Effects of Wollastonite Nanofibers on Biological Durability of Poplar Wood (*Populus nigra*) against *Trametes versicolor*

Ali Karimi,[a,c]* Hamid Reza Taghiyari,[b] Akram Fattahi,[c] Samaneh Karimi,[a]
Ghanbar Ebrahimi,[c] and Asghar Tarmian [c]

The effect of impregnation with wollastonite nanofibers, a nontoxic mineral material, on the biological durability of poplar wood (*Populus nigra*) against a white-rot fungus (*Trametes versicolor*) was studied. Wollastonite nano-suspension with a concentration of 6.3% was used; the size range of the nano-wollastonite (NW) was 30 to 110 nm. Results showed that decay exposed for 16 weeks in accordance with the standard DIN-52176 specifications resulted in a 47.5% mass loss in control specimens, while in the NW-impregnated specimens, only 3.6% mass loss occurred. Mechanical tests on separate sets of specimens impregnated with NW without exposure to the decay organism showed no significant difference in the mechanical properties. Thus, it can be concluded that impregnating poplar wood with NW as a preservative significantly increases the biological durability of poplar wood against deterioration by *Trametes versicolor.* Furthermore, it does not have negative effects on the mechanical properties in the impregnated poplar specimens.

Keywords: Biological durability; Fungal degradation; Impregnation; Nanowollastonite; Poplar

Contact information: a: Department of Biocomposite Technology, Institute of Tropical Forestry & Forest products (INTROP), University Putra Malaysia (UPM), 43400 Serdang Selangor, Malaysia; b: Wood Science & Technology Department, Faculty of Civil Engineering, Shahid Rajaee Teacher Training University (SRTTU), Tehran, Iran*; c: Department of Wood and Paper Science and Technology, Faculty of Natural Resources, Tehran University, Tehran, Iran;*
** Corresponding authors: karimi.ut@gmail.com* & *htaghiyari@srttu.edu*

INTRODUCTION

Poplar is a fast-growing tree that has many commercial applications in Iran. However, it suffers from low biological durability against wood-deteriorating fungi, wood-boring beetles, *etc*. Nanotechnology has been utilized in sciences such as molecular electronics (Pati 2012) and materials extraction (Moghimi 2012). In wood science and technology, nano-silver particles have the potential to increase heat transfer from the surface of wood to its inner part (Taghiyari and Farajpour 2013); they also have antibacterial and antifungal properties. Wollastonite nanofibers were reported to increase the heat-conductivity coefficient and reduce heat-gradient and hot-press time in composite-board manufacturing (Taghiyari *et al.* 2013), as well as to increase the fire-retarding properties (Haghighi *et al.* 2013). Furthermore, wollastonite, a calcium silicate mineral, was found to enhance plant growth and reduced the effects of certain pathogens, including fungi (Aitken 2010). Regarding the environmental aspects and health issues, wollastonite is known to be a nontoxic mineral material that is not hazardous to humans or wildlife; in fact, in reviewing the available epidemiological studies on wollastonite, there was no evidence that wollastonite presents a health hazard; however, further studies on workers exposed to wollastonite dust in the long-run are required before the health hazards of wollastonite can be evaluated in full (Huuskonen *et al.* 1983a; Maxim and McConnell 2005). Also, the long-term health effects due to inhalation of wollastonite appear to be negligible because no correlation of serum angiotensin-covering enzymes in wollastonite workers with slight pulmonary fibrosis was reported (Huuskonen *et al.* 1983b). Based on the literature review above, it can be presumed that because the wollastonite nanofibers in the present study were penetrated deep into the solid wood structure and therefore could not be easily inhaled, there would be no hazardous effects.

Upon review of the aforementioned studies, the objective of this study was to investigate if impregnation with wollastonite nanofibers would have any improving effects on the biological durability of poplar wood without decreasing its mechanical properties. Furthermore, impregnation with many preservatives was reported to adversely affect the mechanical properties in solid woods (Winandy 1995; Colakoglu *et al.* 2003). Wollastonite, a non-reactive mineral material, was predicted to have no significant negative effects on the mechanical properties of poplar wood. Therefore, a complimentary study was also carried out to analyze the effects of impregnation with nano-wollastonite (NW) on the mechanical properties of poplar wood. In the meantime, leaching tests were also carried out to find out if NW can be used for outdoor applications.

