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Effect of metal nanoparticles on hardness in particleboard

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ABSTRACT

Effects were studied of 200 ppm silver and copper nano-suspensions, with size range from 20 to 80 nm, on the hardness of particleboards produced at an industrial scale at the Iran-Choob Factory, Iran. Metal nano-suspensions were added to the mat at two levels of 100 and 150 milli-liters/kg dry weight wood particles, and the results were compared with those of the control panels. Results showed that the high thermal conductivity coefficient of silver nanoparticles broke down part of the resin bonds; it also heat-treated the surface wood particles, resulting in significant decrease in the hardness of treatment with 150 mL/kg. However, in the nanocopper-treated panels, no significant change was observed due to the lower thermal conductivity coefficient of copper; furthermore, as to the formation of higher hydroxyl bonds, it even slightly increased. High significant correlations were determined between most of the physical and mechanical properties of the panels.

Keywords: *Composite board; Metal nanoparticles; Heat transferring property; Metal nanoparticles; Nanotechnology; Particleboard*.

INTRODUCTION

Hot-presses are usually considered to be a bottle-neck for nearly all wood-composite manufacturing factories [1]. Minimum pressing time of a particleboard primarily depends on heat transfer, which in turn varies with thickness, press temperature, closing rate, and mat moisture distribution. When high internal steam pressures are involved, the press-times necessary to prevent damage resulting from the release of gases depend on such factors as resin type, density, press temperature, and total MC [2]. Based on the low thermal conductivity coefficient of wood [3-4], several methods have so far been created to shorten press-time, saving time and energy. However, in the case of urea-formaldehyde (UF) resin, there is a limitation of MC level [5]. Furthermore, due to the more brittleness of UF-resin in comparison to other resins [6], complete curing of the resin would result in the improvement of the properties. Therefore, silver and copper nanoparticles were utilized and reported to successfully decrease hot-press time in particleboard manufacturing at industrial scale [7-8].

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They also reported improved in physical and mechanical properties. However, no results have so far been reported on the effects of metal nanoparticles on the hardness of particleboard. The present study was therefore carried out to investigate if the increased thermal conductivity of the mat may have any significant effect on the hardness of particleboard at different depths of penetration of the ball.

EXPERIMENTAL

Particleboard production

Particleboards were made at the Iran-Choob factory, Ghazvin, Iran. Boards were 16 mm in thickness and 0.7 g/cm^3 in density. Chips were comprised of poplar spp.plus pruned branches of fruit trees. An evenly-formed layer was formed by a spreading head upon a moving caul.

The spreading head provided a continuous particle size gradient between the surface and core layers in a way that fine particles were on the surface layers and coarser particles in the core. Classification of particles was carried out through the use of air stream method. The lengths of particles were randomly formed along the machine direction; this generally made the bending strength across the boards to be approximately 20% lower than the machine direction. Particle size distribution across the width of the boards was in a way that the thickness of particles was about 3 mm in the core of the mat; the thickness was steadily decreased to the surface so that on the surface, there were fine particles with the thickness of about less than 0.2 – 01 mm. The temperature of hot-press plates was fixed at 200°C. The specific pressure of plates was 25 kg/cm^2, and the total nominal pressure of the plates was 200 kgf. The press machine was equipped with electronic sensors measuring evaporation of gases and the pressure to determine press time.

Dimensions of the boards produced on an industrial scale were 530 × 130 × 1.6 cm. Urea-Formaldehyde (13%), plus 1% ammonium chloride (NH_4Cl) as hardener, was used as the resin. It is to be noted that the use of ammonium chloride is not restricted in Iran.

