J. Coat. Technol. Res., **11** (6) 841–852, 2014
DOI 10.1007/s11998-014-9598-3

Mechanical properties of UV-waterborne varnishes reinforced by cellulose nanocrystals

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Abstract There are many instances in the literature of nanocellulose-thermoplastic composites, but there are few studies on coatings reinforced by cellulose nanocrystals (CNCs). The overall objective of this research was to develop organic nanoparticles-reinforced UV-water-based coatings for wood applications and to study the effect, mainly on wear properties, of the final composite coatings. CNC was mixed in the varnishes to improve the mechanical properties of the coatings. One of the key aspects in the technology of nanocomposites remains the dispersion of the nanoparticles within the matrix as well as its affinity with the matrix. To quantify the dispersion, efficient methods of characterization are needed in order to reveal the nanosized particles. In this article, a novel characterization method based on atomic force microscopy was employed to characterize such nanocomposite coatings, by measuring surface nanoroughness, which is clearly correlated with quality of dispersion and mechanical properties. CNC was modified by either alkyl quaternary ammonium bromides or acryloyl chloride. The mechanical properties (abrasion and scratch resistances, hardness and adhesion) were analyzed and compared to the reference varnish without nanoparticles. The modified CNC addition in UV-water-based coatings results in an approximately 30–40% increase in wear resistance (abrasion and scratch), without any loss of appearance.

Keywords Cellulose nanocrystals, CNC, Coating, Dispersion, Surface modification, Mechanical properties, Wear resistance

Introduction

Waterborne coatings

Water-based UV-cured coatings are increasingly used in the wood industry, in view of their performance, very low volatile organic content, hardness, and fast setting (fast curing) properties. UV-aqueous technology is an attractive alternative, since it combines the benefits of UV technology and those of the water-based technology. First of all, the photopolymerization is very fast (a few seconds) and is accompanied by little or no VOC emissions. Second, the use of water as the single solvent reduces the viscosity of formulations to

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promote homogeneous sprayable applications in environmentally friendly and secure conditions.[1] Finally, aqueous coatings promote good adhesion to wood.[2] The UV-aqueous technology also has additional advantages, compared to 100% solid UV coating, since the polymerization of the UV-aqueous coatings is insensitive to atmospheric oxygen and generally coatings producing using this technology have excellent chemical and thermal resistance.[1,3] The aqueous coatings are thin, about 100 μm, only two layers or coats, relative to commercial coatings, which, for parquets for instance, may have up to seven coats. Several additives can be used to improve the mechanical properties, such as aluminum oxide or silica,[4,5] while use of other nanoscale metal oxides (Al_2O_3, SiO_2, TiO_2, ZnO, $CaCO_3$, etc.) has been cited in the literature, in organic varnishes or in aqueous media. These additives are used in order to strengthen the coating for indoor use such as in flooring, or protect the coating from UV radiation attack, in the case of outdoor use. Nanoaluminum oxide is used to strengthen coatings, such as in the study of Bautista et al.,[6] where addition of 5% nanosized SiO_2 to UV-cured acrylics decreased weight loss by abrasion by about 25%. Bauer et al.[7] added functionalized nanoalumina and nanosilica to acrylic coatings, where about 10% addition of such nanoparticles increased abrasion resistance by 40%. Distribution of nanoparticles was characterized with atomic force microscopy (AFM).[7,8] In another work of Bauer et al.,[9] it was shown that nanoalumina particles, at equivalent loading, were three times as efficient as microalumina particles, as far as abrasion resistance was concerned. Adequate dispersion of nanoparticles is always a challenge, in view of their very high specific surface. In order to evaluate the use of an innovative organic-based renewable nanoscale reinforcement, we use organic nanoparticles, cellulose nanocrystals (CNC), as film reinforcement in our study. There are several publications in the literature of nanocellulose-thermoplastic composites, but there are few studies on coatings reinforced by CNC[10] and none which uses CNC as modified in the present study.[11]

CNC

Cellulose is the most abundant organic material on earth (more than 50% of the biomass). Cellulose is the main component of plants and in particular of the cell walls. Cellulose microfibrils, which themselves are associated in layers, form the walls of plant fibers. The presence of hydrogen bonds between the anhydroglucose molecules of the different cellulose chains result in a highly crystalline material. Many products in everyday life are cellulose derivatives, such as cellulose acetate, nitrates, esters, and ethers, some of which are paint components. CNC, which is a new product, is also called 'cellulose whiskers.' These CNCs are bio-based and have a high aspect ratio, as opposed to inorganic nanoparticles, which are usually spherical or plate-like. Generally, the CNC is extracted from the wood by a process of acid hydrolysis (H_2SO_4), with strict control of conditions of time and temperature.[12] The action of the acid removes the amorphous parts of the microfibrils to release only the highly crystalline particles of the original cellulose microfiber. When this level is reached, the hydrolysis is terminated by rapid dilution of the acid. A combination of centrifugation and extensive dialysis is used to completely remove the acid, and, for certain processes, ultrasonic treatments complete the process for dispersing the individual nanoparticles of the cellulose and produce an aqueous suspension.[13] The CNC nanoparticles have the following properties: specific surface area of 300 m^2/g, a Young's modulus of 150 GPa, and a tensile strength of 10 GPa.[14] There are also other types of sources for CNC: cotton CNC, green algae CNC etc.,[15–18] as well as bacterial CNC. CNC was found to be a good reinforcing filler when mixed with aqueous latex matrices.[14,19] Landry et al.[4] have shown that the addition of small concentrations of CNC particles to clear clay-based coatings improves their mechanical properties (abrasion and scratch resistance, hardness). While it is still difficult to incorporate and properly disperse inorganic nanoparticles in an organic polymer matrix,[20] it could possibly be easier to use organic nanoparticles, with proper surface modification. The research hypothesis assumes that CNC as such, and possibly with appropriate modification of its surface, will show high dispersion and stability in the resulting nanocomposite coatings, which are, in this case, transparent coatings (varnishes). Thus in this study, we compare the mechanical properties of varnishes with chemically modified (more hydrophobic) CNC[11] with those of varnishes with either unmodified (hydrophilic) CNC or without CNC.

