Effects of Wollastonite Nanofibers on Biological Resistance of Historical Paper against *Aspergillus Niger*

Hamid R Taghiyari,[a],* Afsaneh Kalantari [b] Amir Ershad-Langroudi [c]

Effect of wollastonite nanofibers on biological resistance of historical paper against *Aspergillus niger* was studied. Specimens from A4 papers were also prepared for comparison purposes. Paper specimens were dipped in aqueous nanowollastonite (NW) with 10, 20, 30, and 40% concentrations and compared with control specimens. In order the nanofibers be fixed on paper specimens, 5% of polyvinyl acetate (PVA) resin was added to all nanosuspensions. Moreover, in order to find out the effect of PVA on fungal growth, a separate set of specimens was prepared dipped in a 5% resin solution, without nanowollastonite content. Results clearly demonstrated the preventing effect of wollastonite nanofibers on the growth of *A. niger*, resulting in significant decrease in weight loss as NW-content increased. It was concluded that as to the mineral, non-toxic, and non-acidic nature of wollastonite, it can effectively be used for paper preservation and conservation purposes. In this regard, NW-content of 20% is recommended to the industry to both achieve a high level of protection against *A. niger*, and keep the preservation costs to the minimum level.

Keywords: Biological resistance; Fungal degradation; Mineral materials; Paper; Wollastonite nanofibers

Contact information: a: Wood Science & Technology Department, Faculty of Civil Engineering, Shahid Rajaee Teacher Training University, Tehran, Iran; b: Islamic Azad University, Central Tehran Branch (IAU – CTB), Tehran, Iran; c: Color, Resin & Surface Coating (CRSC) Department, Polymer Processing Faculty(PPF), Iran Polymer and Petrochemical Institute (IPPI), 14965/115 Tehran, Iran.
** Corresponding author: 0930-2005235; htaghiyari@srttu.edu & htaghiyari@yahoo.com*

INTRODUCTION

Wood has long been a valuable natural renewable material used also in pulp and paper industry. As to the limitations of tree plantation and natural regeneration of trees (Ruprecht et al. 2012; Fernandez et al. 2014), and utilization of their woods and fruits (Miteva et al. 2014), it would be quite vital to preserve and protect wood and papers from physical and biological hazards (Schmidt 2006&2007; Maresi et al. 2013).

In this connection, wollastonite, a calcium silicate mineral, enhances plant growth and reduces the effects of certain pathogens, including fungi (Aitken 2010). As far as the environmental aspects and health issues are concerned, wollastonite is known to be a non-toxic mineral material that is not hazardous to humans or wildlife; in fact, in reviewing the available epidemiological studies on wollastonite, there is no evidence to suggest 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 & McConnell 2005). Also, the long-term health effects due to inhalation of wollastonite appear to be negligible because no correlation between serum angiotensin-covering enzymes and wollastonite workers with slight pulmonary fibrosis has been 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 bound to the resin matrix and therefore could not be easily inhaled, there would be no hazardous effects. So far, wollastonite nanofibers were used in many areas of wood science and technology; wollastonite nanofibers were reported to improve dimensional stability in solid woods (Haghighi et al. 2014) as well as significantly improve biological resistance in solid woods (Karimi et al. 2013) and medium-density fiberboard (Taghiyari et al. 2014ab). This material was also used to improve fire-retarding properties in wood and wood-composite panels (Haghighi et al. 2014). Moreover, its heat-transfer property significantly increased thermal conductivity coefficient in wood-composite panels (Taghiyari & Schmidt 2014; Taghiyari et al. 2014c) and improved all physical and mechanical properties (Taghiyari et al. 2014c), just as the heat transferring property of metal nano-materials (Saber et al. 2013) increased thermal conductivity in wood-composite panels (Taghiyari et al. 2013) and the fungicide effect improved biological resistance against wood-deteriorating fungi (Taghiyari et al. 2014d). However, authors came across to little or no study focusing on the effect of wollastonite on biological resistance of papers. Moreover, due to the fact that materials sometimes react differently as their size substantially decrease (Li 2012), the present study was carried out to find out its possible effects on improving biological resistance against *Aspergillus niger*, as a troublesome fungi attacking papers.

