

# Effects of the Improvement in Thermal Conductivity Coefficient by Nano-Wollastonite on Physical and Mechanical Properties in Medium-Density Fiberboard (MDF)

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The improving effect of an increase in the thermal conductivity caused by nano-wollastonite (NW) on the physical and mechanical properties of medium-density fiberboard (MDF) was studied. Nanowollastonite was applied at 2, 4, 6, and 8 g/kg, based on the dry weight of wood-chips, and compared with control specimens. The size range of wollastonite nanofibers was 30 to 110 nm. The results show that NW significantly ( $p < 0.05$ ) increased thermal conductivity. The increased thermal conductivity resulted in a better curing of the resin; consequently, mechanical properties were improved significantly. Furthermore, the formation of bonds between wood fibers and wollastonite contributed to fortifying the MDF. It was concluded that a NW content of 2 g/kg did not significantly improve the overall properties and therefore cannot be recommended to industry. Because the properties of NW-6 and NW-8 were significantly similar, a NW-content of 6 g/kg can be recommended to industry to significantly ( $p < 0.05$ ) improve the properties of MDF panels.

*Keywords: Minerals; Nanotechnology; Particleboard; Thermal conductivity coefficient; Wollastonite; Wood composite*

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## INTRODUCTION

Composite boards provide a homogeneous structure and the advantage of the use of raw materials without restrictions as to the shape and size. Moreover, the adversity caused by natural regeneration and in environmental conditions (Ruprecht *et al.* 2012) is significantly lower than that in solid woods. It is therefore no small wonder that wood-based composite products are commonly substituted for solid wood in current building structures. Structural and non-structural engineered wood composites such as particleboard, oriented strand-board (OSB), plywood, medium density fiberboard (MDF), laminated veneer lumber (LVL), and thermoplastic/wood fiber blends are now used for both interior and exterior applications. Their use, however, is often limited due to high sensitivity to moisture and decay (Baileys *et al.* 2003), as well as to fire (Ayrilmis *et al.* 2007; Singh and Singh 2012). Therefore, the emergence of new technologies to produce an increasing array of new wood composite products has forced the industry to pursue varied processes and/or treatments to protect these new wood-based products.

The process of hot-pressing is usually considered to be a bottle-neck in nearly all wood-composite manufacturing factories. The minimum pressing time of a wood-composite panel primarily depends on heat transfer, which in turn varies with thickness, press temperature, closing rate, and mat moisture distribution. In the case of urea-formaldehyde (UF) resin, there is a limitation of moisture content (MC) level (Papadopoulos 2006). Furthermore, due to the increased brittleness of UF-resin in comparison to other resins, complete curing of the resin will result in the improvement of the properties. To this end, the addition of metal nanoparticles having a high thermal conductivity coefficient (Drelsh 2013; Khojier *et al.* 2012; Saber *et al.* 2013) has been reported to decrease press time and to improve mechanical properties in particleboard as well as decrease the heat gradient over the profile of composite boards (Taghiyari *et al.* 2013a). However, unusual changes in the properties of materials may occur when the size of a particle is reduced to the nanometer scale (Li 2012).

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 that is not hazardous to humans or wildlife, unlike other mineral insoluble dusts like perlite that was reported to entail risks (Maxim *et al.* 2014a). In fact, a review of the available epidemiological studies on wollastonite provides no evidence to suggest that wollastonite presents a health hazard; earlier studies on workers exposed to wollastonite dust indicated a need for further study of the health hazards to be carried out to come to a final conclusion (Huuskonen *et al.* 1983; Maxim and McConnell 2005). However, a recent study on epidemiology and toxicity of wollastonite summed up that no pleural plaques or interstitial lung disease or decrements in lung function were observed among both never smokers as well as former smokers occupationally exposed to wollastonite (Maxim *et al.* 2014b). They further concluded that wollastonite had relatively low toxicity as currently managed, and that the present occupational limits (OELs) are adequate. Moreover, wollastonite nanofibers were fixed in position by the cured resin in the present study; therefore, there would low possibility for inhalation healthy hazards of composite boards made and installed at work. However, separate studies on the possibility of arising health hazards by wollastonite nanofibers fixed in the wood-composite matrix are encouraged by researchers. Nevertheless, continued medical surveillance of occupationally exposed cohorts would be a reasonable precaution for workers in wollastonite-treated wood-composite manufacturing factories.

The fire-retardant properties of nano-wollastonite, as a silicate mineral ( $\text{CaSiO}_3$ ), have been reported as promising when used in solid woods (Haghighi *et al.* 2014) and wood-composite materials (Taghiyari *et al.* 2013b). Wollastonite nanofibers have also been reported to improve the biological resistance against the wood-deteriorating fungus *Trametes versicolor* in trees (Karimi *et al.* 2013; Maresi *et al.* 2013; Taghiyari *et al.* 2014).

