Nano-Wollastonite in Particleboard: Physical and Mechanical Properties

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The effects of wollastonite nanofibers on the physical and mechanical properties of particleboard were studied. Nano-wollastonite (NW), with the size range of 30 to 110 nm, was applied at 5, 10, 15, and 20%, based on the dry weight of wood chips, and compared with control specimens. Two application methods of NW were used: surface application (SA) and internal application (IA). Density was kept constant at 0.68 g/cm^3 for all treatments. Tests were carried out in accordance with ASTM D-1037 specifications. The obtained results showed that NW formed bonds between the wood chips and improved the physical and mechanical properties, both when applied internally and when applied superficially. However, formation of micro-cavities and decreased integration in the particleboard matrix caused by a reduction in wood chip content resulted in a decrease in the mechanical properties of IA-NW-treated specimens at higher NW consumption levels. It may be concluded that surface application of NW at a 1.5% consumption level can be recommended for use in particleboards.

Keywords: Biotechnology; Minerals; Nanoscience; Particleboard; Wollastonite; Wood-composite

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INTRODUCTION

Wood is frequently modified by engineering processes to produce more homogeneous mechanical properties (Hill 2006; Boonstra *et al*. 2007). The quality of wood can also be affected by rotation period, mono- or mixed-species cultivation (Addo-Danso *et al*. 2012), natural regeneration (Ruprecht *et al*. 2012), light and soil, the density of plants, the interaction between clone-type and stand, initial spacing and alfalfa-intercropping of trees, nanotechnology treatments, drying procedures, hygroscopicity, moisture content, fiber properties, acoustic properties, natural factors, durability, and even diffusion and permeation. Furthermore, the majority of humans world-wide depend upon wood products harvested from forests (Singh and Singh 2012); therefore, efficient use of wood is highly important.

Composite boards offer the advantages of a homogeneous structure and the use of raw materials without restrictions as to the shape and size, and many studies have been conducted to find methods for the limitation of formaldehyde emissions. Another advantage of wood-based composites is that they offer in-process treatment (IPT) options (incorporation during manufacture), as well as post-manufacture treatments (PMT) (Manning 2002). IPT methods offer several distinct advantages not found in solid wood

products (Manning 2002; Ayrilmis *et al*. 2007). The high thermal conductivity coefficient of metal nanoparticles (Narashimha *et al*. 2011; Dongyang 2012; Sadeghi and Rastgo 2012) applied by IPT has been reported to decrease press time and improve mechanical properties in particleboard (Taghiyari *et al*. 2011) and to decrease gas and liquid permeability.

Wollastonite enhances plant growth and reduces the effects of certain pathogens, including fungi (Aitken 2010). As to the environmental aspects and health issues, wollastonite is known to be a non-toxic mineral material that is not hazardous to humans or wildlife (Huuskonen *et al.* 1983a; Maxim and McConnell 2005). Also, the long-term health effects due to inhalation of wollastonite appear to be negligible (Huuskonen *et al.* 1983b).

The fire-retarding properties of nano-wollastonite have been reported to be promising when used in solid woods (Haghighi *et al*. 2013) and wood-composite materials (Taghiyari *et al*. 2013a). Wollastonite nanofibers have also been reported to increase the thermal conductivity coefficient of MDF (Taghiyari *et al*. 2013b) as well as biological resistance against wood-deteriorating fungi *Trametes versicolor* (Karimi *et al*. 2013). Their effects on the physical and mechanical properties of composite boards have not yet been studied. The present study therefore aimed to evaluate the effects of wollastonite nanofibers on the physical and mechanical properties of particleboard.