EXPERIMENTAL

Specimen Procurement

A 70-year old book was purchased from Iran book market. Its density was 92 g/m^2 at 25±2°C, and 42±2% relative humidity (Figueroa et al. 2012). Fifty 40 × 40 mm specimens were cut from its sheets; for each of the control and four NW-treated specimens, ten specimens were prepared. In order to avoid internal difference among specimens, careful attention was taken to cut the specimens from sheets with similar printed area. In order to compare the weight losses of historical paper with A4 paper specimens, similar specimens were also prepared from A4 papers.

Nano-Wollastonite Application

Nanowollastonite (NW) gel was produced in cooperation with Vard Manufacturing Company of Mineral and Industrial Products, Korasan-Jonoobi Province, Iran. The size range of wollastonite nanofibers was 30 – 110 nm. Specifications of wollastonite compounds and formulations are in Table 1. Four concentrations of NW were used in the present study, including 10, 20, 30, and 40%. In order to keep wollastonite nanofibers fixed on specimens, 5% polyvinyl acetate was added to the nanosuspension. Specimens were weighed before and after the NW-application in order to calculate NW-uptake.

Table 1. Compounds and Formulations of the Nano-wollastonite Gel (Taghiyari et al. 2013 & 2014abd)

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	4.67

Fungal Degradation

Specimens were prepared and dried in accordance with the standard specifications BS EN 1275:2005, at 103±2˚C for 24h in a hot air oven. They were first weighed before exposure to *Aspergillus niger* for thirty days in Petri dishes. The incubation was carried out at 27±1˚C and 40±2% relative humidity on Sabouraud's agar. Ten replicate specimens were prepared for each treatment of each paper; totaling, 100 replicate specimens. Following incubation, mycelia were removed and the specimens were dried at 103˚C for 24h and weighed to determine the fungal mass loss.

Statistical Analysis

Statistical analysis was conducted using SAS software program, version 9.2 (2009). Two-way ANOVA was performed to discern significant difference at the 95% level of confidence. Grouping was then made between treatments, using the Duncan's multiple range test. Hierarchical cluster analysis, including dendrogram and using Ward methods with squared Euclidean distance intervals, was carried out by SPSS/18 (2010). Cluster analysis was performed to find similarities and dissimilarities between treatments based on more than one property simultaneously (Ada 2013). The scaled indicator in each cluster analysis shows how much treatments are similar or different; lower scale numbers show more similarities while higher ones show dissimilarities. Regression graphs were made by Minitab software, version 16.2.2 (2010).

RESULTS AND DISCUSSION

Results showed that the maximum and minimum NW-uptakes were found in the NW-40% of A4 specimens (7.96%) and NW-10% of historical specimens (0.63%), respectively (Fig. 1). Generally, A4 specimens absorbed higher amount of NW and PVA resin in comparison to the historical papers with the exception of NW-20% treatment. The exception may be attributed to the variance in NW-uptake because the higher NW-uptake in the NW-20% treatment was not statistically significant. In neither of the two paper kinds, the amount of PVA-resin uptake showed significant difference with the NW uptake in the NW-10% treatment. Historical specimens demonstrated a general lower amount of NW-uptake in all treatments. The lower uptake was due to the lower specific air permeability in the historical paper (Taghiyari 2014). Flow rates in historical and A4 papers were reported to be 5.3 and 195 cm^3/s in historical and A4 papers, respectively (USPTO 2009; Kalantari 2014). Flow rates were calculated according to Gas-3 to be compatible with previous studies (Taghiyari 2014). The higher permeability in the A4 specimens provided higher opportunity for the nano-suspension to penetrate deeper into the texture of specimens and reside there, significantly increasing the uptake in all treatments.