EXPERIMENTAL

Specimen Preparation

Wood specimens were cut from four 7-year-old poplar logs; from each log, two boards were cut. Boards were first dried to the final moisture content of 10%, and then the test specimens were cut from them. Specimens were free from any knots, rots, holes, checks, or other visual defects. In order to have maximum impregnation, specimens were cut from the sapwood of the logs (Taghiyari *et al.* 2010; Taghiyari 2014). The mass loss measurement was carried out according to DIN-52176 standards. The dimensions of the mass loss specimens were 50 × 25 × 15 mm (in longitudinal, radial, and tangential directions, respectively). All specimens were pre-weighed and conditioned at 20 °C and 65% relative humidity for 2 weeks prior to treatment. Specimens were randomly divided into four groups; control and NW-impregnated specimens without exposing them to decaying fungi, and control and NW-impregnated specimens for the tests after exposing them to the decaying fungi; 20 sound specimens were selected for each group.

To determine if the process of impregnation with wollastonite nanofibers had any negative effects on the mechanical properties of poplar wood, separate sets of specimens were prepared to test the mechanical properties, including modulus of rupture, modulus of elasticity, hardness, compression strength parallel to the grain, compression strength perpendicular to the grain, impact strength, and shear strength.

Methods

Nano-wollastonite impregnation

Nano-wollastonite (NW) gel was produced in cooperation with Vard Manufacturing Company of Mineral and Industrial Products, Iran. The concentration of NW was 6.3%. More than 80% of its formulations by mass were composed of CaO and SiO_2

(Table 1). The size range of wollastonite nanofibers was 30 to 110 nm; therefore, with due consideration to the diameter of the vessel elements in poplar (about 50 μm) (Taghiyari *et al.* 2010), a rather uniform spread of NW throughout the specimens could be expected. Specimens were impregnated with the NW suspension using the Bethel process (a full-cell process). Impregnation was carried out under 0.5 atm of pressure for 15 min, followed by 3 atm of pressure for 2 h. Finally, 0.5 atm of pressure was applied for 5 min. Specimens were weighed before and after the impregnation, as well as after being seasoned, to calculate the amount of NW-retention.

Table 1. Compounds and Formulations of the Nano-wollastonite Gel

Nano-wollastonite compounds	Mixing ratio by mass (%)
CaO	39.77
SiO_2	46.96
Al_2O_3	3.95
Fe_2O_3	2.79
TiO_2	0.22
K_2O	0.04
MgO	1.39
Na_2O	0.16
SO_3	0.05
Water	The rest

Fungal degradation

Specimens were biologically sterilized (by autoclave) and exposed to *Trametes versicolor* and incubated at 26 °C and 65% relative humidity for 16 weeks. Two or three specimens were placed in each Petri dish; mass loss tests were carried out according to the standard DIN-52176 specifications. Fungal mycelium growth was measured according to the Willeitner scale (1984). At the end of the test, mycelia were removed and the specimens were dried at 103 °C for 24 h and weighed (W_2) to determine the mass loss caused by fungal decay in comparison to the initial dry weight (W_1), using Eq. 1,

$$ML\ (\%) = \frac{W_1 - W_2}{W_1} \times 100 \tag{1}$$

where ML is the mass loss (%) and W_1 and W_2 are the dry weights (without any moisture content) before and after the exposure to decay exposed, respectively.

Findlay's criterion (1951) was followed to determine the relation between weight loss percentage caused by fungi and wood strength grade, as shown in Table 2.

Table 2. Wood Grading According to the Weight Loss (%) Caused by Xylophagous Fungi and its Strength Grade (Findlay 1951)

Weight loss	Durability grade or resistance category
Lower than 5	Very resistant
5 to 10	Resistant
10 to 20	Moderately resistant
20 to 30	Not resistant
Higher than 30	Perishable or without resistance

Standard test methods

Tests for three-point bending strength, modulus of elasticity, compression strength parallel and perpendicular to the grain, shear strength, and hardness were carried out according to the standard ASTM D-143-83 specifications, using an Instron testing machine, model 1186. For MOR and MOE, the specimen dimensions were 25 × 25 × 410 (mm), center-point loading bar; for the compression strength parallel to the grain, the specimen size was 25 × 25 × 100 (mm); for the impact resistance test, the size was 50 × 50 × 760 (mm); for the compression strength perpendicular to the grain as well as hardness, the size was 50 × 50 × 150 (mm); for the shear strength, the size of specimens was 50 × 50 × 63 (mm). Hardness was measured according to Janka scale, using a ball with 11.3 mm in diameter. Specimens were at a temperature of 20 ± 3 ºC and moisture content of 10% at the time of testing. For all the mechanical tests, the number of replications was 10 specimens. The leaching test was carried out according to the standard BS-5761 (Part II) specifications. Leaching test specimens of 15 × 25 × 50 mm were prepared; they were put in a vessel and enough distilled water was poured in the vessel to cover all the specimens. The vessel was placed in a desiccator; a 4 kPa vacuum pressure was applied for 20 min. The process was repeated for 14 days; then the leaching test was discontinued and leaching was calculated.