EXPERIMENTAL

Specimen Preparation

Wood chips were procured from Shahid Dr. Bahonar Composite-board Company. The chips comprised a mixture of five species, *i.e.*, beech (*Fagus orientalis*), alder (*Alnus glutinosa* L.), maple (*Acer hyrcanum*), hornbeam (*Carpinus betulus* L.), and poplar (*Populus nigra*), from neighboring forests. Dimension of panels was 40 × 40 mm. The thickness of panels was 8 mm. Density was kept constant for all treatments (0.68 g/cm^3) because the wood-composite manufacturers are very strict on the consumption of raw materials and the final costs; therefore, as the present research project aimed at finding a practical solution to the shortage of raw material, density was kept constant. Boarder edges of all panels were trimmed to 5 cm because the integrity and density of the border sections cannot be authenticated. Five replicate panels were produced for each treatment; in total, 45 panels were produced. Replicate specimens for each of the physical and mechanical tests were prepared from different panels. The total nominal pressure of the plates was 160 bar. The temperature of the plates was fixed at 130 °C. The hot-pressing duration was 8 min. Urea-formaldehyde resin (UF) was procured from Sari Resin Manufacturing Company (Sari, Iran). Ten percent UF with a viscosity of 200 to 400 cP, 47 s of gel time, and a density of 1.277 g/cm^3 was used. Specimens were kept in a conditioning chamber (30±2 °C, and 45±3% relative humidity) for 2 months after pressing before the tests were carried out. The moisture content of the specimens at the time of testing was 7.5% because wood has a thermo-hygromechanical behavior, and its properties depends on the combined action of temperature, relative humidity, and mechanical load variations (Figueroa *et al.* 2012). From each panel, one MOR specimen, two WA specimens, two IB specimens, and four hardness specimens were cut; the three hardness specimens were bound together to meet the required thickness of 25 mm.

Methods

Nano-wollastonite application

Nano-wollastonite (NW), a silicate mineral ($CaSiO_3$), gel was produced in cooperation with Vard Manufacturing Company of Mineral and Industrial Products, Iran. The size range of wollastonite nanofibers was 30 to 110 nm. The wollastonite specifications are given in Table 1. NW was applied in two ways: (1) Mixing with UF resin and spraying on the chips before hot pressing (internal application of NW) and (2) Mixing with a water-based paint and spraying on the surfaces of the particleboard specimens 2 months from the date of their production (surface application of NW); all physical and mechanical tests were also carried out 2 months after spraying NW on the surface of the specimens. In both the internal application (IA) and surface application (SA) methods, the consumption levels of NW remained the same (0, 5, 10, 15, and 20%). This way, there were four treatments of IA and four treatments of SA; adding the control treatment, there were nine different treatments. Considering the five replications, 45 panels were produced.

Standard test methods

Physical and mechanical tests, including internal bond strength (IB) tests, were carried out in accordance with ISIRI 9044 PB Type P2 (compatible with ASTM D-1037) specifications (Taghiyari *et al*. 2011). The physical and mechanical testing specimens were cut in accordance with the location and size depicted in Fig. 1. No specimen was prepared from the border parts of the panels, as density of the border was supposed to have high fluctuation; this border part is marked "Safety margin" (Fig. 1). The dimension of the specimens for modulus of rupture (MOR) and modulus of elasticity (MOE) tests was 240 × 75 mm. The static bending test was performed using center-point loading over a 200-mm span. The dimensions of specimens for the internal bond strength (IB), water absorption (WA), and thickness swelling (TS) testing were 75 × 75 mm. A continuous uniform loading rate of 4 mm/min was applied for all MOR, MOE, and IB specimens. Tests on the IB were only conducted in the control and IA treatments. In the SA specimens, nano-wollastonite was applied only on the surface of the specimens produced with the same conditions as in the control specimens. In fact, surface application of nano-wollastonite only affected the surface of the specimens; that is, the central parts of the specimens were not affected in any way. Therefore, SA treatments were assumed to have the same IB as the control specimens. All tests were conducted using an Instron 4486 testing machine. Equations 1 through 3 were used to calculate the final values of MOR, MOE, and IB,

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

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

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

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.

