



Modification of cellulose nanocrystals as reinforcement derivatives for wood coatings



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ABSTRACT

Cellulose nanocrystal (CNC), an emerging renewable nanomaterial, was subjected to carbon chains grafting in order to improve its dispersion and its ability to transfer its rigidity properties into less polar matrixes, especially acrylic wood coatings. Chemical modifications used to this purpose are required to be simple, not affecting the CNC main structure and compatible or synergistic to oligomer reticulation inside the targeted UV-waterborne formulation. Those modifications were carried out using either alkyl quaternary ammonium bromides or acryloyl chloride. These new chemical functionalities, not inducing deep structural changes in modified CNCs, were highlighted through nuclear magnetic resonance, infrared and nitrogen content analyses. CNC derivatives were better dispersed in aqueous acrylic coating as suggested by atomic force microscopy, with a mean surface roughness falling from 9 to 6 nm on the coatings containing unmodified and treated CNCs, respectively. For mechanical evaluations, the coatings including various CNC derivatives were applied on sugar maple wood, a much appreciated material as indoor timber or wooden furniture which requires an efficient surface protection. The abrasion tests indicated that the modified CNCs confer a higher scratch resistance, with an improvement from 24% to 38% for coatings containing CNC derivatives over those with unmodified CNC.

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1. Introduction

The durability improvement of wood products greatly calls for the development of protective coatings with higher performances. The use of various nanoparticles, including common inorganic metal oxides (ZnO, Al₂O₃, TiO₂, CeO₂, etc.) as mechanical reinforcement additives into coatings, represents a significant approach to reach this end [1–5]. However, difficulties encountered in incorporation of inorganic nanoparticles in polymer matrixes (organic), such as incomplete dispersion and adhesion, suggest working with organic nanoparticles. That particularly applies to cellulose nanocrystals (CNC), a new renewable non-toxic product obtained after isolation of crystalline domains from cellulose acid hydrolysis. Indeed, as one of many advantageous characteristics, excellent mechanical reinforcement effects are known with CNC incorporation which has been the subject of a growing interest in nanocomposite materials with polymers [6–10]. This advantage is

much more attractive since wood, compared with other natural sources of cellulose (cotton, hemp, bacteria, green algae, etc.), benefits from a long process experience of its controlled acid hydrolysis, as pulp, and, moreover, represents the most abundant, renewable and sustainable source of CNC [11–13]. Such CNC diversified applications would also permit to foresee a better development potential in the forest industry [8,14]. Some applications, related to low polarity matrix, appear somewhat limited because of CNC surface hydroxyls and consequent hydrophilic nature, in acrylic waterborne coatings, for instance. Thus, to enhance its dispersion and therefore its mechanical reinforcement in a wide range of matrix polymers, CNC should be submitted to appropriate surface modifications.

Thanks to reactive surface of OH side groups, grafting of chemical species is possible to achieve in order to functionalize the CNC surface. In addition, the CNC obtained from sulfuric acid hydrolysis exhibits negative charges at the surface at neutral pH [7,9,15,16], which are due to sulfate ester groups which are able to form ionic bonds with a matching reagent. Based on those reactive sites, some modification studies have been described as for the compatibilization of CNC or cellulose with polymer composites referring to different application fields, as focused on by

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Emanuelsson and Wahlen [17], then Heux and Bonini [18]. In the same way, other authors have silylated CNC, resulting in an improved dispersion in polymers for biomedical and engineering contexts [19,20]. Likewise, firstly activating CNCs surface with tempo-mediated oxidation, thereby creating carboxylic acids surface reactive groups and coupling those with alkylating amines, it was possible to create other CNC derivatives, for example leading to nanoplatelet gels, as stable mimetic nanomaterials [21,22]. In another approach, the CNCs ability to establish ionic interactions have been put to good use in “green”, easy and safe synthesis processes of stable selenium, nickel or titania nanoparticles, notably useful for medical diagnostics, energy conversion or catalytic applications [23–25].

In this communication, we report a preparation of cellulose nanocrystal derivatives by surface chemical modifications using alkyl quaternary amines or acryloyl chloride in simple conditions, the interest being to improve CNC dispersion in varnishes for wood and the mechanical properties of this matrix.