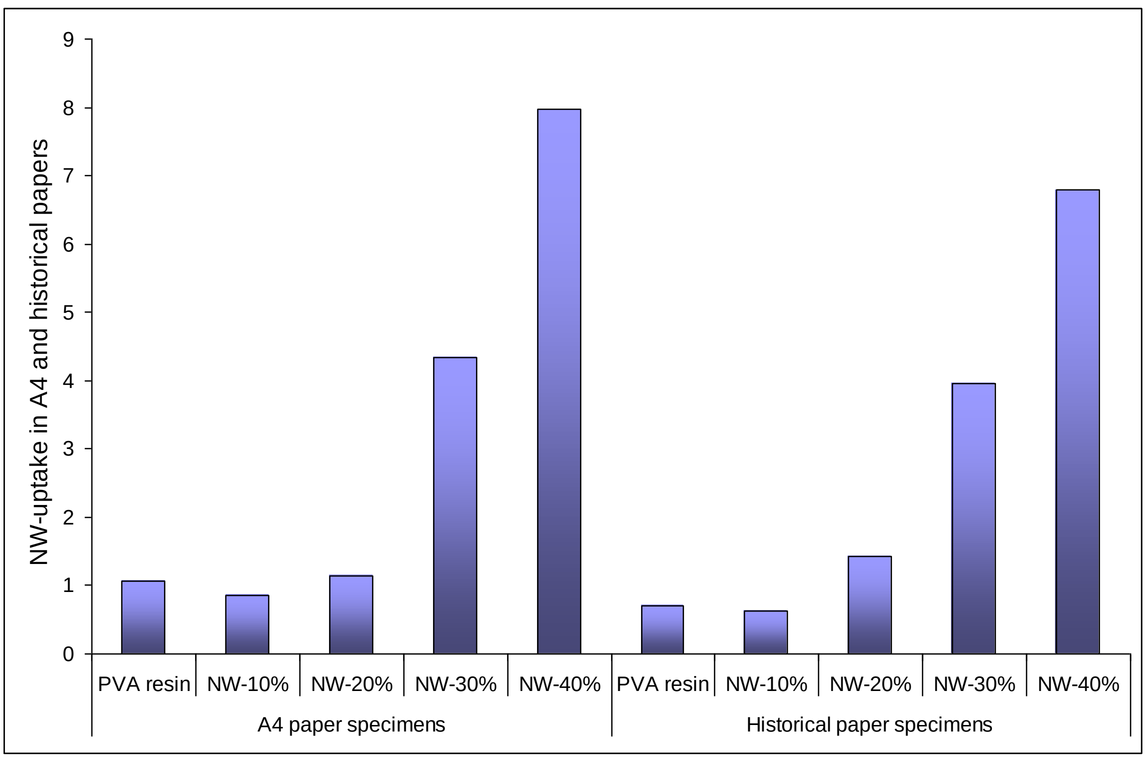

Fig. 1. Nano-wollastonite uptake (%) in the A4 and paper specimens (NW=nanowollastonite; PVA=polyvinyl acetate)

The highest and lowest weight losses were observed in the control historical

(4.5%) and NW-40% A4 paper (1.2%) specimens, respectively. In both papers, the control specimens showed the highest weight losses (Fig. 2). Specimens immersed in PVA resin showed lower weight losses than the control specimens, showing that the thin layer of PVA resin could, to some extent, protect paper specimens from the attack of *A. niger* fungi. Weight losses in the NW-treated paper specimens significantly decreased even in the NW-content of only 10%. This indicated the high impact of NW in preventing the growth of *A. niger* fungi in both kinds of papers. A steady decrease in the weight losses was observed in both papers as NW-content increased, although the decrease was not significant in all cases. All A4 treatments showed higher weight losses in comparison to the historical papers (Fig. 2). The higher weight loss was related to the higher specific air permeability in the A4 specimens; in fact, easier flow of fluid also indicated easier penetration of hyphae into the texture of paper specimens, resulting in higher weight losses. Even the slight lower weight losses in the PVA-coated specimens can be related to the possible lower permeability in this treatment caused by the thin layer of PVA-resin over the paper specimens. However, in order to come to a final firm conclusion, further studies on the permeability of PVA-coated specimens should be carried out.

