

Mold Resistance of Nano and Micronized Particles-Treated Wood After Artificial Weathering Process ^[*]

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Abstract: Wood and wood based materials under outdoor conditions may lose their appearance and performance properties by time. Color differences, cracks, rough surface may occur within a few years in unprotected wood. These undesired formations could be avoided by technical applications such as coatings on wooden surfaces by paints and varnish since such coating materials include special additives in their formulations such as UV absorbents, pigments, etc. Novel systems with nano or micronized particles may have superior properties when compared to conventional wood preservatives.

In this study, it was investigated the effectiveness of Scots pine wood samples impregnated with nano-scale preservatives, micro-scale preservatives and common wood preservatives, against mold fungi before and after artificial weathering process. Accelerated weathering tests of the specimens were performed in a Xenon arc radiation cabinet with water spraying property. Artificially weathered and un-weathered wood specimens were evaluated for resistance to mold fungi according to the ASTM D4445. General mold score results collected before and after artificial weathering process showed that CCA and MCQ-treated specimens had the best performance properties; however, nano zinc oxide-treated wood specimens had the weakest performance against mold fungi.

Keywords: Artificial weathering, micronized copper, mold growth, nano copper, nano zinc.

Mikronize ve Nano Sistemlerle Emprenye Edilmiş Odunun Yapay Yaşlandırma İşlemi Sonrası Küflenmeye Karşı Dayanıklılığı

Öz: Dış hava koşullarında odun ve odun esaslı malzemeler zaman içerisinde görünüm ve performans özelliklerini kaybedebilmekte, korumasız ahşapta birkaç yıl içerisinde renk farklılıkları, çatlaklar, pürüzlü yüzeyler oluşabilmektedir. Bu istenmeyen oluşumlar, ahşap yüzeylerine UV absorbe eden maddeler, pigment gibi özel katkı maddeleri içeren boya ve vernik uygulanmasıyla önenebilmektedir. Nano veya mikronize parçacıklara sahip yeni sistemler, geleneksel ahşap koruyucularla karşılaştırıldığında üstün özelliklere sahip olabilmektedir.

Bu çalışmada nano ölçekli, mikro ölçekli ve geleneksel ahşap koruyucular ile empenye edilmiş ahşabın yapay yaşlandırma işlemi öncesi ve sonrası küf mantarlarına karşı performansı incelenmiştir. Test numunelerinin hızlandırılmış yaşlandırma testleri, yağmurlama özelliği olan Xenon-ark yaşlandırma kabini gerçekleştirilmiştir. Yaşlandırma işlemine maruz bırakılmamış ve yapay olarak yaşlandırılmış odun örnekleri ASTM D4445 standart test metoduna göre küflenme testlerine tabi tutulmuştur. Elde edilen sonuçlar, CCA ve MCQ ile empenye edilen örneklerin en iyi küflenme karşıtı performans özelliklerine sahip olduğunu göstermiştir. Bununla birlikte, nano çinko oksitle empenye edilmiş ahşap numuneleri küf mantarlarına karşı en hassas grup olarak belirlenmiştir.

Anahtar sözcükler: Küf gelişimi, mikronize bakır, nano bakır, nano çinko, yapay yaşlandırma.

INTRODUCTION

Wood is susceptible to biological degradation by fungi, insects and marine borers, depending on its natural durability. Because of this reason, wood protection industry and researchers focus on nano and micro scale chemicals to produce more effective new generation wood protection chemicals, nowadays. (Clausen, 2007; Matsunaga et al., 2007; Clausen et al., 2010, 2011; Akhtari & Nicholas, 2013; Lykidis et al., 2013; Mantanis et al., 2014). The main usage purpose of nano- or macro-scale wood preservation systems is to allow chemical substances to penetrate deeper into the wood uniformly (Mantanis et al., 2014; Mantanis & Jones, 2012; Freeman & McIntyre, 2008; Kartal et al., 2009). Investigations are continuing to better explain the performance of nano- and micro-based wood preservative chemicals against leaching and weathering (Terzi et al., 2016; Mantanis et al., 2014). Terzi et al. (2016) reported that nano-particle forms of some metal oxides for wood protection were successful in terms of biological resistance and leaching. In this study, only nano-B₂O₃ treated and weathered specimens were not effective in preventing decay by *G. trabeum*. Mantanis et al. (2014) focused on the resistance of pine wood treated with zinc and copper based nano chemicals and mold rating results showed that only nanozinc borate could inhibit the mold growth. CCA treated wood were more effective than MCQ and ACQ and nano-CuO treated wood specimens against decay fungi in soil block tests (Kartal et al. 2015). According to recent studies, the effectiveness of nano and micronized particles-treated wood has not been fully elucidated and further research is needed.