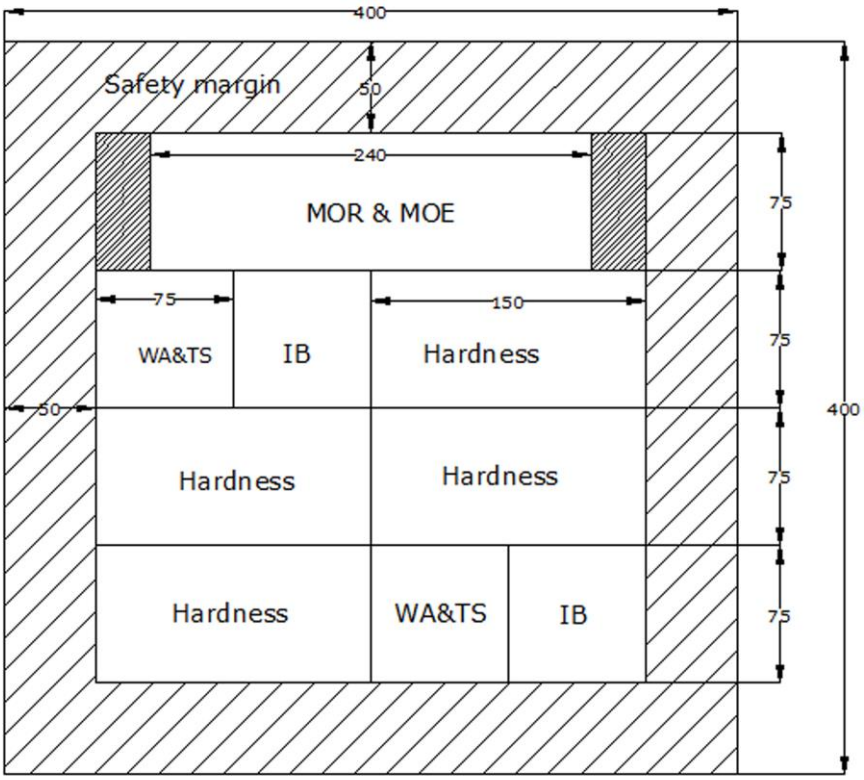

Fig. 1. Schematic diagram of an MDF panel with 50-mm safety margin and the size and location of physical and mechanical specimens (units in mm)

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

Hardness was measured using a modified Janka ball test at 2-, 3-, and 4-mm penetration depths of the hardness ball to evaluate the effects of nano-wollastonite at different penetration depths. Dimensions of the hardness specimens were 75 × 150 mm.

As stipulated in the standard, three specimens were bound together to meet the required thickness of 25 mm; two penetrations were made on each of the flat faces of the specimens, the average of which was considered final for statistical purposes. Loading test was applied at a uniform rate of 4 mm/min.

SEM imaging

SEM imaging was done with a field-emission (FE) SEM at the School of Electrical & Computer Engineering, The University of Tehran. A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energies, resulting in both improved spatial resolution and minimized sample charging and damage.

From each treatment, two specimens were prepared for SEM imaging. Dimensions of the specimens were 15 × 8 mm. Imaging was carried out at five random locations from the core section each specimen.

Statistical analysis

Statistical analysis was conducted using SAS software, version 9.2 (2010). Two-way analysis of variance (ANOVA) was performed on the 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 (2010). 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 how much treatments are similar or different; lower scale numbers show more similarities while higher ones show dissimilarities.

RESULTS AND DISCUSSION

Wollastonite nanofibers significantly decreased water absorption and thickness swelling, both when applied internally and when applied superficially (Figs. 2 and 3). The lowest water absorption was observed when 10 and 15% nano-wollastonite was used superficially. Also, the lowest thickness swelling was seen with SA-NW 10%. Internal application of wollastonite generally caused higher water absorption and thickness swelling in comparison to surface application. The lowest water absorption and thickness swelling in internal application were seen with NW-15 and -10%.

As for the mechanical properties, wollastonite nanofibers decreased the MOR, IB, and hardness (Figs. 4, 6, and 7). The highest MOR value was observed in the control treatment (21.3 MPa). However, internal application of NW resulted in an increase in MOE values (Fig. 5). The highest MOE was observed in SA-NW-20% (33251 MPa). MOE values were significantly increased with all SA treatments. The highest IB was observed in the control specimens (1.13 MPa), and the lowest was found in NW-20% (0.961 MPa).

Hardness was increased as the depth of penetration was also increased. NW-treated specimens resulted in a general decrease in the hardness, although in some cases it was not significant.

