Water-based Nanocrystals Cellulose Coatings

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Introduction

In order to improve its' various properties, inorganic reinforcing agents are added to coatings. Mechanical properties such as abrasion resistance, scratch resistance, impact resistance and hardness can be improved by the addition of inorganic fillers. Optical properties, such as gloss, can also be modified by the addition of these materials. Wettability and adhesion, two closely related properties, can also be modified/enhanced by the addition of some additives. The main inorganic additives used to modify coating properties are silica (fumed or crystalline), aluminum oxide, calcium carbonate, clay and titanium oxide.

Nanocrystal cellulose (NCC) is a renewable and recyclable material. These factors, coupled with the fact that NCC has great mechanical and optical properties, make it a very interesting material that can be produced and used on a commercial scale. As the coating industry uses large amounts and varieties of additives and reinforcing agents, it would benefit greatly from the addition of NCC.

NCC was successfully dispersed in different solvents or polar polymers such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) (Samir and al., 2005; Viet and al., 2007), polyvinyl alcohol (PVA) (Paralikar and al., 2008) and poly(oxyethylene) (Samir and al., 2005). A good dispersion of NCC could be obtained in most cases. These studies have shown that tensile properties can be greatly improved with the addition of NCC. The tensile strength and elongation at break have particularly benefited from the addition of NCC. On the other hand, mechanical surface properties (abrasion resistance, scratch resistance, impact resistance, hardness), which are essential for the coating industry, were not studied.

In this document, the surface properties as well as the optical properties of the water-based nanocomposites prepared are presented. NCC was added to a water-based acrylic lacquer and to a UV water-based varnish.

Method

Nanocrystal dispersible cellulose (D-NCC) extracted from wood with an acid hydrolysis process developed by FPInnovations Paprican was used in this project. Following this procedure, nanocrystal cellulose of 200 nm length, 10 nm in diameter and a specific area of 6000 m^2/g was recovered. NCC powder was milled for 24 hours using a jar mill. The resulting powder was added to two different water based systems: the first one being an acrylic emulsion lacquer, the second one a UV varnish. NCC was added at concentrations ranging from 0 to 5% per weight of the dry coating film.

Different techniques were employed to incorporate NCC to the two coating systems, allowing good dispersion of the latter. The first developed approach is valid for hydrosoluble coatings. In this case, a small quantity of concentrated aqueous suspension of NCC or grinded NCC powder is embedded directly into the polymer resin. The latter is mixed vigorously for 15 to 45 minutes using a high speed mixer or a bead mill. This approach does not apply to hydrodispersible coatings, such as acrylic emulsions. High speed mixing or bead milling can destroy the emulsions.

Another approach was developed for water dispersible resins (emulsions or colloidal dispersion). By adding a highly concentrated aqueous suspension of NCC (10% by weight or more) to the resin and by gently mixing the mixture for at least 30 minutes, NCC can be uniformly dispersed in the acrylic emulsion. The aqueous suspension of NCC could be prepared by adding a low concentrated NCC suspension or from powder. In the last case, a good dispersion can be obtained by the aim of an ultrasonic probe.

Nancomposites formulations prepared were applied on two different substrates: yellow birch panels and steel plates. Steel plates were chosen in order to decrease the effects of the substrate. Mechanical and optical properties were recorded. The hardness was measured by monitoring the damping time of the oscillations of a pendulum swinging in a vertical plane from an initial angle of 6^o to a final angle of 3^o. Experiments were performed according to ASTM standard D 4366 *"Standard Test Methods for Hardness of Organic Coatings by Pendulum Damping Tests"*.

Abrasion resistance was determined using the Taber Rotary Platform Abraser. The abrasives selected for this study are the S-42 sandpaper strips attached to the periphery of the CS-0 resilient rubber wheels. Mass loss was determined after 50 and 100 rotations. These tests were performed according to ASTM standard D 4060.

Impact resistance was determined according to ASTM standard D 2794 "*Resistance of Organic Coatings to the Effects of Rapid Deformation"*. Direct impact was determined using the falling weight test. Samples were subjected to the impact of a 2 lbs weight at different heights. The height at which cracking or loss of the coating was observed was noted as the impact resistance.