CNC dispersion characterization

The choice of the mixing technique plays an important role in the dispersion state of the nanoparticles.[4] There are several types of equipment commonly used in the industry; among those are the high-speed mixer, three-cylinder mill, and ball mill.[4] In our study, a high-speed mixer was used, since it is most appropriate to our system (varnish with CNC) as determined by our previous studies on varnishes with inorganic nanoparticles. The main challenge of mixing CNC particles into a host matrix is to achieve a homogeneous dispersion in order to maximize the macroscopic effects on the mechanical reinforcement. We used atomic force microscopy, AFM, to study the quality of CNC dispersion by measuring surface roughness. Farrokhpay[21] conducted a literature review on the new assessment techniques of painted surfaces and obtained quantitative results on the surface roughness characterization by AFM. Thometzek et al.[22] also used transmission electron microscopy (TEM) and AFM to quantify the surface quality of paintings and correlated the degree of hydrophobicity of the particles with the quality of the dispersion. In this article, we used our own characterization method based on surface roughness measurement by AFM to qualify CNC dispersion in varnishes.[23] Classical dispersion quality analysis by TEM is difficult to apply in this case because of the lack of contrast between the CNC and the continuous organic phase and the difficulty in obtaining freestanding varnish films.

Materials and experimental procedure

The composition of the formulation

The formulation used in this work is composed of the following components: the resin (or binder), photoinitiator, and additives such as defoamer, dispersant, surfactant, and thickener. These chemicals were added in order to minimize foaming, optimize the surface tension, and help CNC dispersion. The typical compositions of the UV-aqueous formulation are presented in Table 1.

The resin selected was Bayhydrol UV 2282 (Bayer MaterialScience), a polyurethane-acrylate (PUA) oligomer emulsified in water that was primarily developed for applications on wood. The photoinitiator used in this research was a bisacylphosphine oxide (Irgacure 819DW, BASF Resins - Inks, and OPV), dispersed in water (45 w/w%).

CNC

CNC used in this project has been prepared by FPInnovations (Canada). To the best of our knowledge, there are no publications on the manufacturing process of the type of CNC used in this paper, since it is a proprietary industrial process, with patent pending.

Prior to shipping the CNC to our lab, the following treatment was done on the CNC by FPInnovations. Samples of the suspension of the CNC were sonicated using a Sonics Vibra-Cell 130 W 20 kHz ultrasonic processor with a 6-mm-diameter probe: typically, 15 ml of a suspension of 2–3% CNC weight was placed in a plastic tube of 50 ml and sonicated at 60% of maximum power until an energy input of more than 3600 J/g CNC was reached. This was performed in an ice bath to prevent the degradation caused by the rapid heating of the suspension.[24]

In water suspension (0.05 w/w%), with the specific material used in this study, the characteristic dimensions of CNC are 6–10 nm (diameter) and 100–130 nm (length). This latter dimension of CNC was measured through dynamic light scattering with a Zetasizer Nano ZS (Malvern Instruments Ltd.).

Cellulose fibers that remain after this treatment are almost entirely crystalline and as such are called “crystalline.” The precise physical dimensions of the crystallites depend on several factors, including the nature of cellulose hydrolysis conditions and specific origin.

The aqueous CNC suspension was then concentrated in a Labconco RapidVap (Labconco, Kansas City, MO, USA) up to 14 w/w%. Such high CNC concentration is required to adjust the CNC loading within the formulation and avoid excessive dilution.

Surface modification of cellulose nanocrystals

Since CNC has an anionic surface at neutral pH, it is possible to modify its surface with hydrophobic cationic surfactants. A similar technique was used by Nypelo et al.[25] to modify hydrophilic silica nanoparticles for coatings.

CNC was chemically modified by the following three different cationic surfactant molecules (Fig. 1), for further use in the formulations (in later discussions, unmodified CNC will be noted CNC). HDTMA and TMA were used to treat the CNC fiber with an hydrophobic coating, while acryloyl chloride was reacted with hydroxyl groups to provide an anchoring group with acrylic reactive sites in the coating.[11] A proprietary hydrophobic grade CNC, modified by FPInnovations, was also used as a reference.

CNC: unmodified CNC

CNC-HDTMA: hexadecyltrimethylammonium bromide (HDTMA-Br)

Table 1: Typical compositions of the formulation (see Table 2 for details)

Component	Chemical structure	Commercial name
Resin	Polyurethane-acrylate	Bayhydrol UV 2282
Defoamer	Ether poly dimethylsiloxane	Foamex 822
Surfactant	Polyether siloxane copolymer	Byk 348
Dispersant	Solution of block copolymer of high molecular weight	Byk 190
Photoinitiator	Bis-acyl phosphine oxide	Irgacure 819DW
Thickener	Polyurethane	RM 2020
Solvent	Deionized water	–

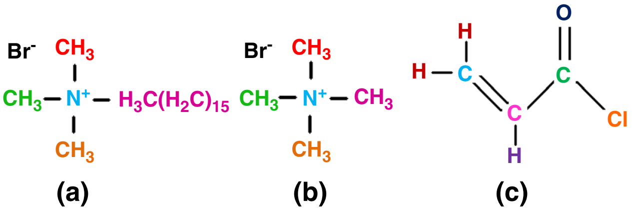

Fig. 1: Chemical formula of hydrophobic cationic molecules: (a) HDTMA, (b) TMA, and (c) acryloyl chloride

CNC-TMA: tetramethylammonium bromide (TMA-Br)

CNC-Acryloyl: acryloyl chloride (C_3H_3ClO)

CNC-FPI: proprietary hydrophobic modified by FPInnovations

The purpose of comparing three types of surface-modified CNCs, CNC-HDTMA, CNC-TMA, and CNC-Acryloyl, with a commercial hydrophobic CNC, CNC-FPI, is to assess whether such surface modifications help in obtaining desirable properties in the coatings where the CNCs are dispersed as reinforcing agents.