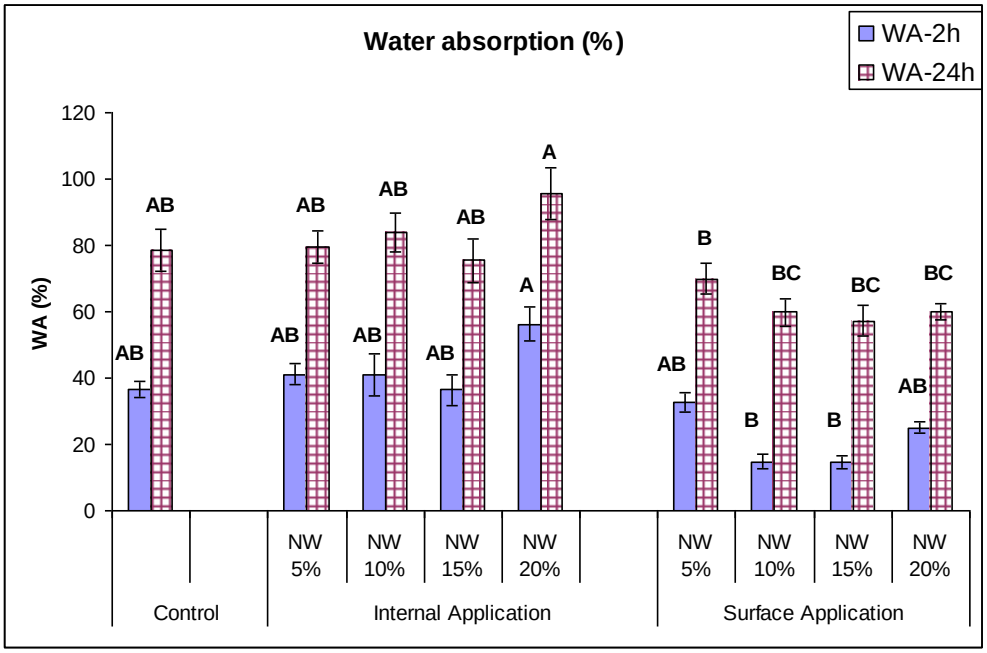

Fig. 2. Water absorption (%) at 2 and 24 h with control and internal and surface application treatments (NW = nano-wollastonite; 5, 10, 15, and 20 = percent of nano-wollastonite consumption levels). Letters on each column indicate Duncan's grouping at the 95% level of confidence.

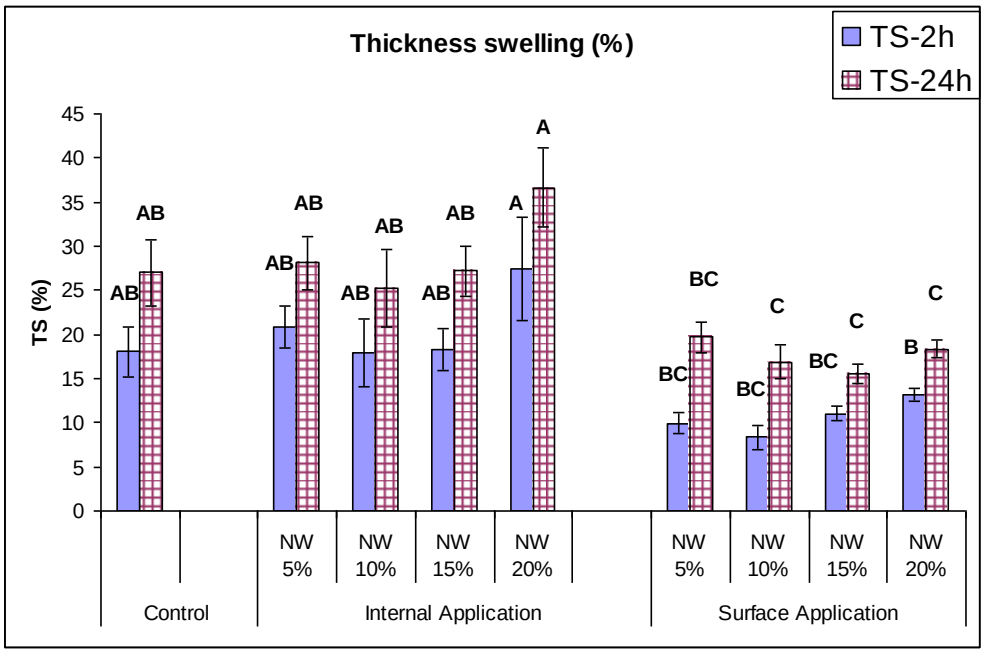

Fig. 3. Thickness swelling (%) at 2 and 24 h in the control and internal and surface application treatments (NW = nano-wollastonite; 5, 10, 15, and 20 = percent of nano-wollastonite consumption levels). Letters on each column indicate Duncan's grouping at the 95% level of confidence.