Effects of wollastonite on the physical and mechanical properties of composite boards have yet to be studied. The present study, therefore, aims to evaluate the effects of wollastonite nanofibers on the physical and mechanical properties in medium-density fiberboard and to find any correlation between the increase in the thermal conductivity of a wood-composite mat and the possible improvements in the physical and mechanical properties.

## EXPERIMENTAL

### Materials

Wood fibers were procured from the Sanaye Choobe Khazar Company in Iran (MDF Caspian Khazar) and comprised a mixture of five species to include beech, alder, maple, hornbeam, and poplar from neighboring forests. The MDF boards were 10 mm in thickness, with a density of 750 kg/m<sup>3</sup>. A HT/MLM-170 hot press (Mehrabadi Mfg. Co., Tehran) was used to apply a total nominal pressure of 160 bars, with a fixed temperature of 160°C for the plates and a hot-pressing time of 7 min. Urea-formaldehyde resin (UF), a thermosetting resin from Sari Resin Manufacturing Company (Sari, Iran) was used at a concentration of 10%, a viscosity of 200 to 400 cP, a gel time of 47 sec, and a density of 1.277 g/cm<sup>3</sup>. The moisture content of the specimens at the time of testing was 7.5 ± 2%. Five replicate boards were made for each treatment, from which two specimens were prepared for each property measurement.

Primarily, the thermal conductivity of wollastonite was studied here; therefore, in order to have a smooth and uniform spread of wollastonite particles and benefit from the maximum surface area of the particles, they were used at nano-scale; further studies may consider the difference between wollastonite at nano as well as regular scale. Nano-wollastonite (NW) gel was produced in cooperation with the Vard Manufacturing Company of Mineral and Industrial Products (Iran). The size range of the wollastonite nanofibers was 30 to 110 nm. Specifications for the wollastonite nanofibers are given in Table 1. Nano-wollastonite was mixed with the UF resin and sprayed on the wood fibers at concentrations of 2, 4, 6, and 8 g/kg (*i.e.*, 2, 4, 6, and 8%) before hot pressing to form the MDF. The results compared the treated MDF with the untreated control. The produced MDF panels were conditioned in a chamber (25 ± 2 °C, 45 ± 3% relative humidity) for two weeks before sample preparation, since the wood has a thermo-hygro-mechanical behavior and its deformation properties depends on the combined action of temperature, relative humidity, and mechanical load variations (Figueroa *et al.* 2012).

### Methods

#### *Standard test methods*

Physical and mechanical tests, including internal bond strength, were carried out in accordance with ISIRI 9044 PB Type P2 (2000) (compatible with ASTM D-1037 2012) specifications. The static bending test was performed using center-point loading over a 380-mm span. The loading speed was 2 mm/min. All tests were conducted using an Instron 4486 testing machine, model 4486 (USA). Equations 1 through 3 were used to calculate the final values of MOR (modulus of rupture), MOE (modulus of elasticity), and IB (internal bond),

$$MOR = \frac{1.5 FL}{bd^2} \text{ (MPa)} \quad (1)$$

$$MOE = \frac{FL^3}{4bd^3D} \text{ (MPa)} \quad (2)$$

$$IB = \frac{F_{\max}}{A} \text{ (MPa)} \quad (3)$$

where  $F$  is the maximum load,  $L$  is the length of loading span,  $b$  is the width of the specimen,  $d$  is the thickness of the specimen,  $D$  is the center deflection at proportional limit load, and  $A$  is the area of the specimen under load.

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

Nano-wollastonite compounds	Mixing ratio by mass (%)
CaO	39.77
SiO <sub>2</sub>	46.96
Al <sub>2</sub> O <sub>3</sub>	3.95
Fe <sub>2</sub> O <sub>3</sub>	2.79
TiO <sub>2</sub>	0.22
K <sub>2</sub> O	0.04
MgO	1.39
Na <sub>2</sub> O	0.16
SO <sub>3</sub>	0.05
Water	4.67

#### *Thermal conductivity measurement*

Thermal conductivity was measured with a KD2-Pro Thermal Properties Analyzer, produced by Decagon Devices Inc. (USA). Heat was applied to a single needle (TR-1) for a time,  $t_h$ , and temperature was monitored in the needle during heating and for an additional time equal to  $t_h$  after heating. The size of needle was 2.4 mm in diameter and 100 mm in length. The temperature during heating was computed from Eq. 4,

$$T = m_0 + m_2 t + m_3 \ln t \quad (4)$$

where  $m_0$  is the ambient temperature during heating,  $m_2$  is the rate of background temperature drift, and  $m_3$  is the slope of a line relating temperature rise to logarithm of temperature.