In the following study, these five types of CNCs were added at concentrations into the liquid coatings as to have a final concentration of 2% in the cured, dry films.

More details about these modifications have been presented in another article,[11] where advantage was taken of the anionic nature of the nanoparticle, whereas these sites were coupled to cationic hydrophobic surfactants. The amount of cationic reactant was adjusted to give a reasonably hydrophobic surface. Tests with too much of these surfactants resulted in an intractable nanopowder akin to powdered Teflon.

Preparation of formulations and samples

Dispersion method

A high-speed mixer (Dispermat, VMA-Getzmann GMBH D-51580 Reichshof) was used to disperse CNC in the varnish formulations. This equipment can produce shear rates comparable to those of industrial mixers. The high-speed mixer consists of a vertical rotary axis with a propeller plate with tooth saws at its periphery, rotating at high speed in a vessel containing the formulation to be dispersed (Fig. 2).

Preparation of formulations

The protocol followed for varnish preparation with CNC (stirring speed: 400 rpm) is presented below:

1. Addition of defoamer to the resin (in a metal container), with 4 min mixing.
2. Addition of surfactant to the above mixture, stirring for 4 min.

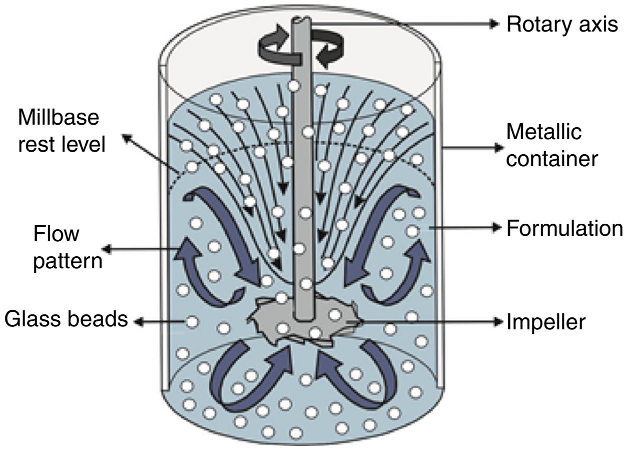

Fig. 2: Principle of dispersion of high-speed mixer

3. Addition of dispersant to the above mixture, stirring for 4 min.
4. Addition of the required amount of deionized water in the above mixture, stirred for 4 min.
5. Addition of CNC gel (14 w/w% in water) gradually with 320 g of beads (glass) in the above mixture, stirring for 10 min (the chemically modified CNC was used in powder form, not gel).
6. Adding the rheological agent, stirring for 4 min.
7. Addition of photoinitiator, stirring for 6 min.
8. Removal of beads by filtration.

An example of varnish formulation with 2% CNC is presented in Table 2.

Results are presented, in various figures, as a function of

- Unmodified, hydrophilic CNC in concentrations of 0.5, 1, 1.5, 2, and 3% (w/w).

- 2% CNC (w/w) in five different types: unmodified hydrophilic CNC, CNC-HDTMA, CNC-FPI, CNC-Acryloyl, and CNC-TMA.

Preparation of the samples

Formulations were applied on sugar maple (*Acer saccharum*) on tangential face. The dimensions of the wood samples were 96 × 96 × 15 mm (Fig. 3). Coatings were applied by spraying. After application (thickness: ~127 ± 15 μm in liquid state), samples were put in a convection oven for 10 min at 60°C to gradually evaporate the water. During this step, the coating passed from a milky white liquid state to a transparent solid state. Film curing was then carried out using a UV oven (ATG 160305 from Ayotte Techno-Gaz, Inc.) equipped with a medium pressure mercury lamp (600 W/cm, model UV Mac 10, Nordson, OH, USA). This is a radical polymerization-type cure or crosslinking. The intensity of incident light measured with a radiometer was in the order of

Table 2: List of chemicals for varnish formulation with 2% CNC (402.98 g)

	Mass (g)	% Dry (w/w)
Resin	366.23	94.34
Defoamer	2.48	0.41
Surfactant	1.53	0.96
Dispersant	4.96	1.29
Deionized water	1.87	–
CNC (14% in water)	22.21	2.00
Rheological agent	1.65	0.21
Photoinitiator	2.05	0.89
Total	402.98	

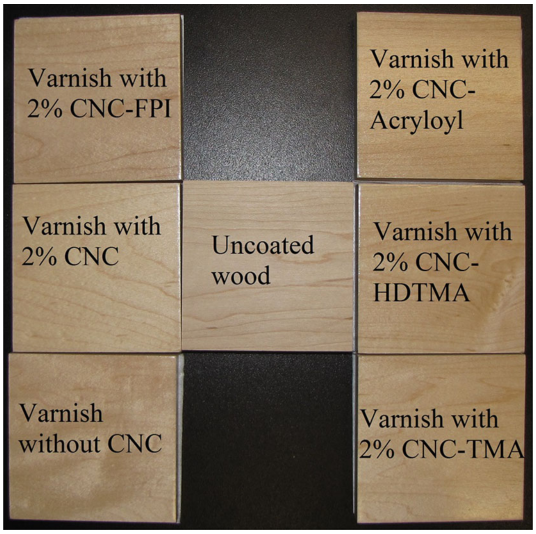

Fig. 3: Wood samples with and without varnish coatings, with and without CNC in the coating, and with modified and unmodified CNC in the coating

570 mJ/cm^2 and the perceived temperature during curing was between 25°C and 30°C. After curing, surfaces of varnishes were slightly sanded with 150 sandpaper, in the direction of wood grain. These steps had to be repeated once again to get a coating ~100 μm thickness. These aqueous coatings were thin, about 100 μm, only two layers or coats, relative to commercial coatings, which for parquets, for instance, may have up to seven coats.