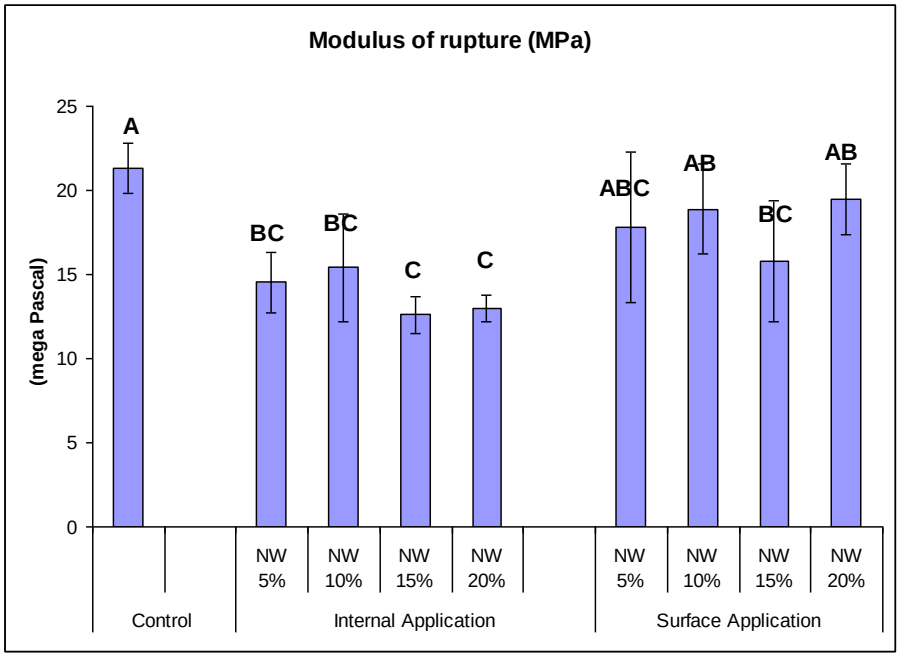

Fig. 4. Modulus of rupture (MPa) in the control and internal and surface application treatments (NW = nano-wollastonite; 5, 10, 15, and 20 = percent of nano-wollastonite consumption levels). Letters on each column indicate Duncan's grouping at the 95% level of confidence.

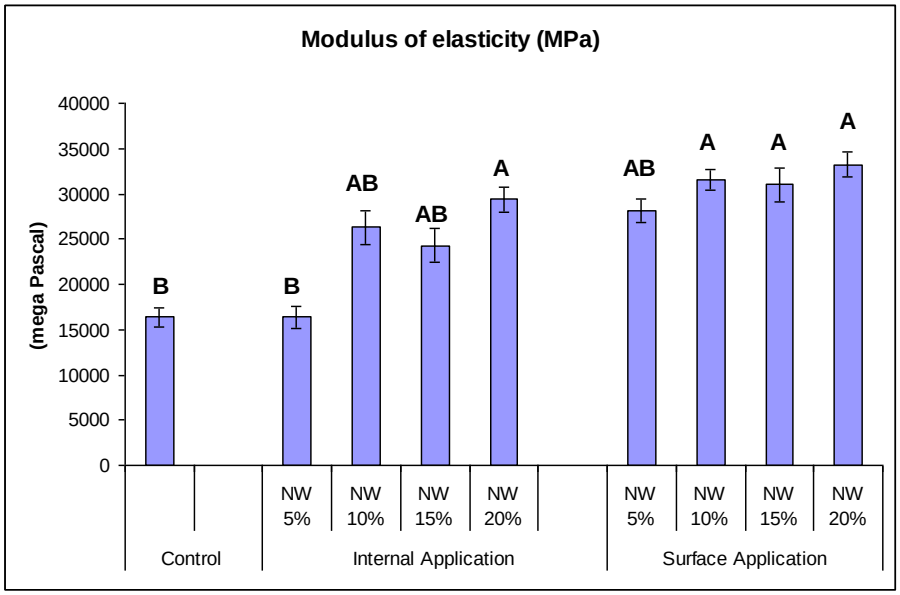

Fig. 5. Modulus of elasticity (MPa) in the control and internal and surface application treatments (NW = nano-wollastonite; 5, 10, 15, and 20 = percent of nano-wollastonite consumption levels). Letters on each column indicate Duncan's grouping at the 95% level of confidence.