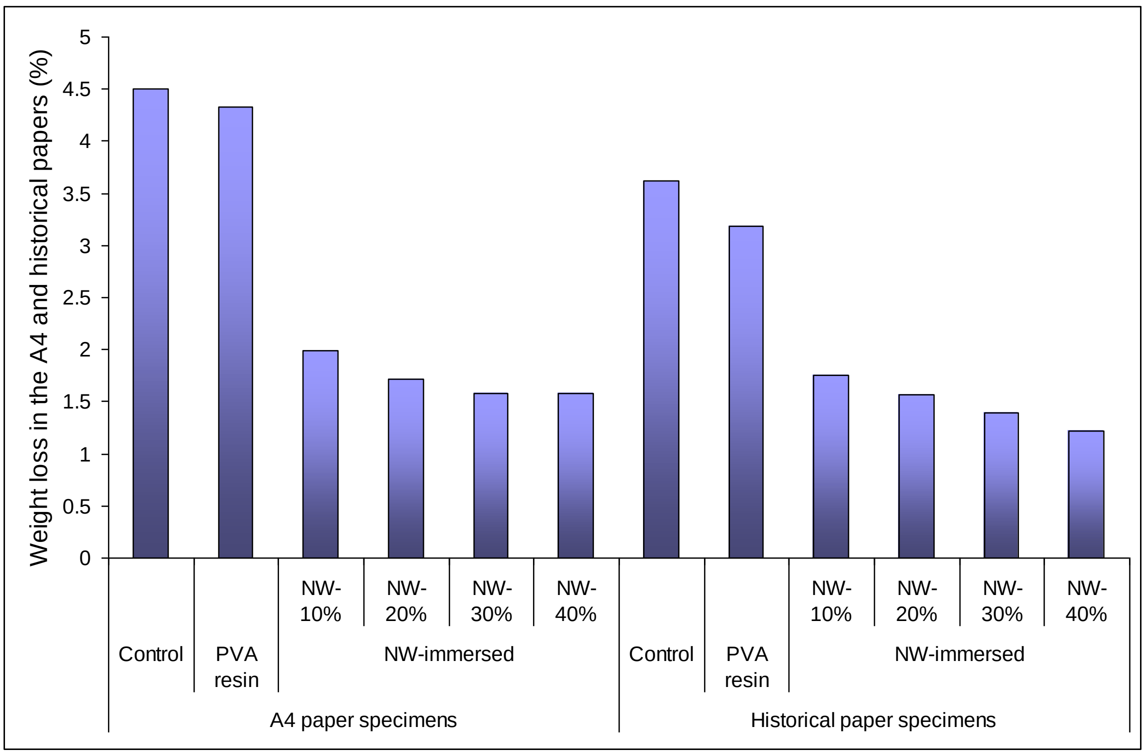

Fig. 2. Weight losses (%) in the A4 and historical paper specimens caused by Aspergillus niger

(NW=nanowollastonite; PVA=polyvinyl acetate)

Cluster analysis based on both properties of NW-uptake and weight loss values showed significant different clustering of the control and PVA-dipped specimens in both papers (Fig. 3). Regardless of the kind of papers, all treatments having the same NW-contents were clustered similarly, showing the higher significant impact of NW in comparison to the kind of paper in preventing the growth of fungi colony over paper specimens. The two lower NW-contents (10 and 20%), as well as the two higher NW-contents (30 and 40%), were closely clustered together. In this regard, and considering the insignificant difference among the weight losses in paper specimens immersed in the four NW-suspensions, NW-content of 20% is recommended to the industry to both achieve a high level of protection against *Aspergillus niger*, and keep the preservation costs to the minimum level.