In Fig. 3, it may be noted that there is no visual difference between the different samples. Thus, the CNC addition does not change the optical properties of the varnish, at least as perceived by the human eye. More details about optical properties of these varnishes will be presented in a subsequent article.

Experimental methods

Atomic force microscopy

AFM observations were carried out using a NanoScope V (Veeco Instruments Inc., Santa Barbara, CA, USA), fitted with a Hybrid XYZ scanner. AFM measurements were done under ambient air conditions in tapping mode. The sensitivity of the tip deviation and the scanner resolution was 0.3 nm. The resolution was set to 256 lines by 256 pixels for all observations. Surface roughness was calculated in 10 μm × 10 μm scan areas, using the classical mean surface roughness parameter R_a. The parameters were calculated by the Research Nanoscope 7.2 software:

$$R_a = \frac{1}{n}\sum_{i=1}^{n} |Z_i - Z_{\text{ave}}|, \tag{1}$$

where R_a is the mean roughness, the arithmetic average of the absolute values of the surface height deviations, Z_i is the current Z value, Z_{ave} is the average of the Z values within the given area, and n is the number of points within the given area : 65,536 in our case. The experimental value for each type of coating was obtained from the average of 12 measurements.

Contact angle

In order to see whether modified CNC had an effect on the hydrophobicity of coatings, contact angle measurements were performed. Water contact angles were taken right after deposition of the water drop on the coated wood surface at laboratory temperature (23°C). The angle was calculated by software FTA200 Dynamic Contact Angle Analyzer (First Ten Angstroms, Inc., Portsmouth, VA, USA). The experimental value for each type of coating was obtained from the average of five measurements.

Viscosity

Viscosity was measured using a DV2T Viscometer at 27°C (Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA). The experimental value for each type of coating was obtained from the average of five measurements.

Adhesion test

To maximize the effectiveness of coatings, it is important that the adhesion of the coating on the wood is maximized, or at least that addition of CNC does not interfere in this respect. The drying of a varnish applied to the wood is accompanied by an increase in the work of adhesion.[2] This increase is accompanied by a decrease in the wood/varnish interface energy.

The adhesion strength of the varnishes was evaluated with the pull-off method according to ASTM D4541. 20-mm-diameter aluminum dollies (Fig. 4) were glued to the cured topcoat films with a two-component epoxy adhesive, Araldite 2011 (Ciba-Geigy Corporation, MI, USA), which needed to cure for 24 h before testing. In order to test only the area bonded under the dollies, a circular groove was machined around these (Fig. 4). The dollies were pulled vertically away with an MTS Systems Corporation Alliance universal testing instrument, model RT/50, with a load cell of 5 kN mounted on the crosshead. The force was applied normal to the surface with a speed of 2 mm/min to the loading fixture. The experimental value for each sample was obtained from the average of 12 measurements.

Hardness

The hardness of dried/UV-cured coatings was determined by measuring the damping number of a pendulum oscillating on the coating according to the standard ASTM D4366 (Pendulum hardness tester, BYK-Garner). The hardness value corresponded to the damping number of the pendulum from 6° to 3° (König pendulum). The experimental value for each type of coating was obtained from the average of 15 measurements.

Abrasion resistance

The abrasion resistance was measured using a Taber Rotary Platform Abraser (Taber Abraser® 5135, Taber Industries, North Tonawanda, NY, USA), according to ASTM D 4060. Two vertical disks of 500 g each, trimmed sandpaper type S-42, rub the sample of varnish on wood, the latter being driven by rotation (Fig. 5). The abrasion resistance is expressed as weight loss caused by the passage of the abrasive surfaces, after 100 cycles of rotations, with the following relationship:

$$M_{\text{loss}} = M_0 - M_{100}, \tag{2}$$

where M_{loss} is the mass loss of the sample after a cycle of 100 revolutions, M_0 is the initial mass of the sample, and M_{100} corresponds to the mass of the sample after a 100 cycle of rotations. The mass loss of a composite coating type corresponds to the average mass loss of 10 samples.

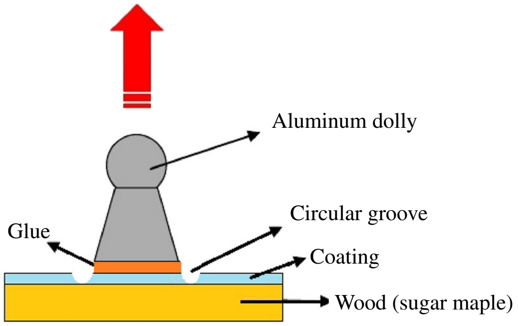

Fig. 4: Diagram of the adhesion measurement set-up

Scratch resistance

To measure the scratch resistance, the surface must be scraped with a standard load for all samples. This test was performed according to ASTM D7027 standard, using a Multifinger Scratch/Mar Tester, model 710, (TABER Industries, North Tonawanda, NY, USA). The samples were scratched with a 10-N load, followed by depth profiling with a profilometer (DekTak 150, Veeco Instruments Inc., Santa Barbara, CA, USA). The experimental value for each type of coating was obtained from the average of 15 measurements.