Optical properties measurements were also performed. Color, gloss and optical clarity measurements were studied. Coating films were applied on LENETA opacity charts. Color was determined by means of a color-guide 45/0 from BYK-Gardner. The CIELAB color scale was used for color measurements. Three basics coordinates (L*, a* and b*) were determined for each sample. They were compared with parameters found for the formulation without NCC. Delta values (ΔL*, Δa* and Δb*) were calculated for each coordinate. Tests were performed according to ASTM standard D 2244. Opacity measurements were also performed with the color-guide 45/0. Finally, the influence of NCC on the gloss level was determined by the micro-tri-gloss equipment from BYK Gardner. This instrument determines simultaneously the gloss at three different geometries, 20^o, 60^o and 85^o.

Results and discussion

Mechanical properties

Two types of coatings were used in this study. Both products can be used in the manufacture of furniture and kitchen cabinets. They have different mechanical and chemical performances. The acrylic lacquer is a thermoplastic coating that has a mechanical and chemical resistance significantly lower than the other product used in this study, a UV water-based varnish. The latter is a thermoset material that has very good mechanical, thermal and chemical resistance. For both products, it was possible to significantly improve the mechanical properties. Few examples are presented here.

Acrylic lacquer

Hardness of the formulations prepared from the acrylic lacquer with different NCC concentrations was studied. Figure 1 shows the obtained results. In order to reduce the effect of the substrate, measurements were made on wood, but also on a standardized steel plates. Adding a small amount of NCC, 1% by weight, leads to a significant increase in the hardness of the lacquer studied. However, when much larger NCC concentrations were used, the hardness decreased to become lower than the one of the original lacquer. NCC is not a very hard additive, such as aluminum oxide; however it is shown that this additive can improve hardness.

Impact resistance measurements were subsequently performed. Results are presented in Figure 2. The falling weight test reveals that NCC can increase the impact resistance of waterborne acrylic lacquer. Formulations prepared with 2.5 and 3.5 %wt of NCC lead to the best results. The limitation of crack propagation by the addition of NCC could explain these results. Similar results have already been achieved through the addition of clay in different coatings. A similar explanation is proposed to explain the improved impact resistance in this study.

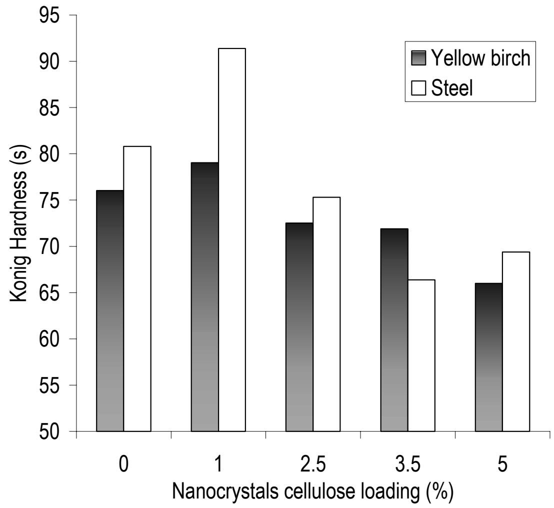

Figure 1: Hardness of the formulations prepared from the acrylic lacquer and different concentrations of NCC

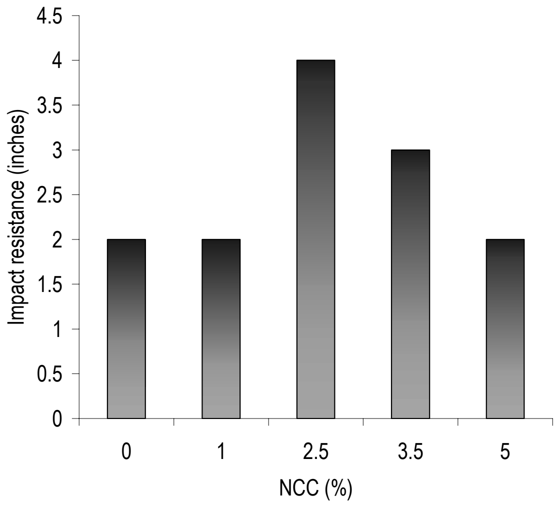

Figure 2: Impact resistance of the formulations prepared from the acrylic lacquer and different concentrations of NCC

UV water-based varnish

The abrasion resistance of UV coatings is in general very good. However, this study has demonstrated that it is still possible to improve this property by the addition of NCC. Indeed, the mass loss recorded for all the formulations with NCC is lower than for the formulation without NCC. Figure 3 presents the mass lost obtained after 100 rotations of S-42 sandpaper strips. This graph shows clearly that NCC can improve the abrasion resistance of the UV water-based coating.