The objective of this study to evaluate mold resistance of nano and micronized particles-treated wood specimens after artificial weathering process and compare with common preservatives.

MATERIAL and METHODS

Wood specimens and treatments: The following commercial wood preservatives and nano particles were tested in the study (% m/m):

i) ACQ - water soluble form of Cu: Osmose Celcure AC-500 (Osmose Naturewood) (Osmose UK Protim Solignum Ltd): Quat (benzalkonium chloride) (4.8%), copper carbonate hydroxide (16.53%), boric acid (5%).

ii) Micronized ACQ - micronized form of Cu: Osmose Micro Pro, (Celcure MC) (Osmose UK Protim Solignum Ltd): Quat (benzalkonium chloride) (10%), micronized copper carbonate hydroxide (17.39%), boric acid (5.23%).

iii) Nano-CuO - nano form of Cu: (NanoArc, 97.5%, 23-37 nm APS Powder, Alfa Aesar, Germany): CuO (97.5%).

iv) CCA: Osmose K-33 e water soluble form of Cu: (Osmose UK Protim Solignum Ltd) CuO (10.5%), chromic acid (29.9%), arsenic penta oxide As₂O₅ (20%), water (39.6%).

v) Nano-ZnO – nano form of Zn: (NanoArc, 99%, 40-100 nm APS Powder, Alfa Aesar, Germany): ZnO (99%).

Water-based preservative solutions were adjusted in order to reach a target elemental Cu and Zn retention level of 0.64 kg m⁻³ in treated wood specimens.

Wood specimens (3 mm x 45 mm x 135 mm) were cut from the sapwood portions of Scots pine (*Pinus sylvestris* L.) lumber. The wood specimens (2 - 4 growth rings/cm) were free of knots and visible deposits of resins, and showed no visible evidence of infection from mold, stain or wood-degrading fungi. The specimens were conditioned to a moisture content of 10-12% in a conditioning room at 22 °C and 65% relative humidity (RH) for 2 weeks before preservative treatment. Pre-weighed wood specimens were vacuum treated for 40 min at 100 mm Hg with each treatment according to the AWWA standard E10 method (AWWA, 2012). All the specimens were treated to a target retention of 0.64 kg/m³ based on Cu and Zn elements, individually. After treatment, the specimens were blotted-dry and re-weighed to check solution uptake.

Accelerated weathering tests: Accelerated weathering tests were performed in a Xenon arc radiation cabinet (Atlas Xenotest Alpha+, ATLAS), which included water spraying according to ISO 4892-2-A1 (ISO, 2006). The radiation source was a Xenon arc lamp (300 to 400 nm), using borosilicate filters. The test consisted of cycles of 102 min of radiation, a black body temperature of 65±5% followed by 18 min of water spray at the same radiation conditions, and a relative approximately 100%. The total duration of the test was 288 h (144 h x 2 periods) for 3 specimens (3 mm x 45 mm x 135 mm) per each test group.

