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Effect of addition of nanosized UV absorbers on the physico-mechanical and thermal properties of an exterior waterborne stain for wood

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ABSTRACT

This study describes the effects of the addition of inorganic nanosized UV absorbers on physico-mechanical and thermal properties of an exterior commercial acrylic-based waterborne stain for wood. Electronic microscopy and water vapor (WV) permeability measurements were performed to characterize the free films of the acrylic stain and resulting nanocomposite coatings. An accelerated weathering method was used to evaluate aging behavior of the coatings on wood through appearance, T_g, abrasion resistance, adhesion strength, hardness and Young's modulus changes. In addition to improving the protection against UV, the doped TiO_2 and silica-coated ZnO nanoparticles in powder form have improved the abrasion resistance and barrier effect against water vapor diffusion of the acrylic stain. For most of nanocomposite coatings, the addition of ZnO hydrophilic nanoparticles in predispersed form has resulted in a decrease in WV permeability, while the adhesion strength and abrasion resistance of those coatings were negatively affected. The addition of ZnO nanoparticles has decreased the T_g of the acrylic stain. Finally, the accelerated weathering has induced an increase in T_g, hardness, Young's modulus (stiffness) and an increase in apparent adhesion strength and abrasion resistance of the coatings. The T_g values of the aged nanocomposite coatings were lower than that of unmodified acrylic stain.

1. Introduction

The interest in waterborne coatings for exterior wood has gained importance due to environmental concerns. Hence, more complex formulations are developed to reduce the VOC content. Otherwise, maintaining forest products as competitive materials in the building industry demands waterborne coatings with high durability, helping in life extension of wood products. The wood coatings are not only decorative, while reducing the maintenance efforts, but also provide protection against UV radiations and moisture uptake. The two lasts points are the main cause of premature aging [1,2]. In general, the waterborne coatings have a higher rate of liquid water and water vapor diffusion in comparison to solventborne alternatives [3,4]. Moreover, the performance of this kind of coating depends not only on appearance preservation by UV resistance but also on mechanical resistance and adhesion retention by maintaining the coating integrity during service life. While a good adhesion of the coating is necessary to protect the wooden substrate, it also prevents the normal motions relative to the wood which a coating makes (expansion, contraction) during weathering. Podgorski and Roux [3] have shown that the evolution of glass transition temperature (T_g) is related with the coatings durability. Enhancing the durability of an exterior coating is related to an increase in the coating flexibility due to a decrease in T_g below the temperature of use [5].

The use of nanoparticles is a convenient way to enhance waterborne coatings durability as their aspect ratio is high and their efficiency is also high when compared to that of micrometric particles. Recent studies have shown that waterborne coatings containing nanosized inorganic UV absorbers are effective against the degradation due to ultraviolet (UV) light exposure [6,7]. TiO_2 while ZnO nanoparticles are mostly used as UV blocking agents [8,9]. ZnO nanoparticles were found also to increase the thermal stability of polymers [10]. Dhoke et al. [11] have shown that increasing the concentration of the ZnO nanoparticles in a silicone modified alkyd–based waterborne coating has enhanced the abrasion resistance. Other investigations have shown that TiO_2 nanoparticles are more effective in reducing the wear rate in different polymers than micro-TiO_2 [12].

In this work, the general objective of this study was to evaluate the impact of addition of ZnO and TiO_2 nanoparticles on the physico-mechanical and thermal properties of a commercial acrylic-based waterborne solid-color stain for exterior wood. In this purpose, several waterborne nanocomposites coatings for exterior wood formulated with ZnO and TiO_2 nanoparticles were evaluated through accelerated weathering. The aging behavior was

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Table 1
Formulation of the acrylic-based waterborne solid-color stain.

Additive	% Wt.
100% acrylic copolymer emulsion resin	36.9
Nonionic alkylaryl polyether alcohol, pigment wetting agent	0.1
TiO_2 rutile, pigment	16.3
Linseed oil emulsion	5.9
Defoamer	0.4
Hydrous calcium magnesium silicate, filler	8.3
Ethylene glycol, co-solvent	2.0
Nonionic urethanes, rheology modifier	2.0
Clay, rheology modifier	0.8
Ester–alcohol, coalescent agent	1.2
Water	17.1
Others	9.0

investigated by appearance changes (color and gloss), thickness loss, and T_g evolution. The mechanical properties of the coatings were studied through adhesion strength and abrasion resistance characterization before and after accelerated weathering. The water vapor permeability of the acrylic stain itself and of the as prepared nanocomposites was studied, on the un-aged coatings only.

2. Experimental

2.1. Wood and coating materials

Black spruce (Picea mariana (Mill.) B.S.P.) wood was flat-sawn in tangential sections and then conditioned in a climate controlled room at a temperature of 20 °C and a relative humidity of 40% until they reached a constant mass. Prior to application of the stains, the wooden boards were disc-sanded on the flat grain with papers of grit 80, 100, and 120 that were used in sequence.