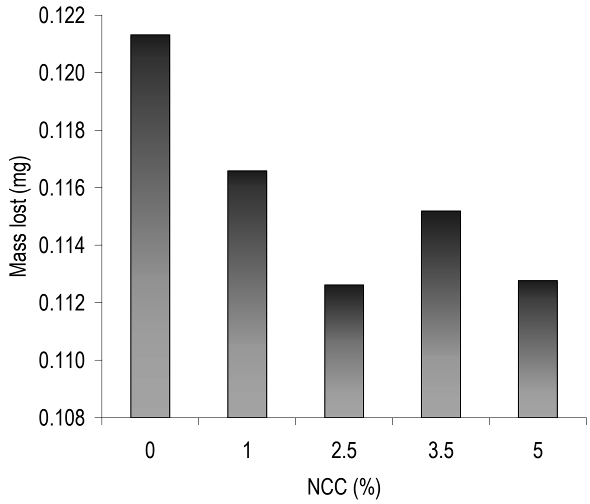

Figure 3: Abrasion resistance of nanocomposite UV varnish formulations prepared from 1 to 5 %wt of NCC

Adhesion to substrate and interlayer adhesion were also studied. A good adhesion is essential so that the product has a good life as well as good mechanical properties. The effect of NCC on the adhesion of UV water-based varnish to the yellow birch panels was examined using two methods. Pull off and cross hatch tests lead to the same results. The addition of NCC creates a better adhesion. Indeed, it was found that, more important the concentration of NCC was, the more important was the adhesion. Figure 4 shows the results of the pull off tests. An important increase can be obtained following the addition of NCC. NCC is a hydrophilic material. Studies of contact angles were performed and demonstrated that the addition of NCC can improve the adhesion. Getting a better wetting can undoubtedly increase the adhesion of coatings to substrate. In order to confirm these results, cross hatch tests were performed. Optical microscopy was performed on the tested samples. Figure 5 presents an image of the UV varnish without NCC and an image of the formulation with 3.5 %wt of NCC. As it is possible to see, the addition of NCC leads to a better adhesion of the UV varnish to the yellow birch panels. It is possible to note that for the sample prepared with the formulation without NCC, significant portions of the coating had been torn from the wood surface.

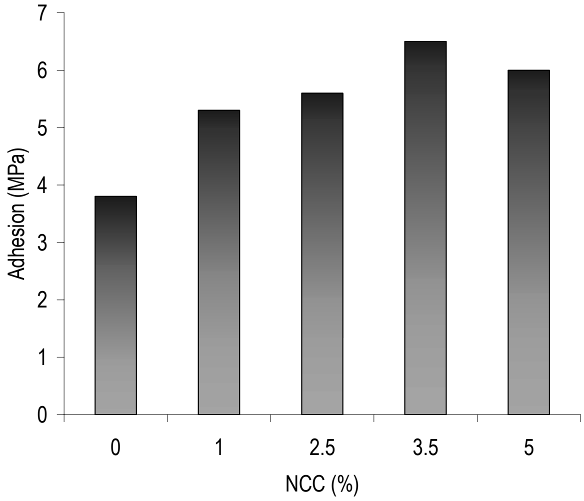

Figure 4: Adhesion of the nanocomposites UV water-based formulations to yellow birch panels