Results and discussion

Coating with unmodified CNC

We characterized surface dispersion degree of nanoparticles in varnishes, as first studied by measuring surface roughness using AFM,[23] since, as discussed above, standard X-ray techniques such as SEM and TEM did not give useful images, for lack of contrast. In

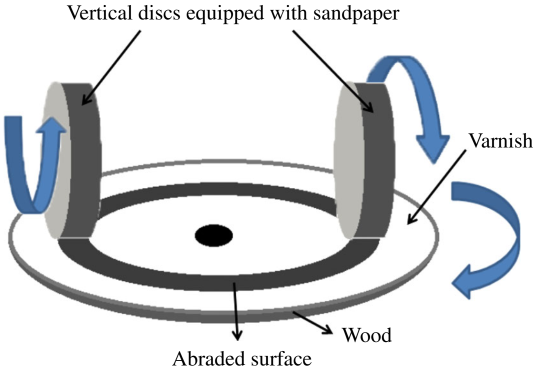

Fig. 5: The abrasion resistance set-up using the Taber Abraser

Fig. 6, the surface roughness measurement results on the effect of hydrophilic i.e., unmodified CNC addition in the varnish, as a function of CNC concentration, are shown. First, before coating application, the wood was sanded; its surface roughness is in the order of microns, since its cellular structure precludes a further lowering of the roughness, even with further sanding with increasingly fine sandpaper. Once coated with the cured water-based varnish (two coats), the roughness is reduced about a thousandfold, to about 5 nm (Fig. 6). This is so because the AFM or any mechanical surface topography characterization apparatus detects only the cured coating surface, which is self-smoothing after liquid coating application, due to the high surface tension in the liquid phase. Thus, there is no direct effect of the wood surface on the surface of the coating even if it is only between 30 μm and 100 μm thick, high gloss can be obtained. Addition of 0.5% of CNC has no effect on the surface roughness. However, when more than 2% CNC is added into the varnishes, there is a significant increase in the surface roughness (around 20 nm). It may originate from the relatively decreasing quality of dispersion of CNC, which can be due to formation of CNC agglomerates. It is important to mention that the poor dispersion of nanoparticles may limit the possible improvement of the mechanical resistance, as well as other properties, such as surface properties, i.e., optical, paramount for appearance of coatings. This is discussed later in the text. One may object that the AFM only characterizes the surface roughness and potential agglomeration of CNC: not in the bulk, but in paints and varnishes, surface appearance is paramount, and any additive must preserve surface appearance. In this case, addition of untreated CNC does not affect the appearance, since even at 3% level of CNC in coating, a roughness of 20 nm is not perceived by the human eye.

These water-based coatings are self-smoothing, but addition of too much CNC interferes with this property. This may be related to increased viscosity. As shown in Fig. 7, the addition of more than 1.5% CNC drastically increases viscosity, but it is still possible to spray the varnishes with up to 3% added CNC. Since varnishes with more than 2% CNC have shown significantly worse dispersion (Fig. 6), no additional experiments were performed on coatings containing higher percentage of CNC than 2%, in the following text.

Effect of surface modification of CNC

In order to improve the CNC dispersion level within the coating, CNC particles were surface modified by three different surfactant molecules[11] (Fig. 1) and a proprietary hydrophobic grade of CNC, modified by FPInnovations, was selected as control sample. The aim of these modifications was to obtain more hydrophobic nanoparticles, which would disperse better in water-based coatings. Indeed a water-based emulsion, such as the coatings used here, is a dispersion of oily resin droplets in water, the latter playing the role of a carrier and a lubricant. Once the water has evaporated, only the hydrophobic phase remains. Our system is an emulsion, a so-called latex two-phase system, which means that the thinner or carrier is hydrophilic (water) and the resin is hydrophobic. To have a good dispersion of CNC in the hydrophobic resin, increasing its hydrophobicity is expected to have a positive effect.[26] For instance, Tigges et al.[27] use hydrophobized ZnO nanoparticles for better dispersion in emulsions, while Nobel et al.[28] mention the advantages of using hydrophobic nanoparticles in coatings. To compare hydrophobicity level of coatings with and without CNCs (modified and nonmodified), we measured contact angles (Fig. 8) on cured coatings with different CNC grades added. The coatings with more hydrophobic CNCs are more hydrophobic, as water contact angles are increased. There is no significant difference of this property between the four grades of hydrophobic CNC. Other measurements on surface properties of these surfactant-treated CNCs are given in a previous publication.[11]

