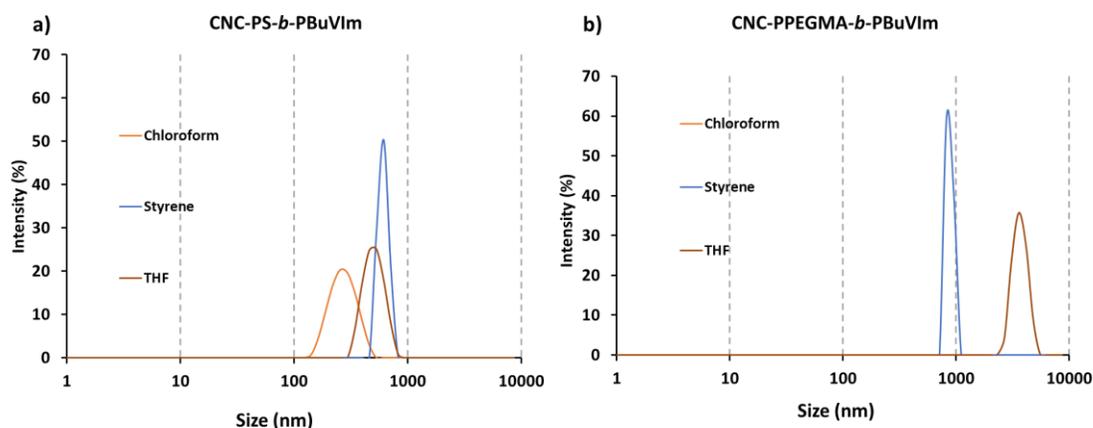
= 15,000 g/mol) using different amounts of added polymer; the  $\zeta$ -potential of each sample was measured, yielding a titration curve (see Figure 2 and Table 1), which confirmed that functionalizing the CNC with higher amount of PBuVIm increases the  $\zeta$ -potential, and it is also useful for estimating the amount of PBuVIm present on the modified CNC. For the functionalization of CNC with both PPEGMA-*b*-PBuVIm and PS-*b*-PBuVIm copolymers we targeted high  $\zeta$ -potential (>30 mV) of the modified CNC in order to ensure a high degree of functionalization. Knowing the amount of PBuVIm necessary to achieve high  $\zeta$ -potential (from the titration curve) and the molar composition of each block copolymer, we estimated the minimum necessary amount of block copolymer we needed to add to a CNC dispersion to achieve a desired  $\zeta$ -potential. We then titrated CNC dispersions with each of the two block copolymers to obtain CNC-PPEGMA-*b*-PBuVIm with  $\zeta$ -potential = 30 mV and CNC-PS-*b*-PBuVIm with  $\zeta$ -potential = 41 mV. Based on these measured  $\zeta$ -potentials, the composition of each block and the titration curve, we could then determine the following compositions for the complexed CNC; CNC-PPEGMA-*b*-PBuVIm- 63 wt% CNC, 37 wt% PPEGMA-*b*-PBuVIm; CNC-PS-*b*-PBuVIm- 71 wt% CNC and 29 wt% PS-*b*-PBuVIm.



**Figure 2.**  $\zeta$ -potential (mV) of CNC functionalized with different amounts (mmol of BuVIm) of PBuVIm (CNC-PBuVIm).

Our next step was to disperse CNC-PPEGMA-*b*-PBuVIm and CNC-PS-*b*-PBuVIm in different common organic solvents ranging from low to high polarity. CNC-PPEGMA-*b*-PBuVIm or CNC-PS-*b*-PBuVIm were dispersed at 0.10 wt% in different organic solvents and stirred overnight with no sonication. After this, the samples were analysed by DLS in order to determine the particle size distribution of the modified CNC in each solvent. Initially, the particle size of native CNC was analyzed in deionized (DI) water and DMSO, showing z-average particle size in DI-water of 70 nm and of 69 nm in DMSO. (NB: these measured values are not strictly correct, since the DLS instrument software assumes a spherical particle). Ideally, the same approximate particle size could be achieved in other more hydrophobic solvents, indicating the presence of individual nanocrystals in the dispersion but this is a very demanding criterion. It is often difficult to assess the degree of dispersion

achieved in other studies, as often the assessment is only visual, although one does cite DLS data.<sup>[18]</sup> In this work, we have chosen the criteria for a “good” dispersion when either CNC-PPEGMA-*b*-PBuVIm and CNC-PS-*b*-PBuVIm in the different organic solvents will have a z-average particle of <1000 nm.



**Figure 2.** Particle size distribution by intensity of CNC-PPEGMA-*b*-PBuVIm (a) and CNC-PS-*b*-PBuVIm (b) in three different solvents.

Figure 2 shows the particle size distribution by intensity of CNC-PPEGMA-*b*-PBuVIm and CNC-PS-*b*-PBuVIm in three different solvents. Table 2 shows the average particle size and PDI of each dispersion and the polarity index of each solvent. Photographs of the different dispersions are shown in Figure S2. The dispersions of CNC-PPEGMA-*b*-PBuVIm in the different organic solvents contained large aggregates (particle size >1000 nm). The picture of the dispersions of CNC-PPEGMA-*b*-PBuVIm (Fig. S2) showed clear aggregates (or precipitates).

**Table 2.** Solvent polarity, average particle size and PDI of CNC-PPEGMA-*b*-PBuVIm and CNC-PS-*b*-PBuVIm in different solvents.

