

Synthesis, characterization and viscoelastic properties of Nanocrystalline Cellulose grafted with Poly(N-isopropylacrylamide)

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ABSTRACT

Nanocrystalline cellulose (NCC) was grafted with the thermo-responsive polymer poly(N-isopropylacrylamide) (Nipaam) via living radical polymerization. Various techniques were used to characterize the physical, chemical, morphological and thermal properties of the resulting material. The viscoelastic properties and the stability of the functionalized NCC were compared to the unmodified NCC using rheometry. The shear viscosity of the NCC suspension decreased slightly with an increase in temperature from 20°C to 45°C, indicating a stable system. The storage modulus and shear viscosity values both exhibited a burst increase at about 32.5°C, which is assigned to be the lower critical solution temperature (LCST) of poly(Nipaam). This indicates the successful functionalization of Nipaam polymer chains on NCC. In addition, the thermodynamic property of poly(Nipaam) also prevailed on the grafted NCC.

Keywords: nanocrystalline cellulose, polymer grafting, poly(N-isopropylacrylamide), rheology

1 INTRODUCTION

Colloids, generally comprise of anisotropic particles, are used in a number of applications ranging from coatings, personal care, food and pharmaceuticals [1]. Onsager has showed that rod like particles can undergo isotropic to nematic phase transitions by increasing their concentrations [2]. Various rod-shaped particles such as fd virus, boehmite, chitin and NCC have been used to show the isotropic to nematic phase transitions [1]. However among these particles, NCC is the most prospective material for colloidal applications because of its commercialization prospect [3]. NCC is a natural, renewable and biodegradable nanomaterial that can be obtained by controlled acid hydrolysis of the amorphous regions of the widely available cellulose sources [4]. The relative low density, low cost, uniform size distribution, high aspect ratios (typically >30-100), high surface area, unique morphology and mechanical properties (rigid rods with 25-

30% strength of carbon nanotubes, stronger than steel) [4-7] makes NCC a very attractive material. NCC can be used to develop an emerging class of nanomaterials, which are expected to capture a new market in transportation, medical and packaging applications, electronics and construction [8,9]. Since NCC has a hydrophilic nature due to the presence of hydroxyl groups on its surface, its application is limited as it is not very compatible with some hydrophobic media such as organic solvents and polymers. As such, the surface modification of NCC is a convenient way to increase the versatility of this material. The presence of hydroxyl groups on the surface of NCC provides the possibility for easy and extensive chemical modification. Incorporating 'intelligent' polymer grafts that can respond to environmental changes such as temperature, pH and light on surfaces can lead to the design of 'smart' materials [10,11,12]. The poly(Nipaam) polymer has a LCST about 32-35°C in water. By changing its chain conformation, poly(Nipaam) can either be hydrophilic below its LCST or become hydrophobic above its LCST [13].

In this work, thermo-responsive poly(Nipaam) was grafted onto NCC via living radical polymerization using the "grafting from" route [14]. Unlike an earlier report which uses never-dried NCC as the substrate for surface modification to yield poly(Nipaam)-g-NCC, we used freeze-dried NCC [15]. Various techniques (FT-IR, SEM, TGA, DSC, DLS, XPS, rheometry and zeta potential) were used to characterize the physical, chemical, morphological, thermal properties of the resulting materials. The viscoelastic properties and the stability of these functionalized NCC were compared to the unfunctionalized NCC using rheometry.

2 EXPERIMENTAL SECTION

Materials. Freeze-dried NCC crystals were purchased from Alberta Innovates Technology Futures (AIFT). 2-Bromoisobutyryl bromide (BriB), 2-dimethylaminopyridine (DMAP), tetrahydrofuran (THF, 99%), *N-isopropylacrylamide* (Nipaam), copper (I) bromide, *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), triethylamine (TEA), acetone, ethanol, methanol, were all obtained from Sigma-Aldrich. 400 mesh copper carbon

TEM grids and Uranyl Acetate (Dihydrate, 99.6%) were purchased from Electron Microscopy Sciences.