The thermal conductivity was then computed from Eq. 5,

$$k = \frac{q}{4\pi m_3} \quad (5)$$

where  $k$  is the thermal conductivity ( $\frac{W}{mk}$ ),  $q$  is the heat input (W), and  $m_3$  is the slope of a line relating temperature

#### *SEM imaging*

A scanning electron microscope (SEM; Hitachi SU8010, Japan) was used at the Thin-Film Laboratory, FE (field emission)-SEM lab, School of Electrical and Computer Engineering, The University of Tehran. The SEM, operated at an accelerating voltage of 15 kV, was equipped with a field-emission cathode in the electron gun that provided a

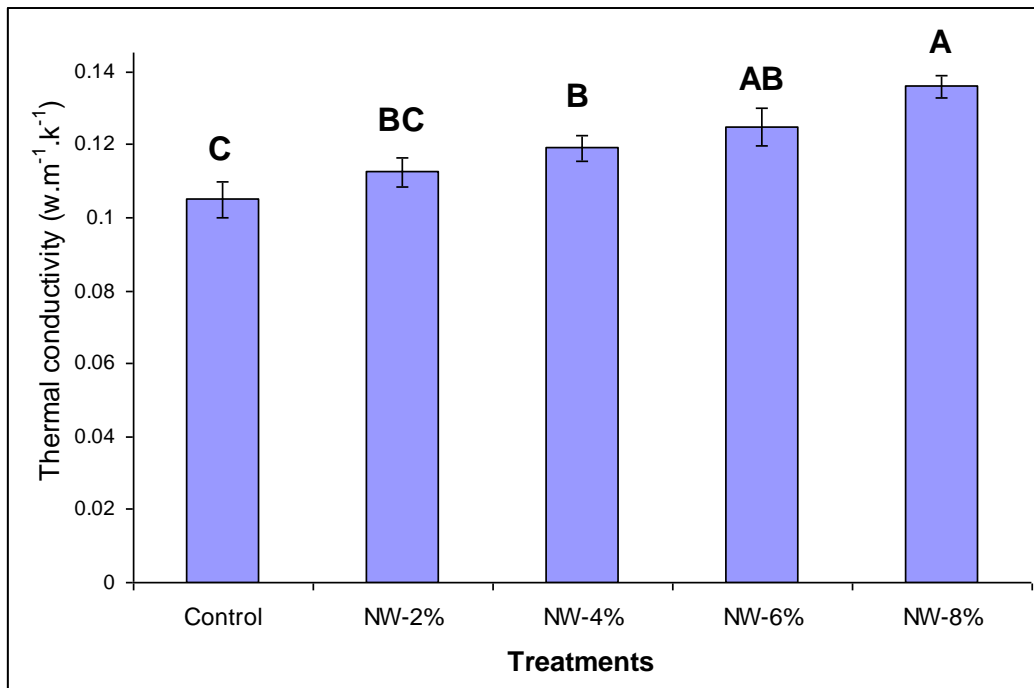
narrow probe beam to improve spatial resolution and minimize sample charging and damage. The samples were mounted on an aluminum stub with double-sided tape and sputter coated with a gold alloy.

### Statistical analysis

Statistical analysis was conducted using SAS software, version 9.2 (Cary, NC USA). Two-way analysis of variance (ANOVA) was performed on the mean data to determine significant differences at the 95% level of confidence. Hierarchical cluster analysis, including dendrograms and Ward methods with squared Euclidean distance intervals, was carried out using SPSS/18, version 18 (IBM; USA). Cluster analysis was performed to find similarities and dissimilarities between treatments based on more than one property simultaneously. The scaled indicator in each cluster analysis shows similarities and differences between treatments; lower scale numbers show more similarities while higher ones show dissimilarities. Fitted-line and scatter plots were created in Minitab software, version 16.2.2 (Minitab Inc.; USA).