Metal nanoparticle application

200 ppm aqueous nanosilver (NS) and nanocopper (NC) suspensions were produced using an electrochemical technique in cooperation with Jafr Sorkhe Fajr Co. (Ltd.). The size range of copper nanoparticles was 20-80 nm. The pH of the suspension was 6-7; two kinds of surfactants (anionic and cationic) were used in the suspension as stabilizer; the concentration of the surfactants was two times the copper nanoparticles. The size of the nanoparticles was monitored by SEM method. The nanosuspensions were added to the resin before mixing the resin with wood particles. The pH and viscosity of the resin were kept constant for all treatments in the present study. Nanosuspensions were used at two levels of 100 and 150 mL/kg wood particle, based on the dry wood basis; therefore, there were three treatments for each nanosuspension (N) as: 1- control, 2- 100 mL of N/kg, and 3- 150 mL of N/kg, totally six treatments. In order to increase accuracy, for each nanosuspension, control panels were also produced to be compared with either nanosuspension. Four boards were manufactured for each treatment. Boards were kept at the warehouse for two weeks before the mechanical and physical tests were done.

Hardness measurement

Hardness tests were carried out in accordance with the ISIRI 9044 PB Type P2 (compatible with ASTM D1037-99) specifications. Location of physical, mechanical, and permeability specimens was the same as carried out by Taghiyari et al. [7]. In order to find out the effects of heat-transferring of nanometal particles [9-11], hardness was measured at five different penetration depths of the hardness ball; that is, hardness loading was measured at 2, 3, 4, 5, and 5.4 mm of the penetration of the ball into the composite-board specimens.

SEM Imaging

SEM imaging was done at thin-film laboratory, FE-SEM lab (Field Emission), School of Electrical & Computer Engineering, The University of Tehran; a field-emission cathode in the electron gun of a scanning electron microscope provided narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage.

Statistical Analysis

Statistical analysis was conducted using SAS software program, version 9.2 (2010). One-way ANOVA was performed to discern significant difference at the 95% level of confidence. Grouping was then made between treatments using the Duncan test. Regression and hierarchical cluster analysis, including dendrogram and using Ward methods with squared Euclidean distance intervals, was carried out by SPSS/18 (2010). Fitted-line plots and regressions were made by Minitab software, version 16.2.2 (2010).

RESULTS AND DISCUSSION

SEM images showed uniform spread of metal nanoparticles over the surface of wood chips in the wood-composite matrix, facilitating easier transfer of heat from the hot-plates of the press to the wood-matrix (Figure 1).

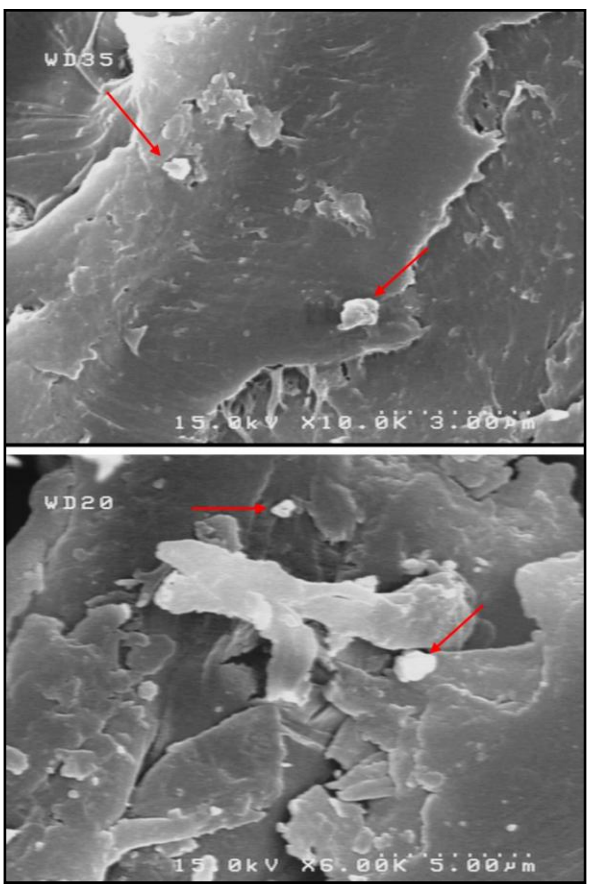

Fig. 1. Scattered copper nanoparticles over the surface of wood chips [8]