Eight coatings formulations based on a commercial exterior waterborne acrylic-based stain for wood (24% pigment volume concentration (PVC)) provided by Sico Inc. (Montreal, Canada – AkzoNobel group) were used in this study. Table 1 provides a brief overview of the waterborne solid-color stain formulation (coating A) that was used as a control to compare with the performance of the nanocomposites coatings. From our subsequent Scanning Electron Microscopy analysis equipped with energy-dispersive X-ray spectrometry, we found this commercial formulation already contained nanoparticles of several kinds, unknown to the producer, and these were due probably to the large size distribution of the grinded micro inorganic pigments/additives added by the commercial formulator.

The ZnO nanoparticles used in this study were VP AdNano ZnO 20, hydrophilic version (approximate primary particle size of 20 nm and specific surface area of 20–25 $m^2\,g^{-1}$) and AdNano Z5, silica-coated version (fully coated with a SiO_2 shell, primary particle size of 10–75 nm [13]), both obtained from Evonik-Degussa (Germany). The doped TiO_2 nanoparticles were Hombitec RM 400 (approximate primary particle size of 10 nm and specific surface area of 110 $m^2\,g^{-1}$) obtained from Sachtleben Chemie (Germany).

The nanocomposite coatings formulations prepared with nanoparticles in powder form are listed in Table 2. Several predispersed systems of 20% (w/w) hydrophilic ZnO nanoparticles were used to prepare the nanocomposite coatings that are listed in Table 3. The preparation procedure was explained in details in a previous paper [14]. The nanoparticles were added to the formulation given in Table 1. Finally, seven coats of the formulated coatings were applied on boards with a Roller Coater machine (model KRF-60 from TruPro International) until the dry average thickness reached 70 ± 5 μm.

Table 2
Formulation of the nanocomposite coatings prepared with nanoparticles in powder form.

Coatings formulation	Type of nanoparticles	% Wt. nanoparticles
A	–	0
B	TiO_2, doped[a]	1
C	ZnO, silica-coated[b]	1
D	ZnO, silica-coated[b]	2

[a] Doped TiO_2 nanoparticles, rutile, 10 nm, 110 $m^2\,g^{-1}$, Hombitec RM 400 (Sachtleben Chemie, Germany).
[b] Silica-coated ZnO nanoparticles, AdNano Z5 (Evonik-Degussa, Germany).

2.2. Accelerated weathering

Accelerated weathering tests were performed in a Xenon arc Weather-O-meter Ci-65 (Atlas Material Testing Technology, USA) following ASTM G155 [15]. The coatings applied on wood were cyclically exposed for 1000 h to UV-A (λ = 340 nm) radiation at 63 °C (temperature on black panel) and relative humidity of 50% for 108 min and water spray for 12 min at the same radiation conditions. The irradiance intensity was 0.35 W m^{-2} nm^1. The panels exposed consisted of 10 samples of each formulation of the nanocomposite coatings including a control of acrylic solid-color stain.

Chromatic coordinates L^*, a^*, b^* were measured with a colorimeter (Byk-Gardner) according to ASTM 1347 [16]. Surface specular gloss of the coatings was measured at 60° angle of incidence through a portable micro-tri-glossmeter (Byk Gardner) according to ASTM D 523 [17]. The thickness loss of the coatings after the weathering cycle was measured with a digital ultrasonic thickness gauge Positector 200 (DeFelsko Corp., NY) according to ASTM D 6132 [18].

2.3. Characterization of coatings

2.3.1. Microscopic observation

In order to study nanoparticles dispersion in the dry film, cross-sections of the un-aged coatings were studied with a Field Emission Scanning Electron Microscope, JEOL JSM-7600F (Jeol Ltd., Japan), equipped with a NORAN energy-dispersive X-ray spectrometry EDS system. The interfacial region between the coating and wood substrate was investigated with a Scanning Electron Microscope JEOL 840A (Jeol Ltd., Japan). The observations were performed on un-aged and aged samples made up of coated wooden cubes of 1 cm^3. Prior to SEM investigation the cross-sections were gold–palladium-coated in a vacuum sputter.

2.3.2. Thermal characterization

A Mettler Toledo DSC 822e differential scanning calorimeter was used for the investigation of glass transition temperature of nanocomposite coatings. The DSC program used was −40 °C (initial temperature), a ramp of 20 °C/min to 60 °C (final temperature), under nitrogen flow. The un-aged samples were analyzed as free films of coatings. The aged samples were collected carefully by peeling and cutting off the wood substrate using a scalpel. Appropriate amount of coatings samples (ca. 15 mg) were sealed in aluminum sample pans. The data were collected and analyzed with Mettler Star^e software version and the T_g was measured as inflection point of the DSC curve.

2.3.3. Water vapors films permeability

The water vapor permeability of un-aged nanocomposites and acrylic latex stain free films was determined through the dry cup method described in ASTM D1653-03 [19]. The mass transfer of the water vapor was monitored by the increasing mass of a cup filled with anhydrous calcium sulphate (indicating Drierite Desiccant)