## RESULTS AND DISCUSSION

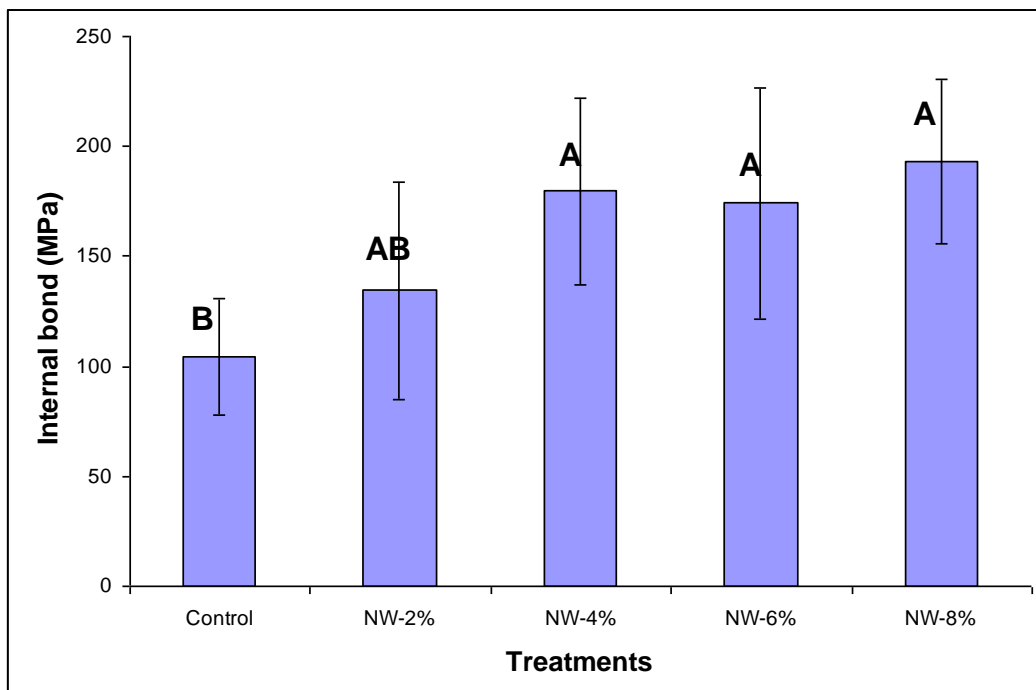
The highest thermal conductivity coefficient was observed in the treatment with the highest wollastonite content that is NW-8% ( $0.136 \text{ w.m}^{-1}.\text{k}^{-1}$ ) (Fig. 1). Control MDF panels showed the lowest thermal conductivity coefficient ( $0.105 \text{ w.m}^{-1}.\text{k}^{-1}$ ); that is, wollastonite nanofibers significantly ( $p < 0.05$ ) contributed to better transfer of heat in a way that thermal conductivity coefficient was increased by more than 29% in the NW-8% treatment.



**Fig. 1.** Thermal conductivity coefficient ( $\text{w.m}^{-1}.\text{k}^{-1}$ ) in the five treatments of the medium-density fiberboards (NW = nanowollastonite content)  
A, B, and C denote statistically significant differences ( $p < 0.05$ )

A gradual increasing trend was observed as the NW-content was increased in the MDF panels. Thermal conductivity of wood was reported to be 0.04 to 0.2 ( $\text{w.m}^{-1}.\text{k}^{-1}$ ), depending on the species and direction from which it is viewed; however, the thermal conductivity of wollastonite was reported as 2.5 ( $\text{w.m}^{-1}.\text{k}^{-1}$ ) (Taghiyari *et al.* 2013c). Therefore, wollastonite nanofibers spread all over the MDF-fibers significantly ( $p < 0.05$ ) contributed to the 29% of increase in the thermal conductivity.

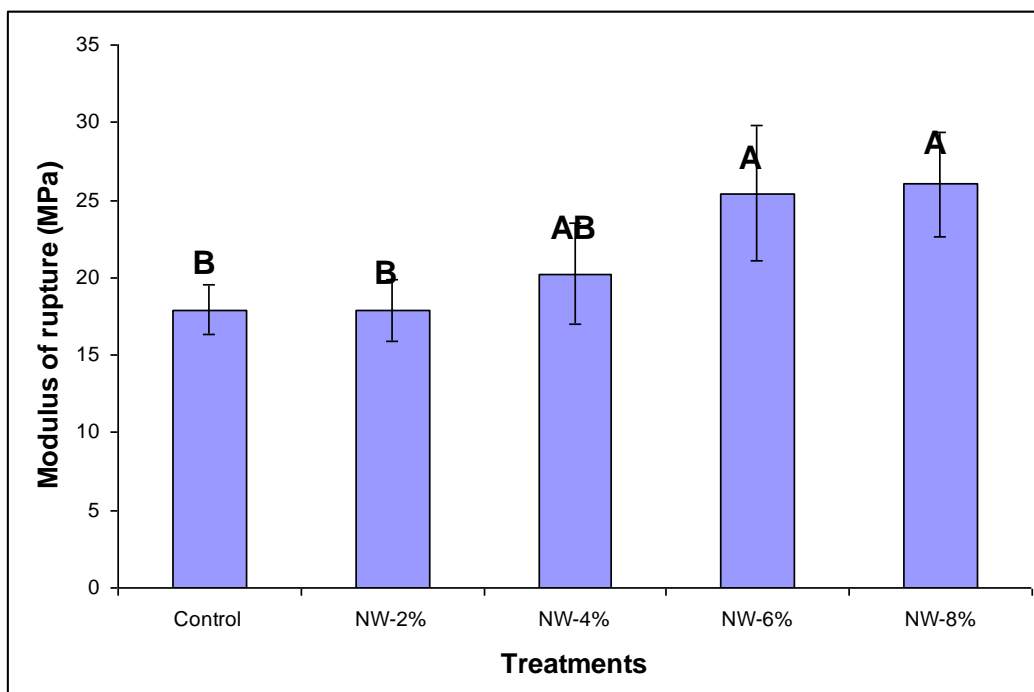
Similarly, the internal bond strength showed significant improvement in the panels treated with wollastonite nanofibers (Fig. 2). The highest IB value was found in the NW-8 treatment (193.3 MPa), showing a more than 85% increase in comparison to the control specimens (104.2 MPa). This improvement was related to two phenomena: first, the increased thermal conductivity of the MDF-matrix due to the involvement of wollastonite nanofibers in the wood-composite matrix; and second, formation of bonds between the nanowollastonite and wood compounds, namely hydroxyl and methoxy groups of lignin and cellulose (Taghiyari *et al.* 2013c). The cited study reported that the preparation of wollastonite composites involved formation of bonds between the hydroxyl and methoxy groups of the benzene cycles in lignin and cellulose. This way, the individual fibers in the MDF-matrix were better connected to each other through a network of bonds formed between the wollastonite compounds and wood functional groups, facilitating the heat transfer and improving the curing of resin in the central part of the mat; ultimately the internal bond significantly ( $p < 0.05$ ) increased.