Results of the tests showed that the maximum hardness in the NS-treated panels was found in the control treatment, at all the five penetration depths of the ball (Figure 2). Furthermore, the load to penetrate the ball at different depths was naturally different; the lowest was observed the 2-mm depth of penetration, and the highest was seen at the 5.4-mm depth. The treatment with 100 mL/kg nanosilver suspension showed no significant difference with the control ones at all depths; however, the treatment with 150 mL/kg nanosilver suspension resulted in almost half the loading pressure at all the depths of penetration. Comparison between the control and 150/mL treatments indicated that 150 mL/kg of nanosilver suspension was too high; so, the theory that part of the UF-resin bonds were de-polymerized [7-8] was proved; however, both research projects reported improved mechanical properties in the treatments with 150 mL/kg content of nanometal suspensions. In the meantime, heat-treatment of wood was reported to decrease the mechanical properties significantly [12-13]; so, another mechanism should also be involved in the process, that is, the heat-treatment of wood particles. In fact, the decrease in the hardness of 150 mL/kg treatment can partially be related to the heat-treatment of the wood particles located at the surface layers of panels. With due consideration of the lower gas and liquid permeability reported for NC-treated particleboards [8] and the decreasing effects of heat-treatment on gas and liquid permeability [9, 14], this theory was strengthened. In fact, similar significant intensifying effects of silver nanoparticles were reported in nanosilver-impregnated specimens at different temperatures [12-13]. Similarly, nano-zycosil (NZ) was reported to significantly decrease gas and liquid permeability in medium-density fiberboard (MDF) [15], though the amount of wood fibers was reduced in the NZ-treated panels. This also proves that any materials added to the wood-composite matrix may affect it in three ways: 1- altering heat-transferring rate to the wood-composite matrix, resulting in better curing of the resin or its breaking down; 2- heat-treatment of the surface wood particles or fibers, affecting their physical properties; 3- altering the compact ratio of the surface and core layers, resulting in physical and mechanical change.