Solvent	Polarity Index <sup>[36-39]</sup>	CNC-PPEGMA- <i>b</i> -PBuVIm		CNC-PS- <i>b</i> -PBuVIm	
		Average size (nm)	PDI	Average size (nm)	PDI
Chloroform	4.1	Out of range	--	266	0.302
THF	4.0	4471	0.473	493	0.006
Styrene <sup>a</sup>	2.4	4551	0.473	1165	0.66

<sup>a</sup>The value for styrene was not found in literature and it is assumed the same value that toluene since they have a similar structure.

The dispersions of CNC-PS-*b*-PBuVIm in organic solvents exhibited much smaller particle sizes than the CNC-PPEGMA-*b*-PBuVIm dispersions (Fig. 2 and Table 2). For CNC-PS-*b*-PBuVIm, average particle diameters <1000 nm were observed for chloroform and THF and some aggregates in bottom are observed in styrene (Figure S2). Further dispersion studies in more organic solvents are underway.

We expected to obtain a good dispersion of CNC-PS-*b*-PBuVIm in styrene (monomer) because of the PS stabilizing block, however, the DP<sub>n</sub> of the PS for this particular block copolymer may not be sufficiently high enough to provide effective stabilization in less polar solvents. Ongoing efforts are underway to refine the design of the two blocks to achieve more effective dispersion in more nonpolar environments.

The analysis of the dispersion of CNC-PPEGMA-*b*-PBuVIm and CNC-PS-*b*-PBuVIm is more comprehensive compared to other reports since the dispersion is analyzed not only qualitatively (visual dispersion) but quantitatively (particle size by DLS). With these

experiments, we observed that DLS can be an important tool to evaluate the dispersion since the particle size can be larger indicating aggregation, which may not be apparent based solely on visual inspection. Based on the results obtained, CNC-PS-*b*-PBuVIm seems to be promising compared to the CNC-PPEGMA-*b*-PBuVIm and is capable of being dispersed in polar and less polar solvents. The dispersion of CNC-PS-*b*-PBuVIm in the different organic solvents used in this work is comparable to, although not as good as, dispersion of DDSA-CNC<sup>[18]</sup>, which dispersed well in very polar and nonpolar solvents (with sizes similar to native CNC). The performance of CNC-PS-*b*-PBuVIm is also comparable with the CNC modified with HDTMA which dispersed well in THF, but only visual analysis was presented in that report.<sup>[5]</sup> Further important considerations are that the dispersions of CNC-PS-*b*-PBuVIm were stable after several months, and that no sonication was used for the dispersion in the corresponding solvents. Comparing the dispersions between both CNC-PPEGMA-*b*-PBuVIm and CNC-PS-*b*-PBuVIm, we can observe that there are important factors that can determine how effectively the modified CNC yields stable dispersions. The first is the nature of the stabilizing block (PPEGMA or PS). Initially, it was expected that PPEGMA would be effective as a stabilizing block (being a polymer soluble in both polar and non-polar solvents), however it did not function as expected, possibly because the PPEGMA block is not sufficiently hydrophobic. The PPEGMA block may also be too long, resulting in poor adsorption on the CNC surface or the DP<sub>n</sub> of the PBuVIm block (PPEGMA-*b*-PBuVIm) was also too long compared to the DP<sub>n</sub> of the PBuVIm (in the PS-*b*-PBuVIm) making the first a very hydrophilic block copolymer. More experiments to understand this phenomenon are currently ongoing. PS, which is known to be more hydrophobic, did yield better dispersions in organic solvents. The other factor will be the DP<sub>n</sub> of each block. In the case of CNC-PPEGMA-*b*-PBuVIm, it may be that the DP<sub>n</sub> of the

PPEGMA block in the PPEGMA-*b*-PBuVIm is too long. In the case of CNC-PS-*b*-PBuVIm, higher DPn of the stabilizing block could improve the dispersion in low polarity solvents (current ongoing work in our labs). Finally, another aspect to consider is the  $\zeta$ -potential. In this study, we are evaluating the materials with a positive  $\zeta$ -potential. Having positive charges on the surface of the CNC could potentially limit the dispersion of the modified CNC in less polar solvents. Ongoing work in our lab is also focusing on modified CNC with  $\zeta$ -potential  $< 5$  mV.

## **Conclusions**

In this communication, we present preliminary results of the non-covalent modification of CNC with a double hydrophilic block copolymer (PPEGMA-*b*-PBuVIm) or an amphiphilic block copolymer (PS-*b*-PBuVIm) synthesized via NMP. The modification process is inexpensive and relatively simple compared to covalent polymer grafting approaches, and it has the potential to be applied as a common industrially viable approach to obtain new polymer-CNC based composites. The modification process involves complexation of the cationic block (PBuVIm) with the negative charges present on the CNC surface while the PPEGMA or PS blocks act as stabilizing blocks in different solvents. It is expected that the molar composition of the block copolymers as well as the DPn of each block could potentially play important roles on the final dispersion properties of non-covalently modified CNC. In this study, only relatively low amounts of polymer were necessary to modify the surface properties of CNC. To the best of our knowledge, this is one of few reports that present a detailed study regarding the dispersibility of CNC in different solvents and the corresponding analysis by DLS. The results presented in this report represent a new approach to modify CNC with a new series of copolymers that are effectively modifying the surface properties

of CNC, potentially leading the development of CNC materials towards industrial applications.

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## Table of contents

We present a simpler and less expensive method to functionalize CNC surface using block copolymers, where a cationic block anchors via complexation to the anionically charged CNC surface and the other block acts as a stabilizing block which provides dispersibility in various organic solvents.