Mold resistance tests: Artificially weathered and treated wood specimens were evaluated for resistance to mold fungi according to the ASTM D4445 (ASTM, 2012). Wood specimens (7 mm tangential x 20 mm radial x 7 cm long) for mold resistance tests cut from the artificially aged wood specimens (3 mm x 45 mm x 135 mm). Three mold fungi, *Aspergillus niger*, *Penicillium fellutanum*, and *Trichoderma harzianum* were grown and maintained on 2% malt agar. Wood specimens (5 specimens per group) were sprayed with 1 ml of mixed mold spore suspension of the three fungi and incubated at 27 °C and 80% RH for 4 weeks. All fungi were obtained from the USDA Forest Service Forest Products Laboratory, Madison, WI, USA. A mixed spore suspension of the three test fungi was prepared by washing the surface of individual 2-wk-old petri plate cultures with 10-15 ml of sterile DI water. Washings were combined in a spray bottle and diluted to approximately 100 ml with DI water to yield approximately 3 x 10⁷ spores ml⁻¹.

The spray bottle was adjusted to deliver 1 ml of inoculum per spray. Wood specimens were sprayed with 1 ml of mixed mold spore suspension and incubated at 27 °C and 80% RH for 12 wk. Following incubation, specimens were visually rated on a scale of 0-5, with 0 indicating the specimen is completely free of mold growth and 5 indicating the specimen was completely covered with mold growth (0: no growth, 1: 20% coverage with mold fungi, 2: 40%, 3: 60%, 4: 80%, 5:100%).

RESULTS and DISCUSSION

Average ratings of weathered and un-weathered wood specimens for resistance to the mold fungi are shown in Fig. 1. Generally, artificial weathering and treatment processes improved the mold resistance of specimens except that ACQ treated – weathered and nano ZnO treated – un-weathered specimens. Mold resistance of control specimens were improved after the artificial weathering process and average mold ratings down under 1.0 from 5.0. Similar results were obtained in previous studies made by researchers. These results could be supported by the products of lignin photodegradation. Because the lignin sub-units that are released during photodegradation are aromatic and therefore fungitoxic (Schoeman & Dickinson 1997; Cerniglia & Crow 1981). The nano or micronized particle based preservatives used in this study have not prevented the growth of mold fungi on un-weathered wood specimens as well as CCA. Mold development was not observed in the un-weathered specimens impregnated with CCA during the test period. MCQ and CCA treated and weathered specimen groups have similar mold inhibition effects on wood specimens. Nano CuO treated specimens have also a good performance against mold growth. The worst mold inhibition performance was observed in nano ZnO treated wood specimens, whether weathered or not. Mold inhibitor effectiveness of CCA and MCQ treated wood specimens were as good as weathered control specimens.

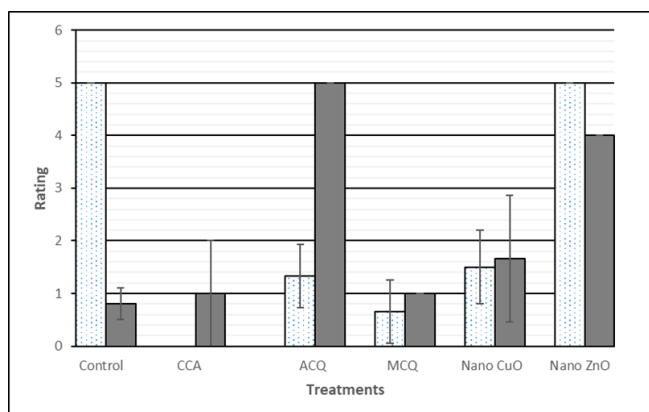


Figure 1. Average mold ratings for un-weathered (dotted bars) and weathered (filled bars) wood specimens (after 4 weeks): 0 indicates no mold growth, 1 = 20%, 2 = 40%, 3 = 60%, 4 = 80%, and 5 = 100% mold coverage.

CONCLUSION

In this study, mold resistance in laboratory conditions of Scots pine wood samples impregnated with nano-scale preservatives, micro-scale preservatives and common wood preservatives were evaluated. Experiments were performed on artificial weathered and un-weathered samples. Results showed that the mold fungi were noticeably inhibited by MCQ, CCA and also nano CuO, while the nano ZnO did not inhibit the mold growth on wood specimens. It was also shown that the artificial weathering process inhibit the mold growth. This can be attributed to the removal or degradation of nutrients on the surface of the wood during the weathering process.

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