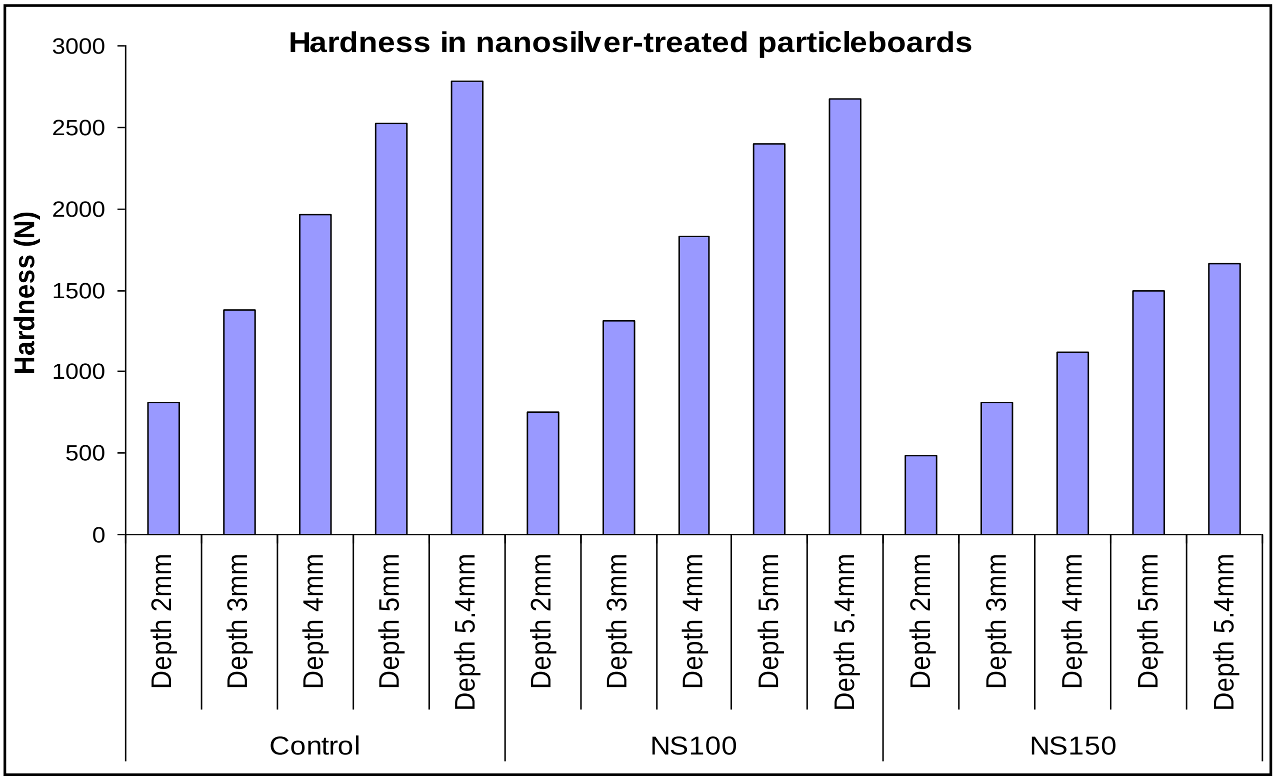

Fig. 2. Hardness in the nanosilver-treated particleboards at five penetration depths of 2, 3, 4, 5, and 5.4 mm (NS=nanosilver; N=Newton)

In the NC-treated panels, though, no significant difference was observed among the three treatments of control, 100 mL/kg, and 150 mL/kg treatments (Figure 3). This also may have the indication that the breakage of resin bonds wouldn't be so serious, as the panels retained their hardness. The maintaining of the bonds was strengthened considering the significant lower gas and liquid permeability in the 150 mL/kg treatment [8]; that is, there were enough more resin-bonds to significantly decrease the permeation of fluids (gas and liquid) through the porous structure. However, as to the lower thermal conductivity coefficient of copper in comparison to silver, it can be concluded that heat-treatment of the surface wood particles was not as severely done in the NC-treated panels as it was in the NS-treated panels. Furthermore, the hydroxyl bonds formed between copper nanoparticles with wood cell structures [16-17] resulted in the slight increase in the hardness.

High significant correlations were found between hardness pressures at different depths of penetration in the six treatments (Figure 4); this showed that the processes involved in the increase or decrease of the hardness at the low depths of 2 or 3 mm also involved in the deeper depth of 5 and 5.4 mm; these processes comprised heat-transferring coefficient of metal nanoparticles, hydroxyl bonds, and heat-treatment of the wood particles.

Similarly, high significant correlations were found between gas permeability versus liquid permeability times of 1st-drop (76.9%) and 50-mm lowering time (79.4%); very high significant correlations were also found between the liquid permeability of 1st-drop versus 50-mm lowering time (99%), as well as between thickness swelling versus water absorption (Figure 5). This clearly indicated that gas or liquid permeability values can be considered as good criteria for prediction of water absorption (WA) and thickness swelling (TS); in fact, permeation property of particleboard, as a porous media, significantly affect its permeation to water, ultimately influencing both the physical properties of WA and TS.