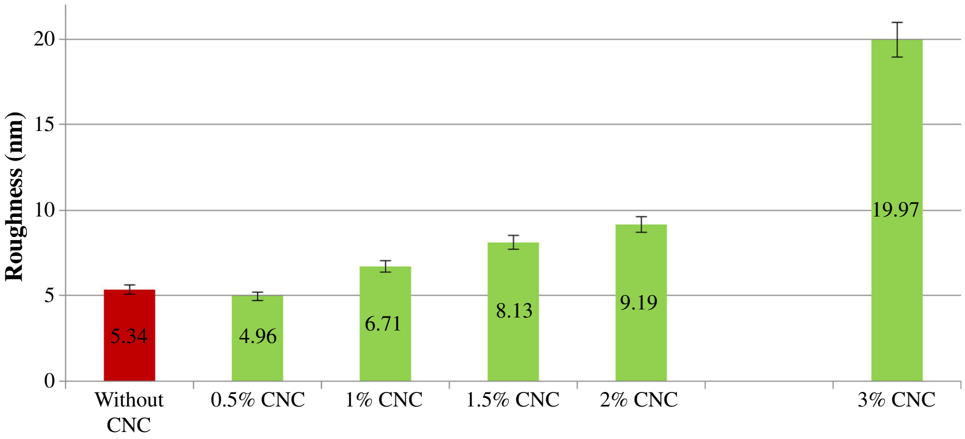

Fig. 6: Surface roughness of varnishes without and with added hydrophilic CNC

To study dispersion properties of varnishes with added modified CNCs, additional roughness measurements were performed by AFM,[23] on cured coatings with no CNC and 2% CNC (w/w), in five different types, as described in experimental section: unmodified (hydrophilic) CNC; CNC-HDTMA; CNC-FPI; CNC-Acryloyl; CNC-TMA (Fig. 9). The surface roughness of coatings incorporating modified CNCs are significantly lower, about 30%, than that of coatings containing same amount of hydrophilic (unmodified) CNCs. Surface roughness of coatings containing modified CNCs, especially those modified by HDTMA, acryloyl chloride, and hydrophobic CNC from FPInnovations are approximately at the same level as for coatings without nanoparticles. This means that the dispersion level of these hydrophobic CNCs is better, at least at the surface, where it is more important, for the final appearance of the coating. Possibly, more CNCs could be incorporated, although high viscosity could become a hurdle to favor the spraying of the formulation. This also shows that having hydrophobic nanoparticles is desirable when working with an emulsion.[20]

Mechanical properties of coatings

Adhesion

To study mechanical properties of these coatings, pull-off tests were performed (Fig. 4). It is important that CNC addition (modified or not) does not worsen the adhesion characteristics of coatings. This study reveals that the adhesion strength of coatings with or without addition of CNC is practically at the same high level (Fig. 10). However, it was noticed that coating with 2% CNC modified with HDTMA presents slightly higher adhesion strength compared with coatings containing CNC modified with TMA and hydrophobic CNC modified by FPInnovations. Since the hydrophobic

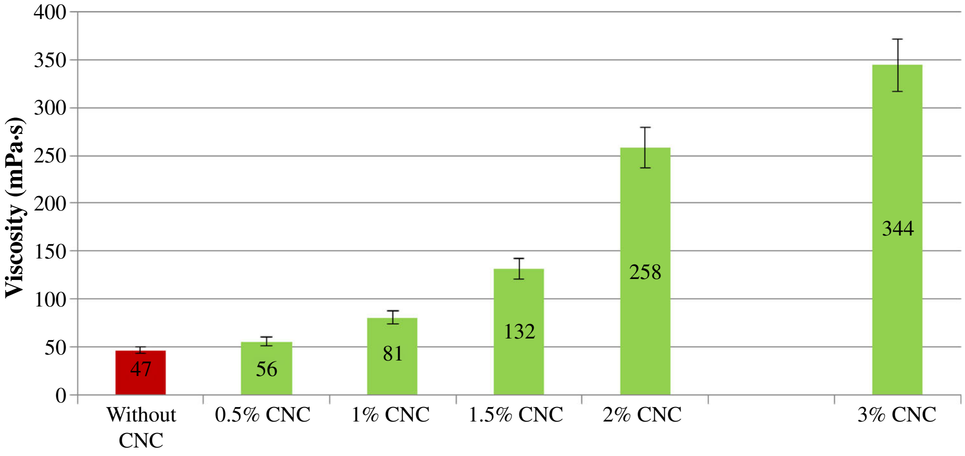

Fig. 7: Viscosity of varnishes formulations without and with addition of hydrophilic CNC

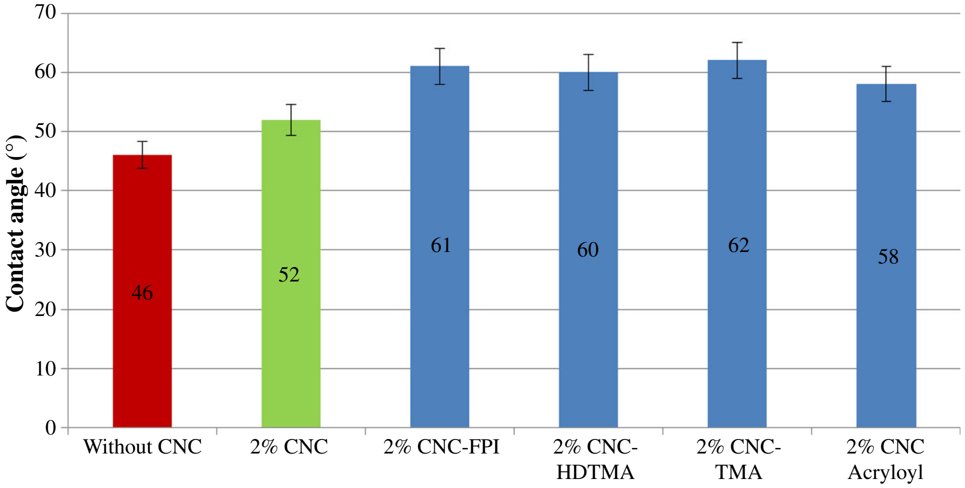

Fig. 8: Contact angle for coatings on wood without and with CNC (unmodified and modified)

CNC has been modified by FPInnovations by proprietary process, it is not possible to determine why it has lesser adhesion strength. Still, this shows that the higher viscosity (Fig. 7) of CNC-based coatings does not interfere significantly with coating adhesion (Fig. 10).

Hardness

Hardness is an important property of coatings, which is related to durability and long-term performance. Any particle or nanoparticle added to the coating would be expected to enhance this property and the system should behave as a true composite. Figure 11 shows König hardness of UV-cured waterborne nanocomposite coatings with and without CNC (unmodified and modified), higher oscillations show that material is harder. This test reveals no significant difference between hardness of coatings with different types of CNC. This is not so surprising since the particles are covalently bonded to the continuous phase, but simply dispersed within. However, we hoped that the acryloyl choride residue on the nanoparticle would have coupled to the acrylates in the continuous phase resulting in an increased hardness, but it failed to do so.

Wear properties

Exploring wear and damage resistance of these nanocomposite coatings is the main purpose of this study. UV coatings are known for their outstanding wear properties, as they cure to a hard finish. To evaluate these characteristics, abrasion (Fig. 12) and scratch (Fig. 13) resistance experiments were performed on the various coatings applied on wood.