2.1 Preparation of Initiator-Modified NCC (BriB-NCC)

The initiator modified NCC and poly(Nipaam)-g-NCC were prepared according to a previously reported procedure with slight modifications [15]. Freeze-dried NCC was reacted with BriB initiator in a ratio of 5:3 with respect to anhydroglucose (AGU) units in NCC. NCC (1.00 g, 6.17 mmol of AGU, equivalent to 18.5 mmol OH groups) was stirred continuously in a 250 mL flask under N₂ gas at room temperature (rt). TEA (2.3 mL, 16.5 mmol) was then added followed by DMAP (2.26 g, 18.5 mmol). BriB (2.30 g, 10.0 mmol) was added dropwise and the resulting suspension was stirred for 24 h at rt. The mixture was centrifuged (12000 rpm at 10 °C for 20 min) twice with dry THF, twice with 1:1 THF:EtOH and once with acetone. The precipitate was allowed to dry at rt.

2.2 Synthesis of Poly(Nipaam)-g-NCC

BriB-NCC was grafted with poly(Nipaam) by surface-initiated single-electron transfer living radical polymerization in a ratio of [NiPAAm]/[AGU] = 100:3. BriB-NCC (300 mg) was dispersed in a water:methanol solvent mixture (100 mL, 1:1) in a 250 mL Schlenk flask. The reaction mixture was degassed under N₂ gas before addition of Nipaam (11.3 g, 100 mmol) and copper (I) bromide (0.143 g, 1 mmol). The suspension was degassed again before addition of PMDETA (0.209 mL, 1 mmol) and resulting mixture was stirred for 24h. The resulting poly(Nipaam)-g-NCC was then centrifuged and dialyzed (MWCO 3500) against deionized water for 1 week.

2.3 Preparation of NCC colloidal suspensions

Colloidal suspensions of unfunctionalized and functionalized NCC samples were prepared by dispersing the material in de-ionized water followed by sonication for 3 min. For our research work, 0.1 wt% suspensions were used for scanning electron microscopy (SEM), dynamic light scattering (DLS) and zeta potential measurements.

2.4 Scanning electron microscopy (SEM)

The morphologies of the samples were investigated by SEM using a Hitachi model S-4800 apparatus equipped with a field emission source and operating at an accelerating voltage of 5 kV or 30 kV. For analysis, a drop of the colloidal suspension was deposited on a carbon-coated copper TEM grid for 3 min and the excess of suspension was wicked off using filter paper. The TEM grid was allowed to dry at RT for 3 min. The sample was then stained by depositing a drop of uranyl acetate solution (2 wt% in water) on the grid for 5 min. The excess solution

was wicked off using filter paper and the grid was dried at rt for at least 24 h prior to imaging.

2.5 DLS and zeta potential measurements

After equilibrating NCC suspensions (0.1 wt%) at room temperature for 10 min, suspensions were placed in a temperature-regulated cell at a temperature of 25.0 ± 0.1 °C. Dynamic light scattering (DLS) measurements were conducted using a Malvern Zetasizer Nano-S instrument working at a 173° scattering angle. This instrument is equipped with a 4.0 mW He-Ne laser ($\lambda = 633$ nm) and an Avalanche photodiode detector. Size distribution were calculated using an inverse Laplace transform algorithm, and the hydrodynamic radii were calculated using the Stokes-Einstein equation. DLS was used to determine the particles size of NCC suspensions in aqueous media. The d_{hyd} (hydrodynamic size) from DLS reported are effective diameter based upon the intensity of scattered light. Zeta potential measurement was performed using the same instrument.

2.6 Rheometry

The dynamic rheology measurement was carried out on an AR-G2 rheometer (TA Instruments, U.S.A.). Cone and plate (2° nominal angle) geometry was used to measure both dynamic oscillatory and steady shear viscoelastic parameters. The strain used for the linear viscoelastic region was determined by performing amplitude sweep experiments at a frequency of 1 rad/s. Temperature control was established with a ThermoCube 200/300/400 (Solid State Cooling Systems Co., USA) kept within ± 0.05 °C of the desired temperature. In order to reduce the testing experimental error, the experiments were repeated twice.

3 RESULTS AND DISCUSSION

Successful grafting of poly(Nipaam) onto the surface of NCC was confirmed by X-ray photoelectron spectroscopy (XPS) and Fourier transform Infrared spectroscopy (FTIR). XPS (Table 1) was used to quantify surface concentration of initiator and poly(Nipaam) grafts on NCC.

Sample	%O 1s	%C 1s	%N 1s	%S 2p	%Br 3d	%Na 1s
NCC	39.3	59.9	0.0	0.4	0.0	0.4
BriB-NCC	28.0	65.6	2.2	0.4	3.6	0.2
Nipaam-NCC	14.4	75.6	10.0	0.0	0.0	0.0

Table 1: Atomic composition (%) by XPS for NCC, BriB-NCC and poly(Nipaam)-g-NCC.