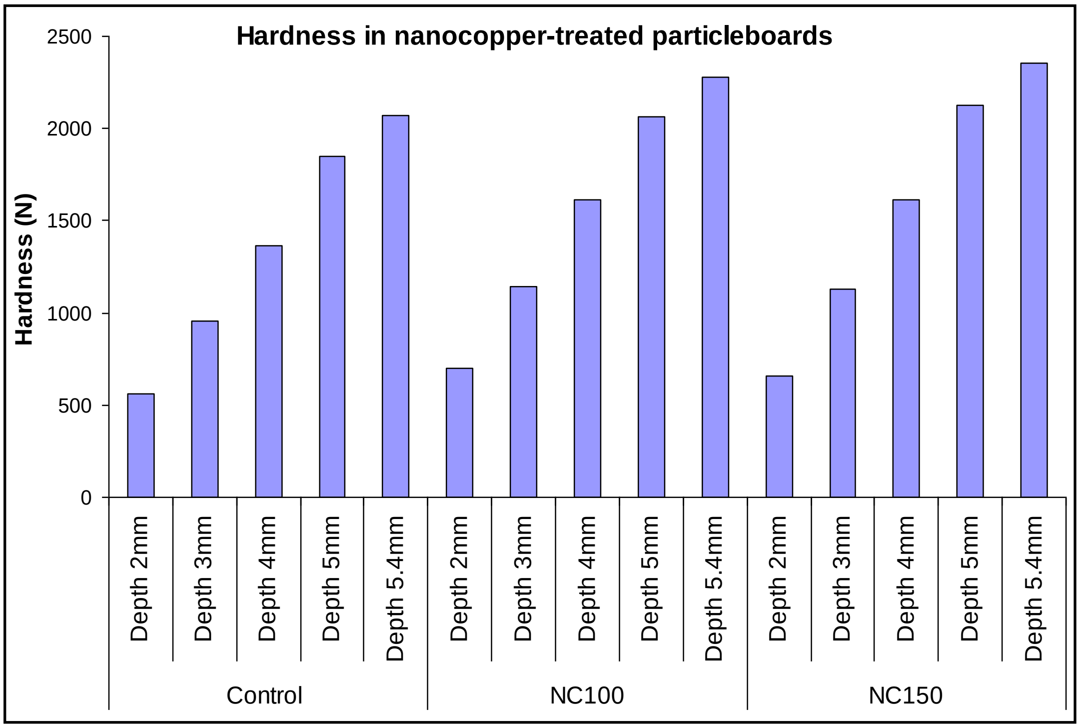

Fig. 3. Hardness in the nanocopper-treated particleboards at five penetration depths of 2, 3, 4, 5, and 5.4 mm (NC=nanocopper; N=Newton)