**Fig. 2.** Internal bond (MPa) in the five treatments of the medium-density fiberboards (NW = nanowollastonite content)  
A and B denote statistically significant differences ( $p < 0.05$ )

The highest MOR value was found in the MDF panels with the highest NW-content of 8% (26 MPa) (Fig. 3). No significant difference ( $p < 0.05$ ) was observed between MOR values in the NW-6 and NW-8 treatments, although NW-8 was slightly

higher than NW-8. In the same way, the lowest MOR value was observed in the control panels (17.9 MPa), although that result was not statistically different from the NW-2 treatment. Wollastonite nanofibers increased MOR more than 45% in the NW-8 treatment in comparison to the control panels. Facilitated transfer of heat contributed in the improvement in the MOR values; moreover, the chemical bonds formed among the hydroxyl groups of the wood cell structure and the wollastonite compounds caused better integration in the composite matrix, resulting in the improved MOR values. A similar significant ( $p < 0.05$ ) improving effect was observed in the MOE values in all NW-treated MDF panels in comparison to the control specimens, although no statistical difference was observed among the NW-treated panels with different NW-contents (Fig. 4). The control treatment showed the lowest MOE value (77.7 MPa). Wollastonite nanofibers increased the MOE to more than 32% in the NW-8 treatment.



**Fig. 3.** Modulus of rupture (MPa) in the five treatments of the medium-density fiberboards (NW = nanowollastonite content)  
A and B denote statistically significant differences ( $p < 0.05$ )

As to the physical properties of water absorption and thickness swelling after 2 and 24 h of immersion in water, no significant changes ( $p < 0.05$ ) were observed, although water absorption increased slightly and thickness swelling decreased slightly in the NW-treated panels (Figs. 5 and 6). The slight increase in the water absorption is related to the formation of hydroxyl bonds between water and wollastonite compounds, increasing the amount of water molecules that the whole wood-composite matrix absorbed in comparison to the control specimens. In the thickness swelling, however, the bonds formed between the wood-cell structure with wollastonite compounds resulted in better integrity of the wood-composite matrix, resulting in lower thickness swelling as NW-content increased.

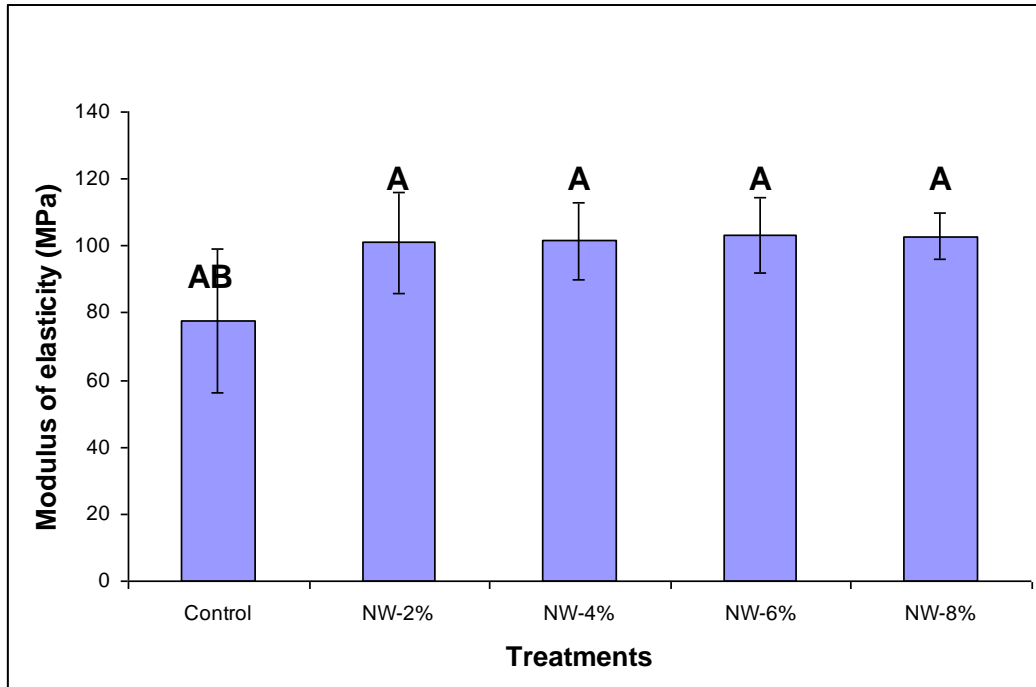


Fig. 4. Modulus of elasticity (MPa) in the five treatments of the medium-density fiberboards (NW = nanowollastonite content)