Both tests revealed that CNC-reinforced varnishes, even with 2% unmodified CNC added, showed improved mechanical resistance. More detailed results about mechanical properties of varnishes (and paints) with hydrophilic CNC were presented in our other publication.[23] Addition of 2% CNC-HDTMA, CNC-Acryloyl, and CNC-FPI improved the mechanical resistance of UV-cured waterborne coatings even further, up to 30–40% (Fig. 12), as a lower amount of

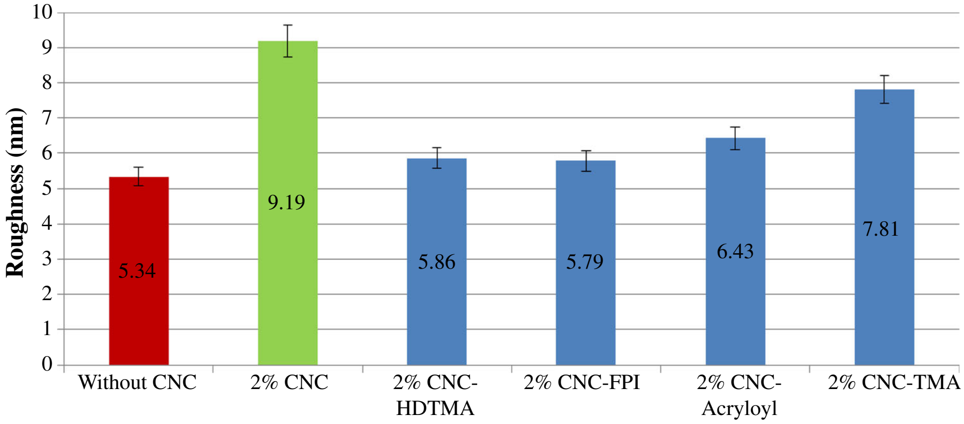

Fig. 9: Surface roughness of varnishes without and with 2% unmodified and modified CNC

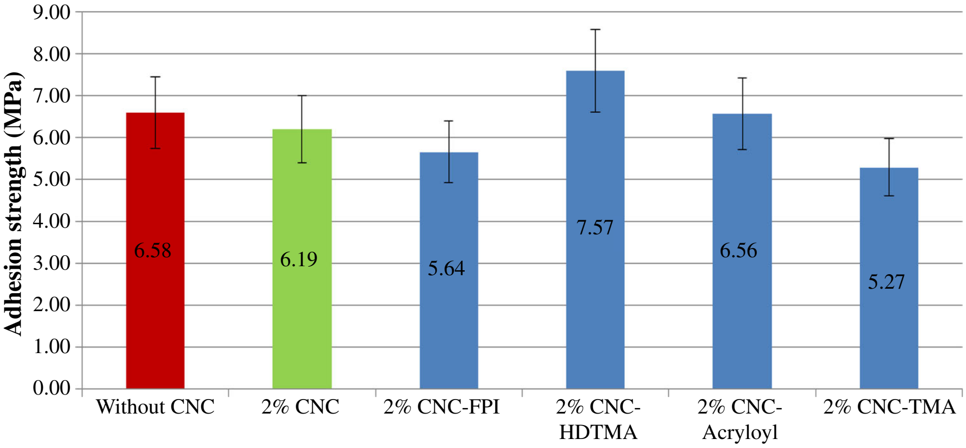

Fig. 10: Adhesion strength of cured varnishes without and with 2% unmodified and modified CNC

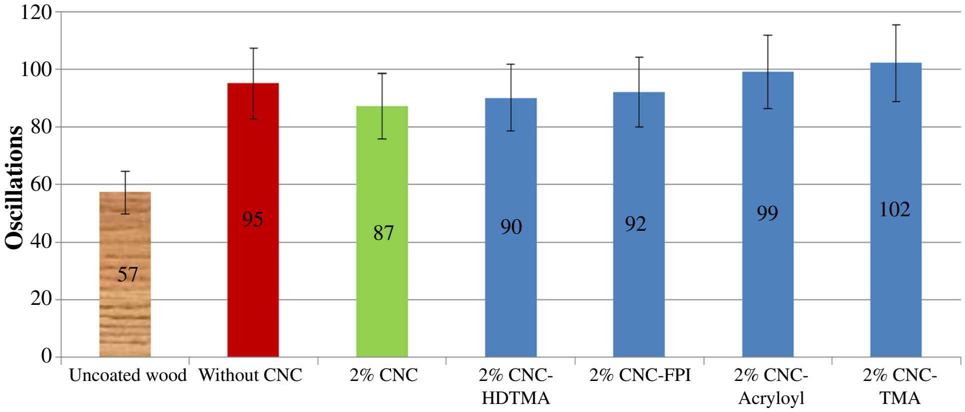

Fig. 11: König hardness of uncoated wood and coated with UV-cured waterborne nanocomposite coatings with 2% unmodified and modified CNC

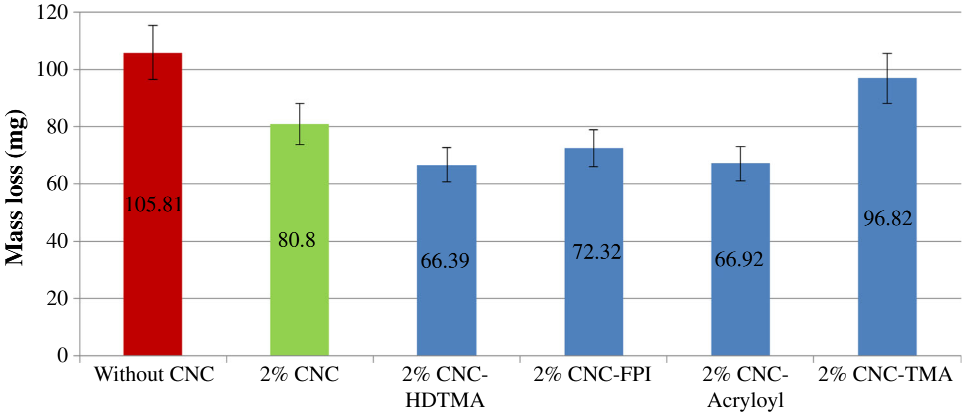

Fig. 12: Mass loss after abrasion resistance test of wood coated with varnishes without and with 2% unmodified and modified CNC