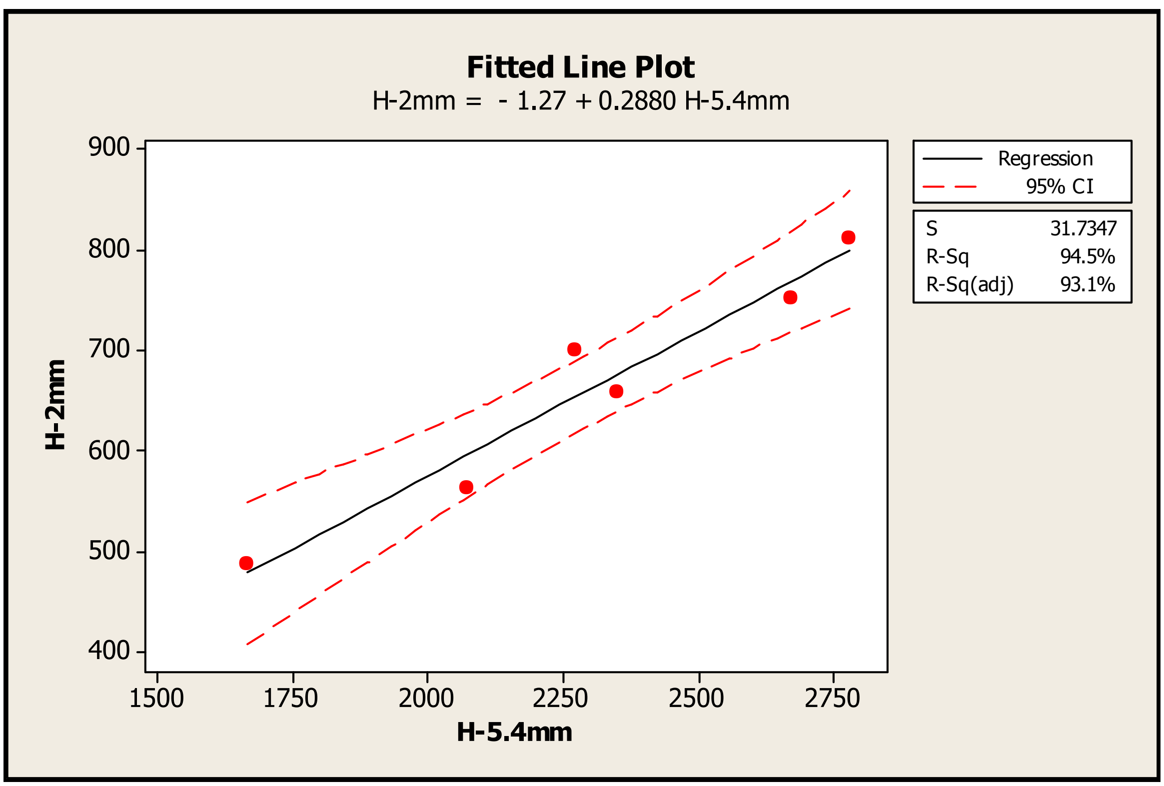

Fig. 4. Fitted line plot between hardness pressures at 2 (H-2mm) versus 5.4 (H-5.4mm) depths of penetration of the hardness ball in the six treatments

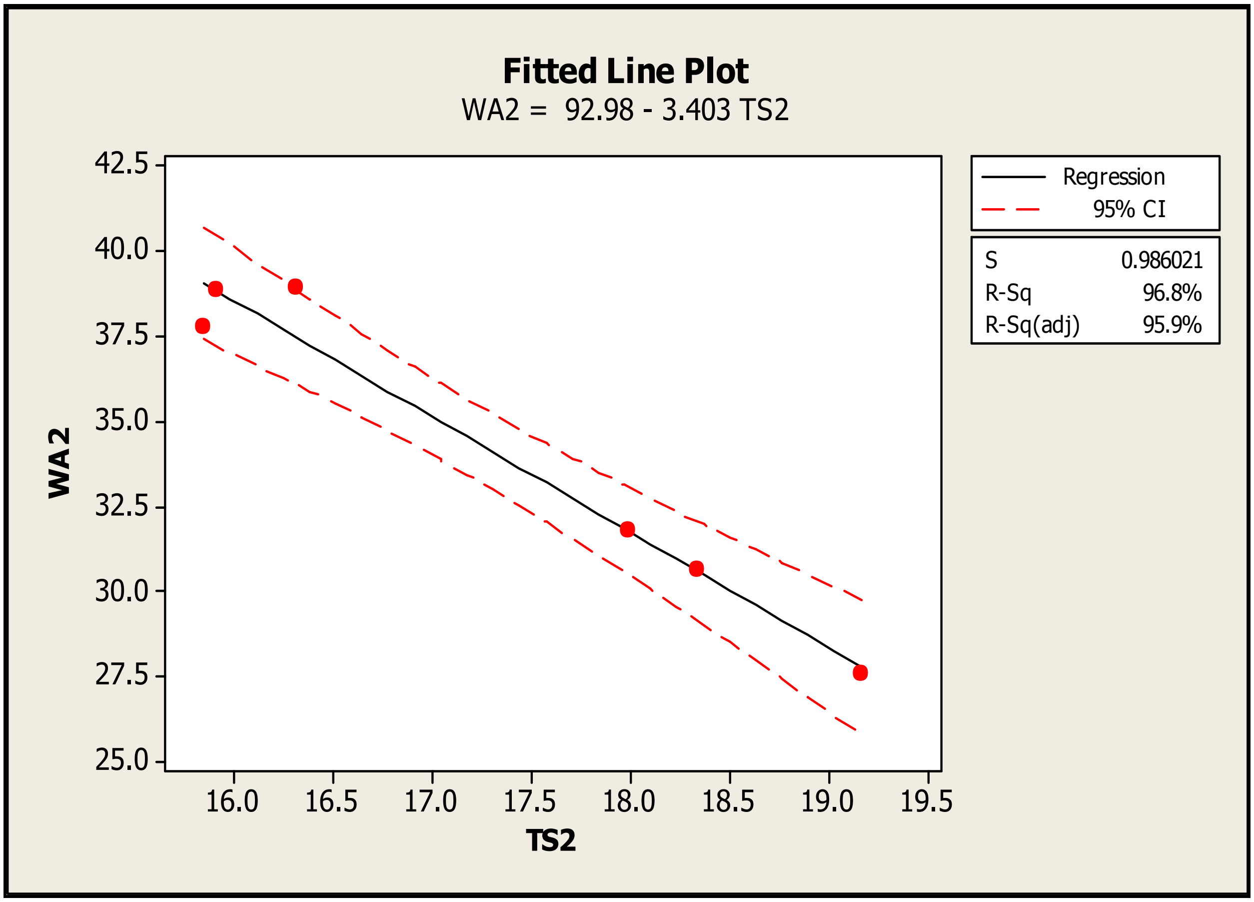

Fig. 5. Fitted line plot between thickness swelling versus water absorption after two hours immersion in water in the six treatments of particleboard (WA=water absorption; TS=thickness swelling)