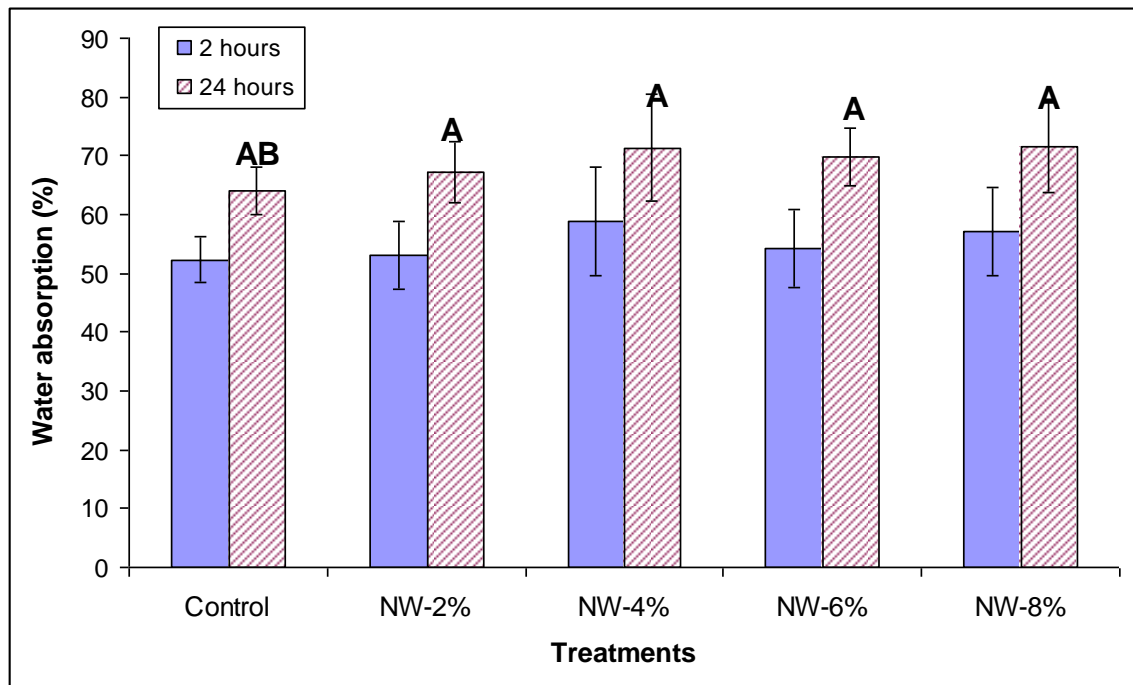
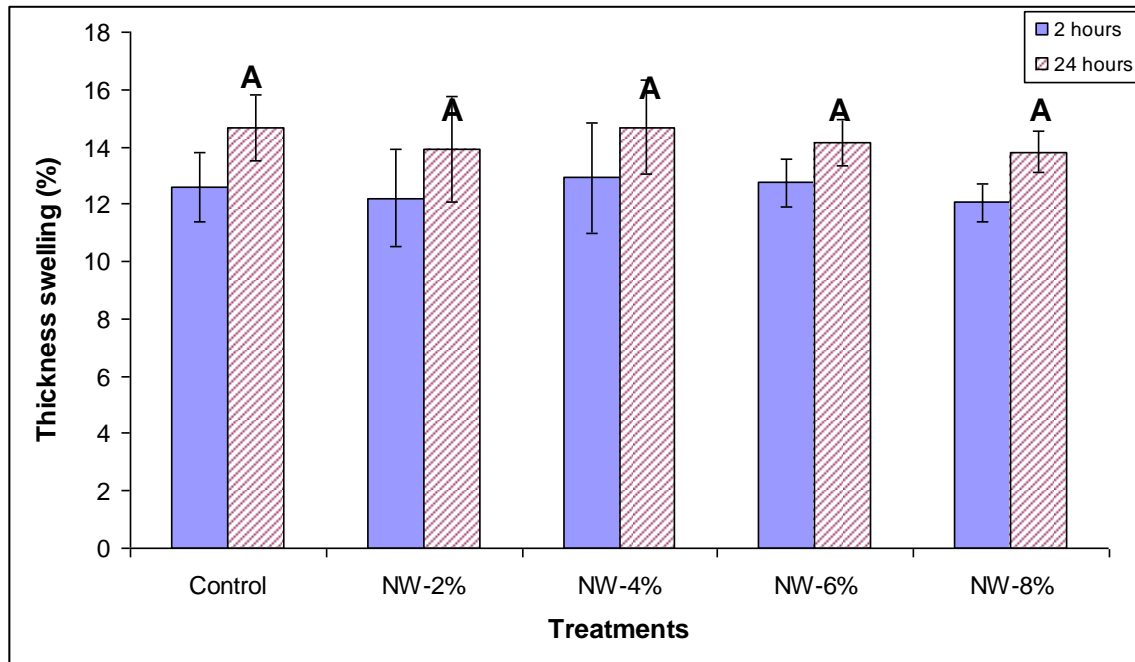
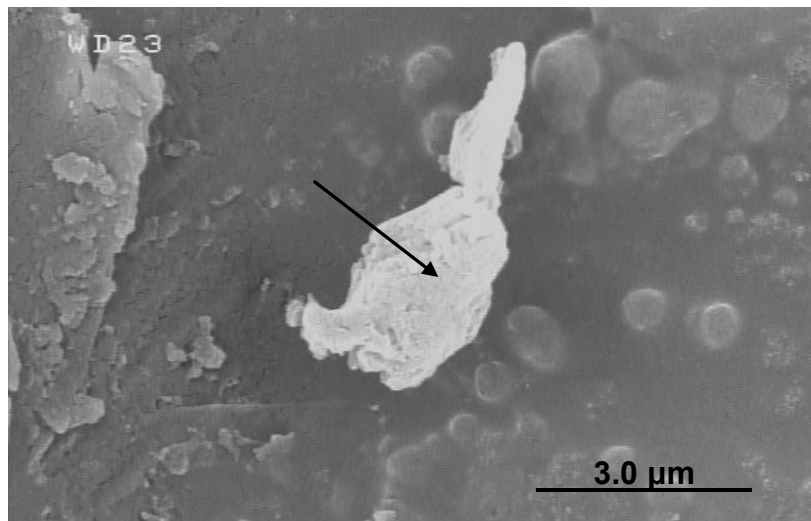