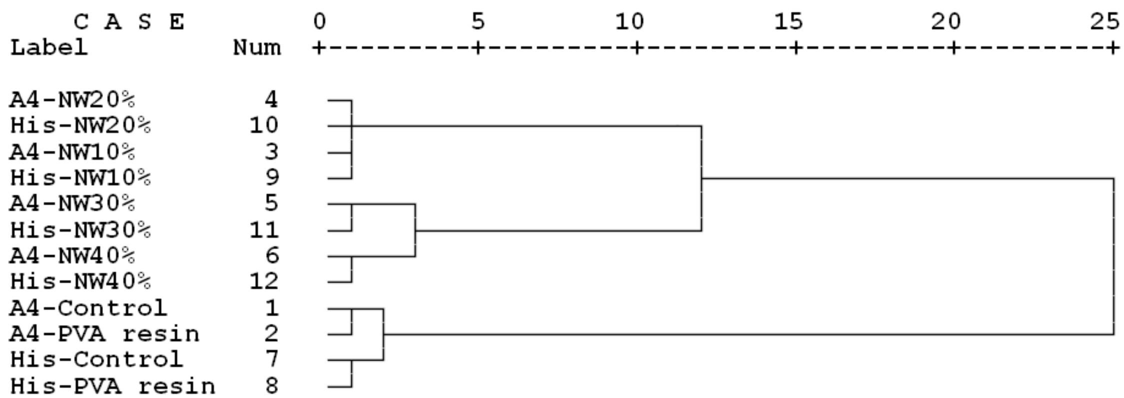

Fig. 3. Cluster analysis of the twelve treatments of two paper kinds, based on two properties of NW-uptakes and weight losses (A4=A4 paper; His=historical paper; NW=nanowollastonite content; PVA=polyvinyl acetate resin)

CONCLUSIONS

1- Wollastonite nanofibers showed significant preventing effect on the growth of *Aspergillus niger* in both historical and A4 papers.

2- The mineral, non-toxic, and non-acidic nature of wollastonite can effectively be used for paper preservation and conservation purposes.

3- NW-content of 20% is recommended to the industry to both achieve a high level of protection against *A. niger*, and keep the preservation costs to the minimum level.

ACKNOWLEDGMENT

We appreciate Dr. Reza Vahid-zadeh, Head of the Conservation and Restoration Department, Islamic Azad University, Central Tehran Branch, for his helpful cooperation and guidance. We are also grateful to Engr. Amin Kalantari, expert in fluid flow in porous media (Towhid Technical School, The 17th Municipal area), for his cooperation on fluid flow measurement of papers.

REFERENCES CITED

Ada, R. (2013). Cluster analysis and adaptation study for safflower genotypes. Bulgarian Journal of Agricultural Science 19(1): 103 – 109.

Aitken, E. (2010). Analyses of the Effect of Silicon on Fusarium Wilt on Banana, Horticulture Australia, Sydney, NSW, Australia.

Fernandez-Puratich H, Oliver-Villanueva JV (2014) Quantification of biomass and energetic value of young natural regenerated stands of *Quercus ilex* under Mediterranean conditions. BOSQUE 35(1): 65 – 74.

Figueroa M, Bustos C, Dechent P, Reyes L, Cloutier A, Giuliano M (2012) Analysis of rheological and thermo-hygro-mechanical behaviour of stress-laminated timber bridge deck in variable environmental conditions. Maderas: Ciencia y Tecnologia 14:303–319

Haghighi Poshtiri A, Taghiyari HR, Karimi AN (2014) Fire-retarding properties of nano-wollastonite in solid wood. Philippine Agricultural Scientist 97(1): 52 - 59.

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(2), 291-304.