Wollastonite nanofibers significantly increased water absorption and thickness swelling (at both 2 and 24 h) with IA-NW-20% (Fig. 2); however, these qualities also tended to increase in other treatments. The reason may be traced to the equality of the density in different treatments; that is, in the boards treated with NW, fewer wood chips were used, and the integrity and compactness of chips were therefore decreased compared to the control specimens. Thus, water can penetrate the specimens through the

micro-cavities caused by the decreased compactness of the boards; the micro-cavities mostly formed in the core section of the panels (Fig. 8). In the IA-NW-5, -10, and -15% treatments, the water-repellent property of NW prevented the specimens from absorbing significantly more water than the control specimens; however, in the IA-NW-2-%, the number of micro-cavities formed was high enough to significantly increase water absorption and thickness swelling. Furthermore, surface application showed generally smaller amounts of water absorption and thickness swelling in comparison to the internal application of NW (Figs. 2 and 3). This proves that surface protection against penetration of water could be more effective in the short-time tests (2 and 24 h). Still, long-term water absorption and thickness swelling tests should be carried out to have a better scope of the effects of NW on WA and TS.

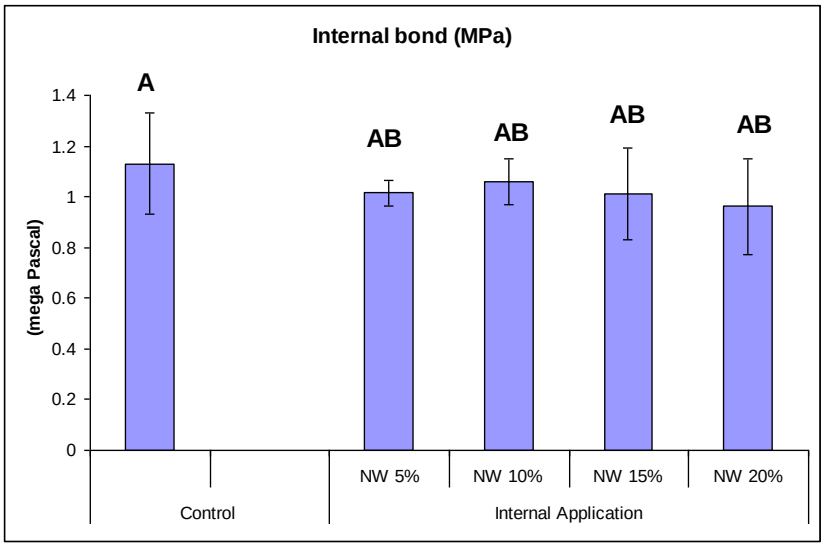

Fig. 6. Internal bond (MPa) in the control and internal application treatments (NW = nano-wollastonite; 5, 10, 15, and 20 = percent of nano-wollastonite consumption levels. Letters on each column indicate Duncan's grouping at the 95% level of confidence.