Unmodified NCC has atomic composition of oxygen and carbon only. Trace amount of sulphur and sodium was also found, which arise from the hydrolysis and neutralization processes used at AITF. The BriB-NCC sample showed the presence of bromine, confirming that NCC was modified with the initiator. A significant decrease in oxygen and increase in nitrogen contents confirmed the successful grafting of poly(Nipaam) on NCC surface.

Compared to the unfunctionalized NCC and initiator-modified NCC, the poly(Nipaam)-g-NCC samples showed two new FT-IR peaks at 1652 and 1540 cm^{-1} (Table 2) for amide stretch and amide bend of poly(Nipaam).

Sample	Size (nm)	Zeta (mV)	FT-IR (cm^{-1})
NCC	87.2 \pm 1.2	-58.2 \pm 0.5	-
BriB-NCC	83.7 \pm 0.7	-45.8 \pm 1.1	-
Nipaam-NCC	126.9 \pm 0.4	-14.8 \pm 0.6	1652, 1540

Table 2: DLS, zeta potential and FT-IR analyses on NCC, BriB-NCC and poly(Nipaam)-g-NCC.

By DLS, an increase in the nanomaterial dimension was observed for poly(Nipaam)-g-NCC compared to NCC and BriB-NCC. Through grafting, the surface properties of nanoparticles were altered due to a decrease in charge density on the surface of NCC. This was reflected by an increase in the zeta potential values from -58.2 ± 0.5 mV for NCC to -14.8 ± 0.6 mV for poly(Nipaam)-g-NCC. As such the latter formed a less stable colloidal suspension in water compared to NCC.

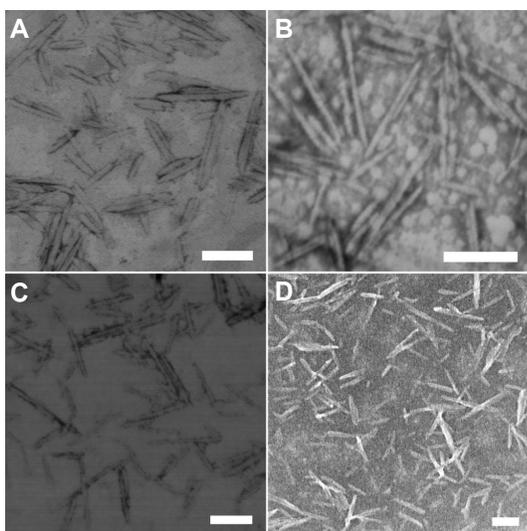


Figure 1: SEM of NCC (B), BriB-NCC (A) and poly(Nipaam)-g-NCC (C,D) dispersed in water. Images A, B, C were taken in TE mode at an accelerating voltage of 30 kV and D is in SE mode at 5 kV. Scale bar = 100 nm

By SEM imaging (Figure 1), a retention of the rod-like structures were observed for BriB-NCC and poly(Nipaam)-g-NCC. Therefore, chemical modification did not alter the structure and morphology of NCC.

Thermogravimetric analysis on TGA 500 (TA instrument) was used to investigate the thermal stability of the materials. Samples were heated up to 600 $^{\circ}\text{C}$ under nitrogen at a heating rate of 20 $^{\circ}\text{C}/\text{min}$. Figure 2 shows the thermograms of NCC, BriB-NCC and poly(Nipaam)-g-NCC. The thermograms of NCC shows the typical degradation behavior observed in literature [16,17]. The curve for poly(Nipaam)-g-NCC is comparable to poly(Nipaam), confirming grafting on NCC surface. The presence of grafted species on NCC surface delays the thermal degradation of NCC by acting as an insulator.

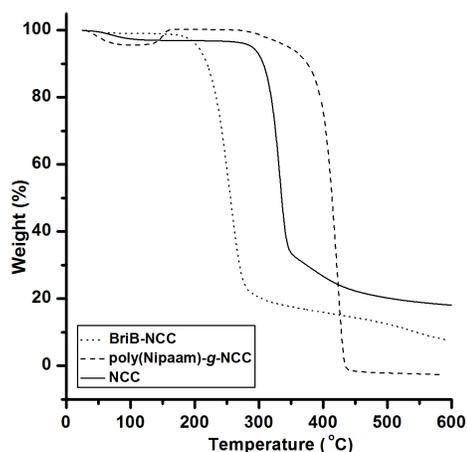


Figure 2: Thermograms of NCC, BriB-NCC and poly(Nipaam)-g-NCC.