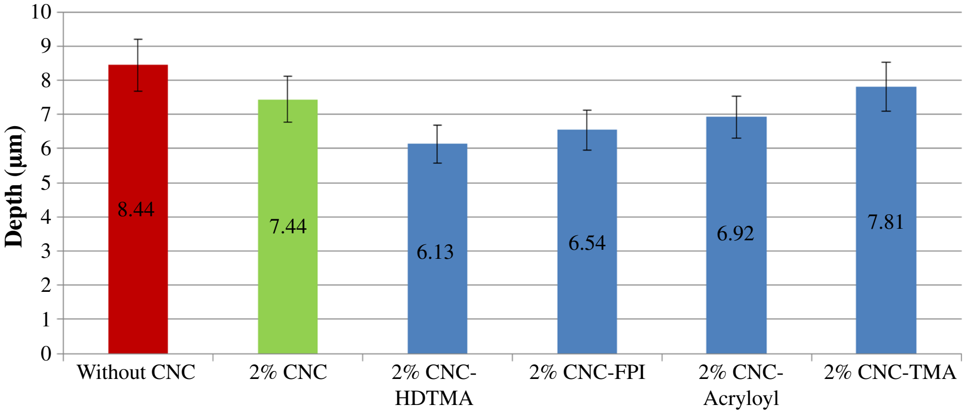

Fig. 13: Depth of scratches after scratching the varnishes without and with 2% unmodified and modified CNC

material was abraded from the surface following the test. In comparison with the results found with CNCs, a significantly lower resistance to abrasion can be noted following nanosilica addition at 2% level to coating formulation. However, much larger amounts of alumina than CNC, up to 40%, can be added to coatings.[7]

The scratch resistance was improved about 20–30% for the same CNC-reinforced varnishes (Fig. 13), as depth of scratches decreased with addition of the same hydrophobic CNC. Addition of CNC-TMA did result in improving the scratch resistance, which can be due to its lower dispersion state in the varnish (Fig. 9). If we relate dispersion level (Fig. 9) with mechanical resistance (abrasion and scratch: Figs. 12 and 13), some correlations can be shown. It turns out that the varnishes which have good CNC dispersion are much more resistant. So we can note that efficient dispersion is the key in improving the mechanical resistance of the resulting nanocomposite varnish. It is reasonable to think that the CNC chemical modification did not change mechanical or structural characteristics of CNC itself and helped to make the CNCs more compatible with the coating matrix, which should favor its dispersion.[11] Similarly, Bauer et al.[7,9,20] obtained increased abrasion resistance of UV-cured acrylates with the use of hydrophobized silica and alumina nanoparticles. These results also suggest that characterization of dispersion with AFM, although being a surface phenomenon, does reflect the quality of the dispersion in the bulk, which is related to bulk wear and scratch resistance.

Not all nanoparticle addition gives positive results. In another study by Sow,[29] UV-waterborne varnishes reinforced with inorganic nanoparticles of alumina and silica evidenced increased mass loss upon abrasion, as compared to varnishes without nanoreinforcement, indicating a decrease of mechanical resistance of coatings, possibly because particles were not hydrophobized, which could have created weak interfaces between the filler and the matrix. In addition, hardness of above mentioned coatings was decreased by about 50%,[5] despite an increase in adhesion strength. In contrast, our results show an increase of mechanical resistance, due to the presence of CNCs. We believe that varnish strengthening is due to proper CNC dispersion within the organic varnishes due to right hydrophobic/hydrophilic balance of modified CNCs, as well as its intrinsic features (high aspect ratio and Young's modulus). Furthermore, we may speculate that geometrical characteristics of CNCs may serve as nanostrusses, which can reinforce the binder matrix, like metallic fixtures for the modern high-resistance buildings, but at the nanolevel.

Conclusion

In this study, the influence of addition of nanoparticles of CNC on the properties of water-based UV-cured coatings for wood products was studied. It was shown that it is possible to improve the quality of the dispersion of CNC in coatings using simple chemical reactions made on the surface of CNC. Dispersion was characterized by measuring the surface roughness by AFM. For these varnish formulations, an optimum concentration of CNC (2%) was found. Varnishes with 2% CNC-HDTMA, CNC-Acryloyl, and CNC-FPInnovations gave approximately the same roughness as reference coating (without CNC nanoparticles), which suggests a good CNC dispersion state. The impact of the CNC addition in the paint and varnish formulations was assessed. Hardness and adhesion test show that addition of CNC does not worsen mechanical characteristics of neat varnishes, while in the case of CNC-HDTMA these were even improved. The effect of CNC on varnish formulation behavior differs significantly in terms of abrasion and scratch resistance. The property which is of greatest interest, wear resistance, was increased by 40% with addition of 2% of surface-modified CNC with HDTMA. From all tests done in this study, we can conclude that varnishes with 2% CNC-HTDMA and CNC-Acryloyl are the most efficient. In next paper, we will examine properties of those varnishes (and corresponding paints) following accelerated aging and weathering.

Acknowledgments Thanks to the Fonds de Recherche Nature et Technologie du Québec, the Conseil de Recherches en Sciences Naturelles et Génie du Canada, and Arboranano for funding this research as well as FPInnovations' pilot plant for the production of CNC.

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