Statistical Analysis

Statistical analysis was conducted using the SAS software program, version 9.2 (2010). Two-way ANOVA was performed to discern significant differences at the 95% level of confidence.

RESULTS AND DISCUSSION

Extra specimens were also impregnated under the same conditions to study whether NW nanofibers had been impregnated into the heart of the specimens. Once cut from the middle, it was clear that NW-suspension penetrated into the deepest parts of all specimens. Similar deep penetration was also reported for silver nanoparticles under the same impregnating conditions (Taghiyari 2012, 2014). However, further studies should investigate if NW has any effects on the cutting tools, the impregnation utensils, *etc*.

The average amount of NW retention in all the specimens based on their dry volume was calculated to be 0.032 g/cm^3 (with the standard deviation of 0.004); that is, 0.032 g of wollastonite nanofibers were deposited in the porous structure of the specimens. The leaching test revealed that an average of 0.0013 g/cm^3 (with standard deviation of 0.0001) wollastonite nanofibers was leached; that is, only 4% of the wollastonite nanofibers leached out of the specimens. This showed that the stability of wollastonite nanofibers would enable them to be used as a preservative in the wood products industry.

The Willeitner scale showed distinct evidence of fungal colonization (100%) on untreated wood. However, impregnation with wollastonite nanofibers inhibited fungal growth to a noticeable extent, as displayed in Fig. 1. In the control specimens (Fig. 1-A), mycelium grew freely all over the two specimens in Petri dish; however, mycelium growth was significantly limited in the specimens that were impregnated with nano-wollastonite (Fig. 1-B).

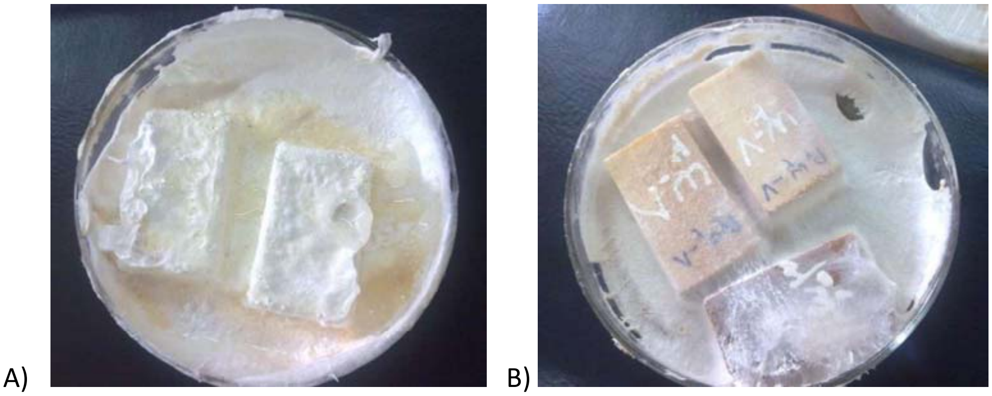

Fig. 1. Mycelium growth of *Trametes versicolor* fungus on control poplar specimens (A) and NW-impregnated poplar specimens (B)

The average value for mass loss was 47.5% (1.2 standard deviation) in the control specimens after 16 weeks of exposure to decaying fungi, while the mean amount of mass loss in the NW-impregnated specimens was only 3.6% (0.7 standard deviation) (Fig. 2). There were significant differences in the amount of mass loss between the control and NW-impregnated specimens. According to the Findlay scale, ASTM D-2017 (1981), wood with a weight loss of more than 30% is classified as perishable or without resistance; therefore, the control poplar specimens were classified as perishable, while the NW-impregnated specimens, with less than 5% weight loss, were classified in the very resistant category.