2. Experimental

2.1. CNC derivatives synthesis and characterization

CNC was provided under freeze-dried form by FPIInnovations pilot plant (Celluforce, Waterloo, Québec, Canada), from a sulfuric acid hydrolysis process of commercial bleached softwood kraft pulp source. In both following preparation approaches, the CNC used was previously dispersed in a solvent (deionized water or 1,4-dioxane according to involved method) by stirring at room temperature for 2 h. For the first modification method, in 60 mL of deionized water overall, various quantities of hexadecyltrimethylammonium bromide (HDTMA) or tetramethylammonium bromide (TMA) (Sigma–Aldrich, $\geq 99\%$) were mixed with 2 g of CNC, that is, from 0.1 to 14 mmol quaternary ammonium by weight of CNC. Each reaction mixture was vigorously stirred for 4 h at ambient temperature. In the second method, the reaction was based on the 1-methylimidazole (1 MIM) catalyzed esterification described by Connors and Pandit [26] and implying an alcohol and an anhydride. The expected result of this kind of grafting, with an ionic bond being created, should resist the environment of the aqueous liquid coating and replace most of the charged $-\text{SO}_2$ groups at the surface of the CNC with hydrophobic moieties, thus encouraging dispersion in the oily phase of the coating emulsion. In the present case, the synthesis consists in performing the reaction on the CNC (4 g) with acryloyl chloride (110.5 mmol, Sigma–Aldrich, $\geq 97\%$), being carried out with the catalyst 1-methylimidazole (6.1 mmol, Sigma–Aldrich, 99%) in 80 mL of 1,4-dioxane. The reaction was stirred overnight under nitrogen atmosphere at 50 °C. This second kind of grafting should also satisfy the same requirements as the precedent one, as well as creating an additional cure site with the acrylate phase, thus anchoring the CNC in the continuous cured. Both employed reaction types were performed in very simple conditions: at room temperature or around it, use of one reactant and mostly water as solvent, and, once, use of a moderate quantity of catalyst. All products from these methods were obtained after concentration of resulting mixtures by centrifugation at $1500 \times g$ for 15 min (Thermo IEC), supernatants removal, and five washing cycles with 420 mL of warm deionized water to remove excess of unreacted CNC, quaternary ammonium salts or acryloyl chloride. Finally, after the last supernatant removal, powdered products were recovered by freeze-drying. In this way, various treated CNCs were obtained according to the type, the length and the ratio of the used reactant in regarding the substrate. For all products, as molar weight of CNC is not exactly defined, usual definition of yield is not applicable in this context. Thus, to have an indication of crude

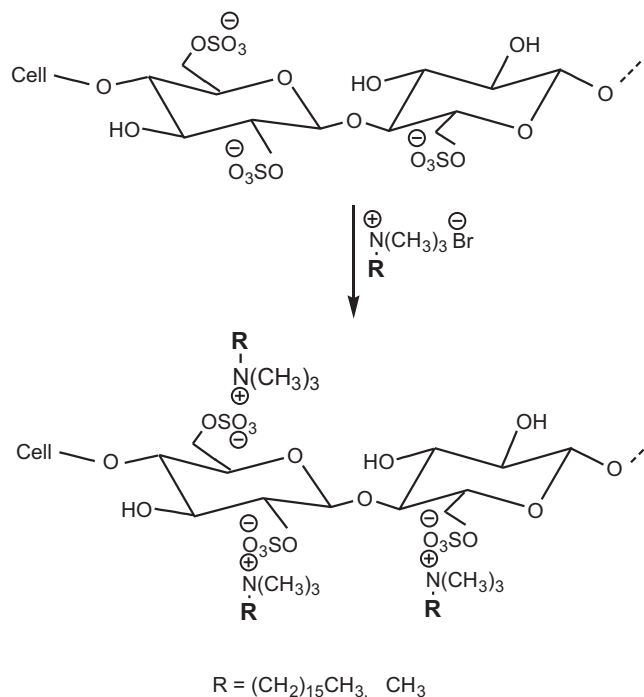


Fig. 1. Reaction between CNC and quaternary ammonium salts (hexadecyltrimethyl- or tetramethyl-ammonium bromide).

quantitative results from preparations, we defined mass yield as the ratio of product weight to the CNC weight (Figs. 1 and 2).

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy measurements from unmodified CNC and its synthesis derivatives were carried out using a PerkinElmer Spectrum 400 Series instrument. Data were collected from 600 cm^{-1} to 4000 cm^{-1} wavelength range with 64 scans for each sample. Concerning only samples with HDTMA-modification, to appreciate the qualitative intensity of the CH aliphatic bands, a flat baseline correction was done between 2750 and 3000 cm^{-1} and the spectra were normalized to the OH group [27], which were not likely to be modified in this case after reaching moisture equilibrium of samples, as checked by constant mass. The solid state CP/MAS ^{13}C NMR analyses were run with a Bruker Avance 300 spectrometer at a frequency of 75 MHz. All spectra were recorded using the technique of cross-polarization and rotation with magic angle spinning with 7-mm tubes. The samples were spun at 4000 Hz. The time of contact for cross-polarization was adjusted to 1 ms, and 3000 scans were recorded. Nitrogen content of derivatives from synthesis, i.e. the grafted CNC, with quaternary ammonium salts were determined by a PerkinElmer 2410 Nitrogen Analyzer.

2.2. Preparation of nanocomposite coatings and application

The base resin, Bayhydrol UV 2282, is an UV-curing polyurethane acrylate dispersion (about 39 wt%) in water, used especially for wood coating and purchased from Bayer Material Science. To this resin, for obtaining the neat formulation, a photoinitiator and additives (defoamer, surfactant, dispersant and thickener) were added and mixed one by one, each 5 min, through a high speed disperser (Dispermat, VMA-Getzmann GmbH D-51580 Reichshof), glass beads being also added to improve the shear rate. Water (6 wt%) was added to adjust the viscosity of the UV-waterborne formulation. CNCs were dispersed into the neat formulation at a loading of 2 wt% at the same time as glass beads addition with a higher shear for 10 min. After glass beads removal by filtration, the formulation was coated (thickness of

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