Fig. 5. Water absorption (%) in the five treatments of the medium-density fiberboards (NW = nanowollastonite content)





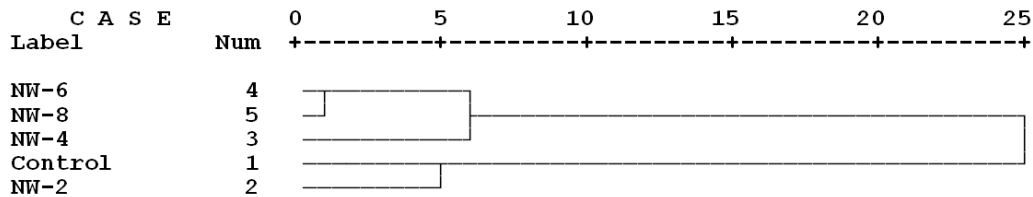
**Fig. 6.** Thickness swelling (%) in the five treatments of the medium-density fiberboards (NW = nanowollastonite content)



**Fig. 7.** SEM image showing nano-wollastonite (arrow) on wood fiber

Cluster analysis of the five treatments based on all the properties measured (MOR, MOE, IB, water absorption (WA), and thickness swelling (TS) after 2 and 24 h immersion in water, and thermal conductivity coefficient) showed that control panels (NW-4, NW-6, and NW-8) were significantly ( $p < 0.05$ ) categorized in a different cluster in comparison to NW-treated panels (Fig. 8). This demonstrated the significant effects ( $p < 0.05$ ) of wollastonite nanofibers on the improvement in the overall properties in the NW-treated MDF panels. However, NW-2 treatment had a tendency to be clustered

together with the control specimens, showing more similarity between these two treatments. This implied that NW-content of only 2% did not have significant ( $p < 0.05$ ) improving effects on the overall properties. As to the NW-6 and NW-8 treatments, their close clustering showed significant ( $p < 0.05$ ) similarity between these two treatments. It can therefore be concluded that the lower NW-content of 6% is recommended to industry to keep the production expenses lower and to improve the properties to the optimum level as well.



**Fig. 8.** Cluster analysis of the five treatments based on all physical and mechanical properties as well as thermal conductivity coefficients measured in the present study (NW = nanowollastonite; 2, 4, 6, and 8 = nanowollastonite contents)

## CONCLUSIONS

1. Wollastonite nanofibers significantly ( $p < 0.05$ ) improved the thermal conductivity coefficient in the wood-composite matrix in MDF.
2. The increased thermal conductivity coefficient in the NW-treated MDF panels resulted in a better heat-transfer from the hot-press plates to the core section of the composite mat; consequently, the internal bond increased.
3. Formation of bonds between the wood-cell structure and wollastonite compound, as well as better curing of the resin due to the improved thermal conductivity, caused the mechanical properties of MOR and MOE to significantly ( $p < 0.05$ ) improve. The physical properties of WA and TS, though, did not improve as much as the mechanical properties.
4. A wollastonite content of 2% was not enough to significantly ( $p < 0.05$ ) improve the properties. Moreover, the overall properties of NW-6 and NW-8 were similar. Therefore, an NW-content of 6% can be recommended to industry to both improve the properties of MDF panels and keep production expenses low.