The large difference between the mass loss in the control and NW-impregnated specimens implies that there is a great opportunity to apply wollastonite nanofibers in improving the biological durability of solid woods. Previous studies have reported several benefits of wollastonite in wood and wood-composite industries, such as enhanced thermal conductivity of medium density fiberboards (Taghiyari *et al.* 2013), increased fire-retarding properties of solid woods (Haghighi *et al.* 2013), and its nontoxic properties. Thus, it can be concluded that wollastonite is a promising preservative and fire-retardant that can be used in wood-based materials. However, the authors are still working on its possible improving effects against wood-boring beetles and termites to come to a final comprehensive conclusion.

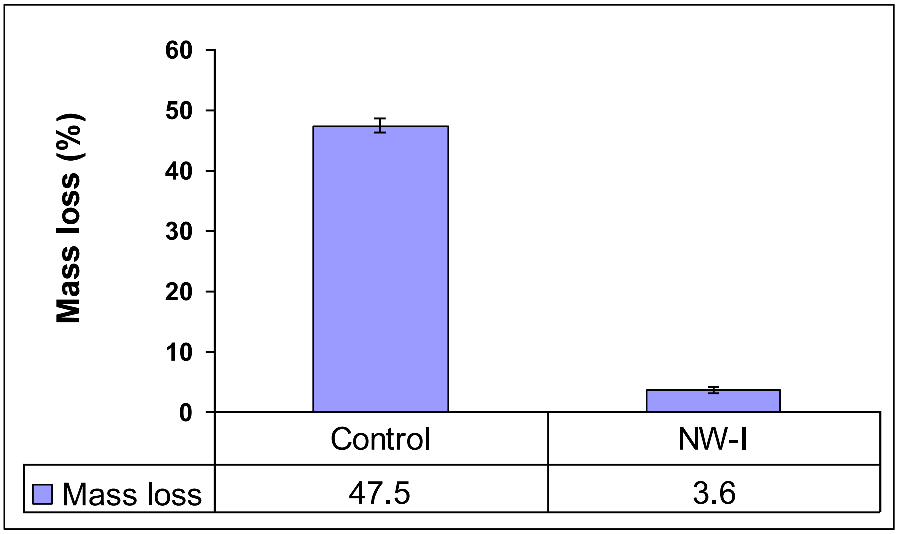

Fig. 2. Mass loss (%) in the control and NW-impregnated specimens (NW=nano-wollastonite; I=impregnated)

Once exposed to the decaying fungi, specimens were kept in the conditioning room for four weeks (20 °C and 65% relative humidity). The average hardness in the specimens exposed to decay was only 0.33 kN (Table 3); NW increased the hardness to 0.74 kN, which is more than a 120% increase. The same increasing effect was found in the compression strength parallel to the grain (Table 4); decay exposed decreased compression parallel to the grain to only 4.82 kN, while NW increased it to more than 8 kN; that is, wollastonite nanofibers resulted in a 70% increase in the average values of the compression strength parallel to the grain. Although hardness and compression parallel to the grain showed significant improvement by impregnation with NW, they were lower than those of the control specimens (Table 3); complimentary studies must be carried out to find out the optimum concentration of NW.

Results showed that NW-impregnation did not have significant decreasing effects on the mechanical properties (Table 3); in some cases, there was even an apparent increasing effect, though not significant, on properties such as hardness, MOE, and shear strength. Many preservatives have been reported to have negative effects on the physical or mechanical properties of solid woods (Winandy 1995; Colakoglu *et al.* 2003); therefore, the fact that the mechanical properties were not decreased by the NW-impregnation process can be considered another advantage of this new formulation.

Table 3. Mechanical Properties of the Control and Nano-wollastonite-Impregnated Specimens (at moisture content of 10%)

Mechanical Properties	Treatments	
	Control	NW-impregnated
Hardness (kN)	2.22 (0.34)	2.29 (0.38)
Hardness after exposure to decaying fungi	0.33 (0.01)	0.74 (0.03)
Compression strength parallel to the grain (kN)	20.67 (1.35)	19.65 (1.67)
Compression strength parallel to the grain after exposure to decaying fungi (kN)	4.82 (0.28)	8.18 (0.35)
Modulus of rupture (MPa)	74.8 (8.6)	71.6 (9.3)
Modulus of elasticity (MPa)	8280 (53)	8850 (61)
Compression strength perpendicular to the grain (kN)	24.8 (0.65)	24.5 (0.59)
Impact strength (m/kg)	1.49 (0.09)	1.41 (0.12)
Shear strength (kN)	14.1 (0.8)	19.4 (1.2)

* Figures in parenthesis are the standard deviations.