Kalantari A (2014) Study on the effects of nano-wollastonite on biological resistance of historical paper against *Aspergillus niger*. MS Thesis at Islamic Azad University, Central Tehran Branch (IAU – CTB), Tehran, Iran.

Karimi A, Taghiyari HR, Fattahi A, Karimi S, Ebrahimi Gh, Tarmian T (2013) Effects of wollastonite nanofibers on biological durability of poplar wood (*Populus nigra*) against *Trametes versicolor*. BioResrouces 8:4134–4141

Li D (2012). Nanostructuring materials towards conventionally unachievable combination of desired properties. Journal of Nanomaterials & Molecular Nanotechnology 1(1): dx.doi.org/10.4172/2324-8777.1000e102.

Maresi G, Oliveira Longa CM, Turchetti T (2013) Brown rot on nuts of *Castanea sativa* Mill: An emerging disease and its causal agent. iForest 6:294–301

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

Miteva D, Dimov K, Nacheva I, Todorov Y, Doneva M, Metodieva P, Tsvetkov T (2014) Modern technological approaches for ensuring of harmless and quality fruits. Bulgarian Journal of Agricultural Science 20: 243-245

Ruprecht, H., Vacik, H., Steiner, H., and Frank, G. (2012). ELENA – a methodological approach for the long term monitoring of the natural regeneration of natural forest reserves dominated by Norway-spruce (*Vaccinio piceetea*). *Austrian* Journal of Forest Science 129(2), 67-105.

Saber, R., Shakoori, Z., Sarkar, S., Tavoosidana, Gh., Kharrazi, Sh., Gill, P. (2013). Spectroscopic and microscopic analyses of rod-shaped gold nanoparticles interacting with single-stranded DNA oligonucleotides. IET Nanobiotechnology 7:42–49.

Schmidt O (2006) Wood and tree fungi. Biology, damage, protection and use. Springer Verlag Berlin Heidelberg.

Schmidt O (2007) Indoor wood-decay basidiomycetes: damage, causal fungi, physiology, identification and characterization, prevention and control. Mycological Progress 6(4): 261 – 279; DOI 10.1007/s11557-007-0534-0.

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

Taghiyari HR (2014) Effects of nanosilver-impregnation and alfalfa-intercropping on fluid transfer in downy black poplar wood. Maderas-Cienc Tecnol. 16(1): 49 – 62.

Taghiyari HR, Schmidt O (2014) Nanotechnology in wood-based composite panels. International Journal of Bio-Inorganic Hybrid Nanomaterials 3(2): 65 – 73.

Taghiyari HR, Bari E, Schmidt O, Tajick Ghanbary MA, Karimi A, Tahir PMD (2014a) Effects of nanowollastonite on biological resistance of particleboard made from wood chips and chicken feather against *Antrodia vaillantii*. International Biodeterioration & Biodegradation 90: 93 – 98.

Taghiyari HR, Bari E, Schmidt O (2014b) Effects of nanowollastonite on biological resistance of medium-density fiberboard against *Antrodia vaillantii*. European Journal of Wood and Wood Products 72(3): 399 - 406 DOI 10.1007/s00107-014-0794-8.

Taghiyari HR, Ghorbanali M, Tahir PMD (2014c) Effects of the improvement in thermal conductivity coefficient by nano-wollastonite on physical and mechanical properties in medium-density fiberboard (MDF) BioResources 9(3): 4138 – 4149.

Taghiyari HR, Moradi-Malek B, Ghorbani Kookandeh M, Farajpour Bibalan O (2014d) Effects of silver and copper nanoparticles in particleboard to control *Trametes versicolor* fungus. International Biodeterioration & Biodegradation 95: 69 – 72.

USPTO (2009) Gas permeability measurement apparatus; patent number 8079249.

Article submitted: September 6, 2014; Peer review completed: October 2, 2014; Revised version received and accepted: November 24, 2014; Published: December 10, 2014.