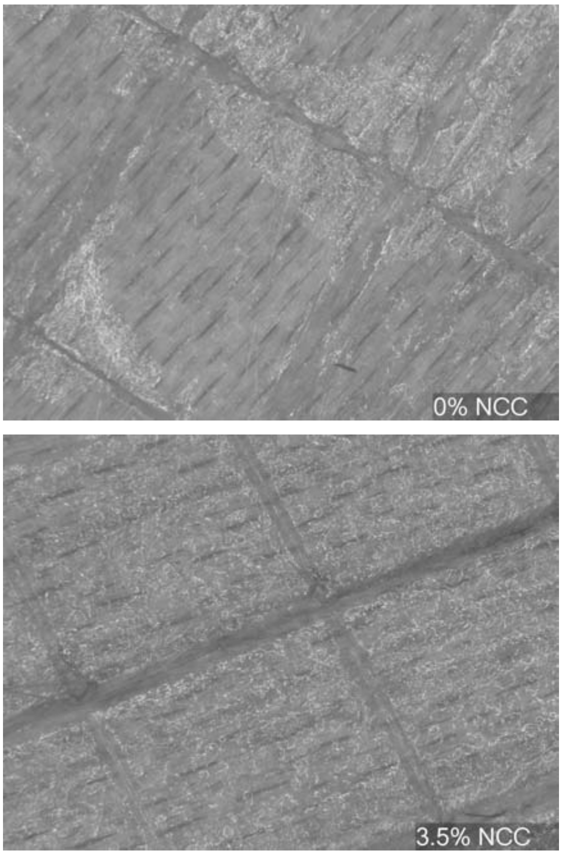

Figure 5: Cross hatch experiments performed on UV water-based varnish without NCC and with 3.5 %wt of NCC

The interlayer adhesion was also found to be improved through the addition of NCC. Figure 6 presents an image of the UV varnish formulation without NCC. This picture shows that the adhesion between the two layers is low. Indeed, a separation of the two coating layers was observed. Similar experiments were performed for the formulations with NCC. In all cases, interlayer adhesion was found to be very good. No separation of the coating layers could be observed.

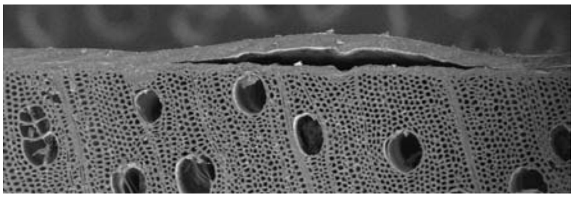

Figure 6: Scanning electron microscopy image of the UV varnish without NCC

Optical properties

Dispersion of NCC in coatings leads to changes in appearance. The gloss was found to be modified by the addition of D-NCC. Moreover, according to the method of incorporation of the NCC in coatings (suspended in water, grinded NCC powder, added directly into the coating, etc.), the effect on the gloss will be different. In general, it was observed that when the concentration of NCC increased, gloss decreased. Table 1 presents the gloss values found for the two coating systems. In both cases, it was found that NCC decreases significantly the gloss.

Table 1: 60° Gloss of the acrylic lacquer and UV varnish formulations

% NCC	Acrylic Lacquer	UV varnish
0	58.7	38.9
1	43.1	28.4
2.5	33.7	23.3
3.5	32.1	13.4
5	25.3	14.0

For the acrylic lacquer, the values found were compared with those of formulations prepared with a commercial mating agent, fumed silica. Figure 7 presents the comparison of NCC and silica. The silica mating agent was found to have a greater mating power than NCC, however this additive also leads to an important opacity increase. Figure 8 presents the opacity values for the formulations prepared with silica and NCC. The formulation prepared with 1 %wt of silica leads to the same opacity than the formulation prepared with

5 %wt of NCC. Moreover, at concentrations of 3.5 %wt or more of silica, the viscosity becomes very important and it is impossible to prepare high quality films. On the other hand, the addition of NCC hardly changes the viscosity of the finishing products used in this study. Figure 9 presents the effects of the addition of NCC and silica on the viscosity of the acrylic lacquer.