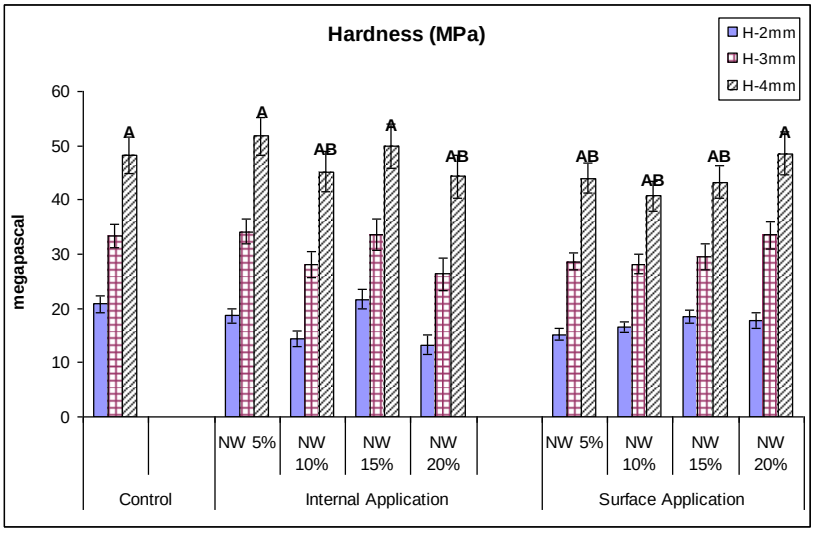

Fig. 7. Hardness (MPa) for 2-, 3-, and 4-mm penetration of the modified ball in the control and internal application treatments (NW = nano-wollastonite; 5, 10, 15, and 20 = percent of nano-wollastonite consumption levels). Letters on each column indicate Duncan's grouping at the 95% level of confidence.

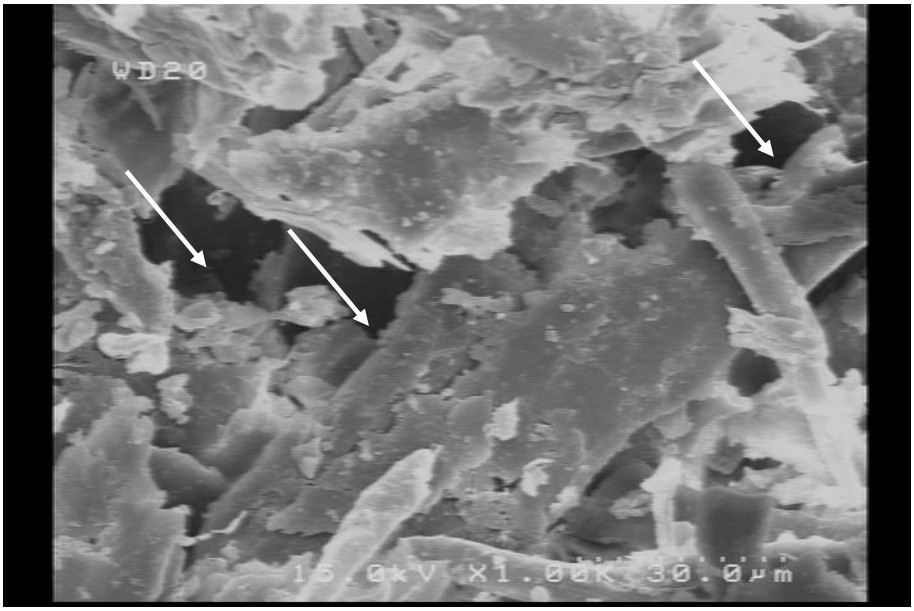

Fig. 8. SEM image showing cavities formed in the core section of IA-NW-20% treatment

NW application resulted in a decrease in MOR (Fig. 4). However, little difference between treatments was observed, although they were significantly divided into different groups. This can indicate some sticking property of NW in particleboard; that is, wollastonite nanofibers contributed to sticking the chips together, although NW-treated particleboards had small wood chip contents and consequently less compactness. In fact, two factors worked simultaneously: first, the increased micro-cavities formed in the structure of the boards resulted in decreased physical or mechanical properties; second, the sticking properties of wollastonite nanofibers contributed to the abovementioned properties. This contribution was related to the formation of bonds between the nanowollastonite and wood compounds, namely hydroxyl and methoxy groups of lignin and cellulose (Taghiyari *et al.* 2013b). The cited authors reported that wollastonite composition made bonds with the hydroxyl and methoxy groups of the benzene cycles in lignin and cellulose. Two types of similar bonding were also reported to form between nanoclay compounds and lignin network, significantly improving the properties of the wood-composite (Rangavar 2005). From one side, the Al in $Al(OH)_3$ made reaction with methoxy groups in lignin; and from the other side, the hydroxyl groups of $Al(OH)_3$ made a complex bond with the lignin. The formation of the bonds continued, significantly fortifying the composite-matrix. Furthermore, higher thermal conductivity of the composite mat due to the wollastonite nanofibers (Taghiyari *et al*. 2013b) contributed to a better resin cure, resulting in higher MOR.