The onset decomposition or initial decomposition temperature (T_i) for each sample was critical for establishing the temperature window for differential scanning calorimetry (DSC), hence avoiding the degradation of compounds. DSC experiments were then carried out with a DSC1000 differential calorimeter (TA instrument) fitted with a liquid N_2 cooling system. The samples were placed in closed hermetically DSC pans. The heating and cooling rates were 10 and 5 $^{\circ}\text{C}/\text{min}$, respectively. DSC experiments were performed to study the thermal transition for each compounds and determine the glass transition temperature (T_g), which indicates the temperature where the compound loses its rigidity. Only the poly(Nipaam)-g-NCC sample showed a T_g at 142.0 $^{\circ}\text{C}$. This value is higher than that observed for poly(Nipaam) at about 130 $^{\circ}\text{C}$ [18], since reducing the mobility of the polymer chains by anchoring them on NCC surface results in an increase in the glass transition [19].

The rheological measurements were carried out on a 1wt% poly(Nipaam)-g-NCC suspension in water and a 1wt% NCC suspension was used as control. The dynamic oscillation properties of poly(Nipaam)-g-NCC suspension were shown in Figure 3 as a function of temperature. The

storage modulus (G') and loss modulus (G'') were almost constant until the temperature reached 32.5 °C, indicating the suspension was stable. However, sharp increases were observed for both G' and G'' , which were assigned to the phase transition of poly(Nipaam). After 35.0 °C, G' and G'' were relatively stable, indicating the phase transition of poly(Nipaam) was completed.

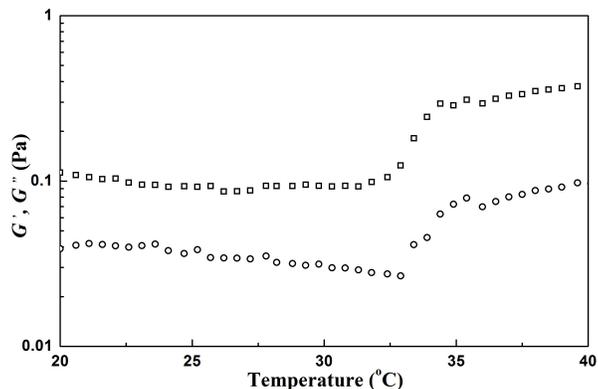


Figure 3: Graph of dynamic storage modulus (G' , \square) and loss modulus (G'' , \circ) of 1.0 wt% poly(Nipaam)-g-NCC suspension in water as a function of temperature.

This phase transition was further validated by the steady shear test (Figure 4) using a shear rate of 40 s^{-1} . The viscosity of poly(Nipaam)-g-NCC exhibited a sharp increase from 32.5 to 35.0 °C, indicating the phase transition for poly(Nipaam) from hydrophilic to hydrophobic. The viscosity of NCC remained unchanged, suggesting stability in the test temperature range.

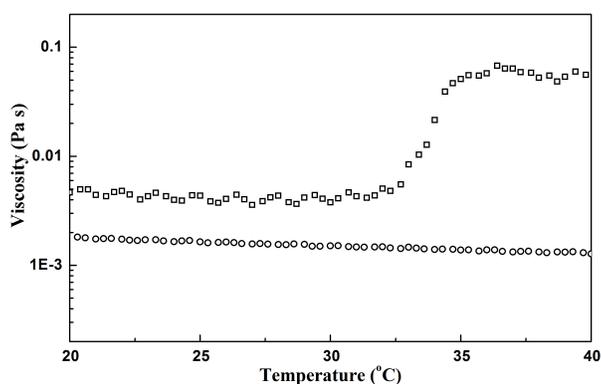


Figure 4: Graph of viscosity of 1.0 wt% poly(Nipaam)-g-NCC (\square) and 1.0 wt% NCC (\circ) suspensions in water as a function of temperature.

4 CONCLUSION

NCC was successfully grafted with the thermo-responsive polymer Nipaam. It was observed that the resulting surface modified NCC showed a thermo-

responsive behavior. NCC is known to show isotropic to nematic phase transitions by increasing its concentration. Adding a thermo-responsive property to NCC will allow further tuning of the phase transitions. We are currently investigating other responsive polymer grafting on NCC and their rheological properties.

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