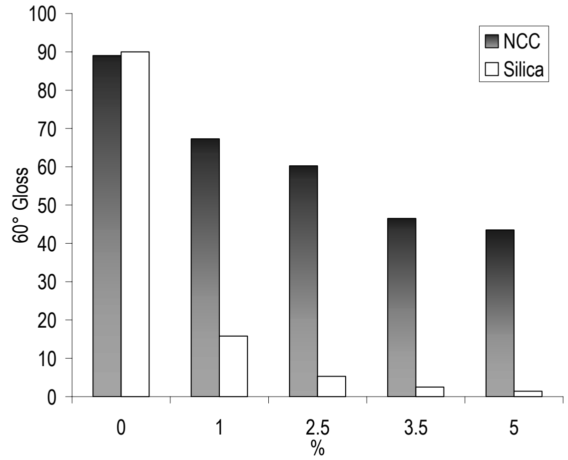

Figure 7: Gloss of the formulations prepared with NCC and a silica matting agent

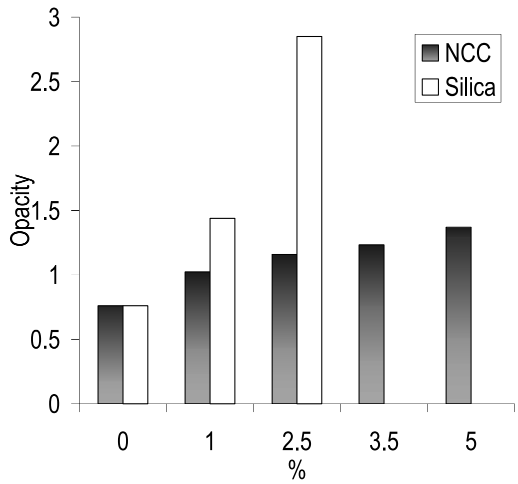

Figure 8: Opacity values for the formulations prepared with NCC and silica

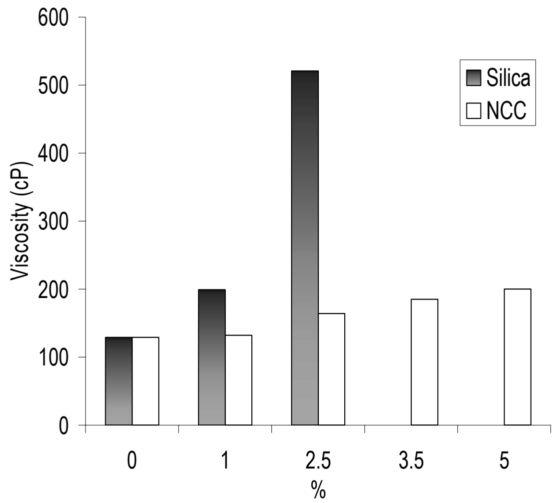

Figure 9: Viscosity of the formulations prepared with NCC and silica

Finally, Figure 10 presents the color change with the addition of NCC and silica. The addition of the silica mating agent significantly affects the brightness of the coating. Indeed, important whitening was observed following the addition of silica. In return, the addition of NCC affects only slightly the color of the coatings. Parameters a* and b* were not significantly changed by the addition of NCC and silica.

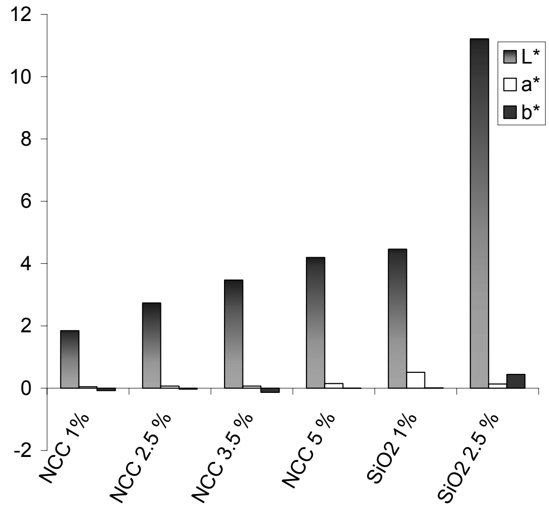

Figure 10: Color parameters (L*, a* and b*) of the formulations prepared with NCC and silica

Conclusion

In this study, nanocrystal cellulose was added to two different systems: an acrylic lacquer and a UV water-based varnish. Mechanical properties of the surface were studied. This study showed that NCC can significantly improve the mechanical performances of the coatings. Abrasion resistance and hardness are among the properties that were improved. Optical properties were also modified by the addition of NCC, such as Gloss, color and opacity. The main changes come from the gloss. NCC was found to decrease significantly the gloss of both coating systems. However, when compared with other mating agents, especially silica, NCC has less important mating properties. In return, the color and opacity changes remain very low when NCC is added compared to silica.

Initial results are encouraging and suggest that NCC could take on as an important market share product in the coatings industry. Several studies should still be made to improve the dispersion of the NCC in water-based coatings.

References

Azizi Samir, M.A.S., Alloin, F. & Dufresne, A. 2005, A review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field, Biomacromolecules, 6, 612-626.

Viet, D., Beck-Candanedo, S. & Gray, D.G. 2007 Induced phase separation in cellulose nanocrystal suspensions containing ionic dye species, Cellulose, 14, 109

Paralikar, S.A., Simonsen, J., Lombardi, J., 2008, Poly(vinyl alcohol)/cellulose nanocrystals barrier membranes, J. Membrane Sci., 320, 248-258

M.A.S. Azizi Samir, L. Chazeau F. Alloin, J.-Y. Cavaill, Dufresne , J.-Y. Sanchez, 2005, POE-based nanocomposite polymer electrolytes reinforced with cellulose whiskers Electrochimica Acta 50, 3897–3903