MOE values were significantly improved by all IA treatments, with the exception of NW-5% (Fig. 5). Surface application showed a higher improving impact on MOE values in all treatments, showing the importance of surface quality in the elastic behavior of the boards; that is, NW nanofibers contributed to the integrity of the surface properties, causing the increase in MOE values with NW-treatments.

Wollastonite nanofibers also decreased the internal bond in all NW-treated treatments (Fig. 6). In fact, the micro-cavities formed due to the decreased chip content decreased the integrity and compactness of the wood chips in the particleboard matrix, leading to decreased IB values.

Hardness values were also influenced by two factors: the first was the improving effects of NW on bond formation between the wood chips, and the second was the decreasing effect of the micro-cavities formed by the decreased wood chip content in the particleboard matrix. In IA-5 and -15%, the amount of wollastonite compensated for the micro-cavities, and an increasing trend was therefore observed (Fig. 7); however, in the IA-10 and -2% NW contents, the micro-cavities overcame the extra bonds formed by wollastonite nanofibers.

Cluster analysis of the nine treatments based on all the physical and mechanical properties clearly showed that surface and internal applications were clustered quite differently (Fig. 9). This implied a significantly higher impact of surface application, compared to internal application, on the physical and mechanical properties. Study on the effects of surface application on physical properties and MOE (Figs. 2, 3, and 5) implied that SA had a high significant effect on the physical properties as well as MOE; in fact, the great impact of SA on these properties ultimately resulted in clear distinct clustering of the IA and SA treatments. IA-NW5 was closely clustered with the control specimens; this shows that a consumption level of 5% is not enough to significantly affect the properties when applied internally. Similar results were obtained from IA-NW-10 and 20%.

NW nanofibers improved the properties in the NW-20%; however, less wood-chip integration plus the formation of micro-cavities in the particleboard matrix resulted in a final significant decrease in the properties; consequently, the end-results were comparable to those of the NW-10% content level.

As for the surface application of NW, the cluster analysis clearly showed that all consumption levels of SA-NW significantly improved the physical and mechanical properties. SA-NW-5 and 10% are clustered closely together, showing their similarity. However, the best properties were obtained when 15% and 20% of NW were used superficially. In this regard, SA-NW-15% is recommended to decrease the production costs.

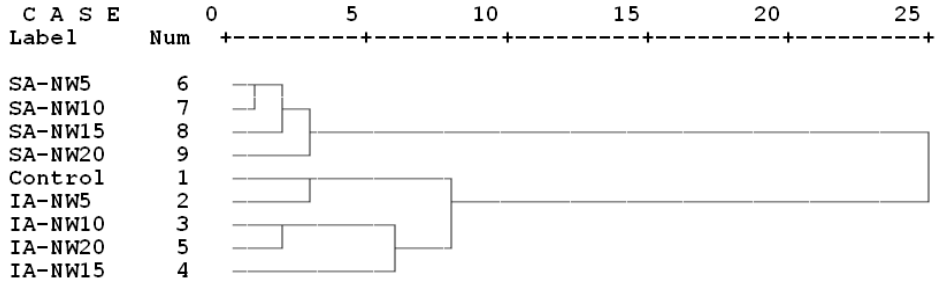

Fig. 9. Cluster analysis of the control and surface and internal application treatments (IA = internal application; SA = surface application; NW = nano-wollastonite; 5, 10, 15, and 20 = percent of nano-wollastonite consumption levels)

Since both SA and IA methods showed some advantages and also disadvantages, the authors are planning to work on combining the two methods together and analyze the results of SA and IA, mixed together.

CONCLUSIONS

1. Wollastonite nanofibers contribute to bond formation between wood chips when applied internally; consequently, they can improve the physical and mechanical properties of particleboard; however, the formation of micro-cavities in the particle-board matrix can lead to decreased properties in NW-treated specimens due to the decreased wood chip content.

2. A NW content of 5% did not significantly improve the physical and mechanical properties; while, NW-20% decreased these properties due to the decreased amount of wood chips used and the consequent decreased integration of wood chips in the particleboard matrix, when the density of the boards was kept constant.

3. SA-NW-15% is recommended to improve the physical and mechanical properties of particleboard.

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