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## REFERENCES CITED

- ASTM D1037-99. (2012). "Standard test methods for evaluating properties of wood-base fiber and particle panel materials".
- Aitken, E. (2010). *Analyses of the Effect of Silicon on Fusarium Wilt on Banana*, Horticulture Australia, Sydney, NSW, Australia.
- Ayrilmis, N., Candan, Z., and White, R. (2007). "Physical, mechanical, and fire properties of oriented strandboard with fire retardant treated veneers," *European Journal of Wood and Wood Products* 65(6), 449-458.
- Baileys, J. K., Marks, B. M., Ross, A. S., Crawford, D. M., Krzysik, A. M., Muehl, J. H., and Youngquist, J. A. (2003). "Providing moisture and fungal protection to wood-based composites," *Forest Products Journal* 53(1), 76-81.
- Drelsh, J. (2013). "Nanoparticles in a liquid: New state of liquid?" *Journal of Nanomaterials & Molecular Nanotechnology* 2(1), 1-2.
- Figuroa, M., Bustos, C., Dechent, P., Reyes, L., Cloutier, A., and 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(3), 303-319.
- Haghighi Poshtiri, A., Taghiyari, H. R., and Karimi, A. N. (2014). "Fire-retarding properties of nano-wollastonite in solid wood," *Philippine Agricultural Scientist* 97(1), 45-52.
- Huuskonen, M. S., Jarvisalo, J., Koskinen, H., Nickels, J., Rasanen, J., and Asp, S. (1983). "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.
- ISIRI 9044. (2000). "Wood and wood-based panels: Specifications," *Institute of Standards and Industrial Research of Iran*.
- Karimi, A., Taghiyari, H. R., Fattahi, A., Karimi, S., Ebrahimi, G., and Tarmian, A. (2013). "Effects of wollastonite nanofibers on biological durability of poplar wood (*Populus nigra*) against *Trametes versicolor*," *BioResources* 8(3), 4134-4141.
- Khojier, K., Zolghadr, S., and Zare, N. (2012). "Structural, electrical, and optical properties of molybdenum oxide thin films prepared by post-annealing of Mo thin films," *International Journal of Bio-Inorganic Hybrid Nanomaterials* 1(3), 199-207.
- Li, D. (2012). "Nanostructuring materials towards conventionally unachievable combination of desired properties," *Journal of Nanomaterials & Molecular Nanotechnology* 1(1), 1-2.
- Maresi, G., Oliveira, Longa, C. M., and 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.
- Maxim, L. D., Niebo, N., and McConnell, E. E. (2014a). "Perlite toxicology and epidemiology – A review," *Inhal. Toxicol.* 26(5), 259-270.
- Maxim, L. D., Niebo, R., Utell, M. J., McConnell, E. E., and Segrave, A., M. (2014b). "Wollastonite toxicity: An update," *Inhal. Toxicol.* 25(2), 95-112.
- Papadopoulos, A. N. (2006). "Property comparisons and bonding efficiency of UF and PMDI bonded particleboards as affected by key process variables," *BioResources* 1(12), 201-208.

- 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, G., Kharrazi, S., and Gill, P. (2013). "Spectroscopic and microscopic analyses of rod-shaped gold nanoparticles interacting with single-stranded DNA oligonucleotides," *IET Nanobiotechnology* 7(2), 42-49.
- Singh, T., and Singh, A. P. (2012). "A review on natural products as wood protectant," *Wood Science and Technology* 46(5), 851-870.
- Taghiyari, H. R., Moradiyan, A., and Farazi, A. (2013a). "Effect of nanosilver on the rate of heat transfer to the core of the medium density fiberboard mat," *International Journal of Bio-Inorganic Hybrid Nanomaterials* 2(1), 303-308.
- Taghiyari, H. R., Rangavar, H., and Nouri, P. (2013b). "Fire-retarding properties of nano-wollastonite in MDF," *European Journal of Wood and Wood Products* 71(5), 573-581.
- Taghiyari, H. R., Mobini, K., Samadi, Y. S., Doosti, Z., Karimi, F., Asghari, M., Jahangiri, A., and Nouri, P. (2013c). "Effects of nano-wollastonite on thermal conductivity coefficient of medium-density fiberboard," *Journal of Nanomaterials and Molecular Nanotechnology* 2(1), 1-5.
- Taghiyari, H. R., Bari, E., Schmidt, O., Tajick Ghanbary, M. A. T., Karimi, A., Tahir P. M. D. (2014). "Effects of nanowollastonite on biological resistance of particleboard made from wood chips and chicken-feather against *Antrodia vaillantii*," *International Biodeterioration & Biodegradation* 90, 93-98.

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