CONCLUSIONS

1. The results showed that nano-wollastonite (NW) can significantly increase the biological durability as well as hardness and compression strength parallel to the grain of polar wood that is subsequently exposed to the decay organism *Trametes versicolor*.

2. Results of the tests on the NW-impregnated specimens without exposure to the decaying fungi also showed that impregnation of poplar specimens with NW did not have significant decreasing effects on its mechanical properties. It can thus be concluded that a NW suspension can be used to improve the biological durability of poplar wood.

REFERENCES CITED

Aitken, E. (2010). *Analyses of the effect of silicon on Fusarium wilt on banana*, Horticulture Australia, Sydney, NSW, Australia.

Colakoglu, G., Colak, S., Aydin, I., Yildiz, U.C., and Yildiz, S. (2003). "Mechanical properties of laminated beech veneer lumber," *Silva Fennica* 37(4), 505-510.

Findlay, W. P. K. (1951). *The Value of Laboratory Test on Wood Preservatives. (S1): Convention*, British Wood Preserving Association.

Haghighi Poshtiri, A., Taghiyari, H. R., and Karimi, A. N. (2013). "The optimum level of nano-wollastonite consumption as fire-retardant in poplar wood (*Populus nigra*)," *International Journal of Nano Dimension (IJND),* (in press).

Huuskonen, M. S., Jarvisalo, J., Koskinen, H., Nickels, J., Rasanen, J., and Asp, S. (1983a). "Preliminary results from a cohort of workers exposed to wollastonite in a Finnish limestone quarry," *Scandinavian Journal of Work, Environment, and Health* 9(2), 169-175.

Huuskonen, M. S., Tossavainen, A., Koskinen, H., Zitting, A., Korhonen, O., Nickels, J., Korhonen, K., and Vaaranen, V. (1983b). "Wollastonite exposure and lung fibrosis," *Environmental Research* 30, 291-304.

Maxim, L. D, and McConnell, E.E. (2005). "A review of the toxicology and epidemiology of wollastonite," *Inhalation Toxicology* 17(9), 451-466.

Moghimi, A. (2012). "Solid phase extraction of amount Cu (II) using C18 disks modified Schiff base-chitosan grafted multiwalled carbon nanotubes," *International Journal of Bio-Inorganic Hybrid Nanomaterials* 1(2), 105-114.

Pati, R. (2012). "Molecule for electronics: A myriad of opportunities comes with daunting challenges," *J. of Nanomaterials & Molecular Nanotechnology*, (dx.doi.org/10.4172/2324-8777.1000e104.)

Taghiyari, H. R., Karimi, A. N., Parsapajouh, D., and Pourtahmasi, K. (2010). "Study on the longitudinal gas permeability of juvenile wood and mature wood," *Special Topics & Reviews in Porous Media* 1(1), 31-38.

Taghiyari, H. R. (2012). "Correlation between gas and liquid permeability in some nanosilver-impregnated and untreated hardwood," *Journal of Tropical Forest Science* 24(2), 249-255.

Taghiyari, H. R., and Farajpour Bibalan, O. (2013). "Effect of copper nanoparticles on permeability, physical, and mechanical properties of particleboard," *European Journal of Wood Products* 71(1), 69-77.

Taghiyari, H. R., Mobini, K., Sarvari Samadi, Y., Doosti, Z., Karimi, F., Asghari, M., Jahangiri, A., and Nouri, P. (2013). "Effects of nano-wollastonite on thermal conductivity coefficient of medium-density fiberboard*," J. of Molecular Nanotechnology* 2(1), (http://dx.doi.org/10.4172/2324-8777.1000106).

Taghiyari, H. R. (2014). "Effects of nanosilver-impregnation and alfalfa-intercropping on fluid transfer in downy black poplar wood," *Maderas-Cienc. Technol.* 16(1).

Willeitner, H. (1984). *Laboratory Tests on the Natural Durability of the Timber Methods and Problems*, Document International Research Group on Wood Preservation.IRG/WP/2217.

Winandy, J. E. (1995). "Effects of waterborne preservative treatment on mechanical properties: A review," American Wood-Preservers' Association; The Forest Products Laboratory; 91st Annual meeting, 21-24 May, 1995, New York, USA.

Article submitted: April 4, 2013; Peer review completed: April 29, 2013; Revised version accepted: June 11, 2013; Published; June 14, 2013.