High significant R-squares were also found in between MOR versus IB (98%), between MOE versus IB (89%), and MOR versus TS24h (92%). These high R^2 also prove that different mechanical or physical properties are closely dependant on each other and can be predicted by one another; furthermore, as to the fact that the resin bonds formed between the wood particles, significantly affect these physical or mechanical properties, it can also be concluded that any factor affecting these bonds would eventually have similar effects on other properties as well. Therefore, the authors are working on adding metal nanoparticles to only the core section of composite-board mats. This way, the possible negative effects of breaking down the resin bonds due to high accumulation of heat in the surface layers would be eliminated; furthermore, the over-heating and the consequent extra heat-treatment of wood particles located on the surface layers would also be prevented.

Cluster analysis of the three treatments of nanosilver panels (control, NS-100, and NS-150) based on the hardness loading strength values showed that NS-150 was clustered quite differently (Figure 6). This clearly showed the effect of extra heat-transferring effect caused by silver nanoparticles on the hardness of particleboards. However, cluster analysis of the three nanocopper treatments showed different results; both NC-100 and NC-150 levels of nanocopper consumption had significant improving effects on the hardness values at different depths of ball penetration, resulting in significant similar clustering of NC-100 and NC-150; however, the control treatment was clustered quite differently (Figure 7).

Fig. 6. Cluster analysis of the three treatments of nanosilver panels based on hardness loading strength values at six depths of penetration of the hardness ball (NS=nanosilver)

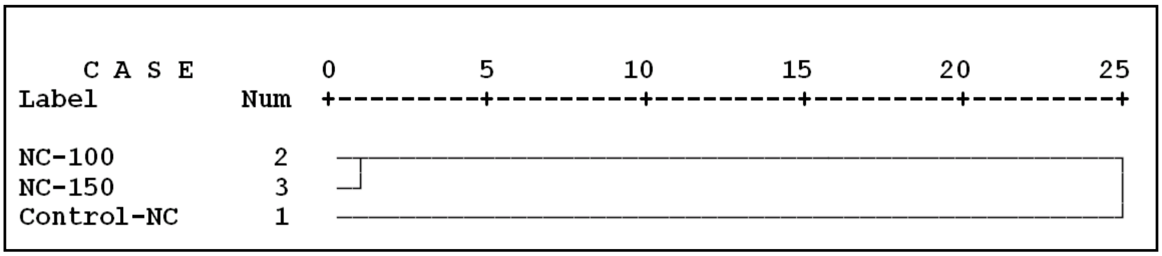

Fig. 7. Cluster analysis of the three treatments of nanocopper panels based on hardness loading strength values at six depths of penetration of the hardness ball (NC=nanocopper)

CONCLUSIONS

The effects of silver and copper nanoparticles at two consumption levels (100 and 150 mL/kg dry wood particles) on hardness in particleboard were studied here; correlations between different physical and mechanical properties were also calculated and interpreted. It was revealed that higher thermal conductivity coefficient of silver nanoparticles (at the higher consumption level of 150 mL) resulted in the de-polymerization of part of the resin bonds in the surface layers of particleboard, resulting in slight decrease in hardness. Lower thermal conductivity coefficient of copper made the hardness of NC-treated panels to be of no significant difference with those of control specimens. In was also revealed that other mechanisms were also involved; that is, the surface particles were somehow heat-treated as to the high temperature of the hot-press plates; the heat-transferring property of metal nanoparticles intensified this process. The hydroxyl bonds formed in the NC-treated panels contributed in maintaining the hardness of the treatment with 150 mL of nanocopper/kg.

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