

Physical Properties of Medium Density Fiberboard Produced with the Addition of ZnO Nanoparticles

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The use of wood-base panels in humid environments, in general, presents low durability due to contact with water. In order to increase durability and reduce the attack of fungi, studies had been developed using resin with zinc oxide (ZnO) nanoparticles. This work aimed to produce medium density fiberboard with urea-formaldehyde resin and melamine-formaldehyde adding 0.5% and 1.0% of ZnO nanoparticles for the physical properties evaluation. All treatments were classified as medium density according to ABNT NBR 15.316-2 (2015) with values ranging between 550 and 800 kg*m⁻³. No differences were found between the two commercial adhesives used. The addition of 1.0% of nanoparticles resulted in lower density panels, higher moisture contents, and, after immersion in water for 24 hours, higher values of swelling in thickness. These results are explained by the lower compaction of the boards due to rapid cure of the adhesive using higher percentages of ZnO nanoparticles. The best treatment of the panels was with melamine-formaldehyde resin and 0.5% of nanoparticles.

Keywords: Fiberboard; Physical characteristics; Nanotechnology

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INTRODUCTION

Wood panels have a great number of applications in the civil construction and the furniture industry, especially particulate and fiber panels. The production of medium density fiberboard (MDF) panels is carried out by a continuous hot-pressing process with the addition of adhesives. The adhesives employed by the industry are urea-formaldehyde and melamine-formaldehyde. Dimensional changes may occur, decreasing the mechanical strength of MDF panels when exposed to more aggressive conditions. To lessen the possible negative effects on the panels, other materials can be added during the manufacturing process in addition to the products already used. New studies have the objective of improving properties of the panels in terms of physical and mechanical performance and durability of the product.

In this context, nanoparticles are an example of materials that show good results, such as a decrease of swelling and lower mass gain when in contact with water. Research on the synthesis of nanomaterials is mainly focused on controlling their shapes, sizes, and compositions. Each of these factors is key in determining the properties of the materials and lead to different technological applications (Ghorbani *et al.* 2017).

Weichelt *et al.* (2010) developed nanocomposites for use in ultraviolet resistant coatings using zinc oxide nanoparticles in wood panels for outdoor use. The suitability of these panels for use under outdoor conditions was ensured by increasing the elasticity of the coatings and decreasing the water permeability of the panels.

The use of ZnO nanoparticles on wood-based panels has shown good performance against fungal attack (Reinprecht *et al.* 2018); however, it should not impair the physical and mechanical properties of the boards. So, it may be possible to add a nanomaterial that allows better performance of the panels especially in humid environments, such as kitchens and bathrooms.

Gupta *et al.* (2018) evaluated the application of high conductivity nanoparticles for improving the thermal and mechanical properties of MDF as well as using a urea-formaldehyde resin in their composition. The authors added multi-walled carbon nanotubes (CNTs), aluminum oxide (Al_2O_3) nanoparticles, and activated carbon nanoparticles to the adhesive. Activated carbon and Al_2O_3 nanoparticles increase the amount of heat transfer during the pressing process, improving the physico-mechanical properties of the MDF. In addition, activated carbon nanoparticles significantly reduce formaldehyde emissions from the panel production process.

Kumar *et al.* (2013) evaluated the effects of Al_2O_3 nanoparticles on the physical, mechanical, and heat transfer properties of MDF. The nanoparticles were added at two levels, 0.5 wt.% and 1.0 wt.% of the dry weight of wood fibers. The resin used was urea-formaldehyde. The temperature profile inside the panel and the thermal conductivity were improved by the addition of Al_2O_3 nanoparticles, subsequently improving the adhesion of the fibers in the MDF. The modulus of rupture and the modulus of elasticity also showed improvement over the control panels and the thickness swelling decreased.

Furthermore, nanoparticles can be applied on the surface of boards. Nosál and Reinprecht (2017) applied zinc oxide (ZnO) nanoparticles to the surface layer of medium density particleboard (MDP) to improve their anti-bacterial and anti-mold properties. Melamine-formaldehyde resin and ZnO nanoparticles, in the amounts of 0.1%, 0.3%, 0.6%, and 1.0%, were used for the impregnation of white decorative paper in MDP panels. The presence of ZnO increased the surface mold resistance of panels intentionally contaminated with microscopic fungi by approximately 50%.

Soltani *et al.* (2013) studied the effect of four different concentrations of zinc oxide nanoparticles used in the treatment of beech wood by the submersion method in order to evaluate the dimensional stability and swelling for 24 hours. Beech wood was thermally treated at 60 and 120 °C after impregnation of nanoparticles. The results indicated that the nanoparticles of ZnO provided modification in the wood, improving the dimensional stability and reducing its hygroscopicity. In addition, Fourier Transform Infrared Spectroscopy (FTIR) analysis indicated a strong interaction between the nanoparticles and the chemical components of the wood. Thermal treatment effectively improved the effects of nanoparticles.

One of the great challenges of adding nanoparticles to wood panels is finding the optimum percentage of application for improving the physical and heat transfer properties of the product without adversely affecting its mechanical properties.

Taghiyari (2013) determined the effects of the addition of silver nanoparticles and zycosil nanoparticles on the mechanical resistance of MDF. The study concluded that nanoparticles did not positively influence the mechanical strength of the panels.

Gao *et al.* (2011) presented the effects of copper oxide nanoparticles on the physical and mechanical properties of oriented strandboard (OSB) using phenol formaldehyde (FF)

resin. The copper oxide nanoparticles had no beneficial effects on the mechanical properties and dimensional stability of OSB panels. However, the addition of nanoparticles did result in the acceleration of FF resin reactions and in an increase of heat transfer in the wood strands mattress.

Reinprecht *et al.* (2018) studied the addition of four different percentages (2, 6, 12 and 24%, by weight) of ZnO nanoparticles in wood particulate panels produced with MUF resin. The use of nanoparticles improved the resistance of the boards against biological agents; however, there were no major changes for the different percentages tested. The presence of zinc oxide nanoparticles in the particulate panels decreased its internal bonding and did not influence swelling in thickness and water absorption after 2 and 24 h and resistance in static bending.

The present work evaluated the physical performance of MDF panels produced with eucalyptus fibers, the addition of zinc oxide nanoparticles in proportions of 0.5% and 1% based on fiber dry weight, and urea formaldehyde and melamine-formaldehyde resins.

EXPERIMENTAL

The fibers used for the production of MDF panels were wood fibers of *Eucalyptus grandis* hybrid H103 donated by a timber company (Eucatex, Salto, Brazil). The adhesives used, urea-formaldehyde (UF) with the solids content of 66% and melamine-formaldehyde (MF) with the solids content of 65.9%, were donated by Momentive Indústria Química. The catalyst contained the following: ammonium sulfate with the solids content of 13.10%, emulsion of paraffin with the solids content of 57.2% (provided by Eucatex), water, and ZnO nanoparticles obtained from the sol-gel method from the synthesis of zinc nitrate and gelatin in the ratio of 1:1 (Favarim and Leite 2018).

The work was carried out over a total of six treatments, which were divided between panels produced with the UF and MF adhesives. Table 1 shows the nomenclature of the treatments, the type of adhesive used, and the percentage of nanoparticles used for each treatment. The proportion of materials and the production process of the panels are described below.

Table 1. Characteristics of the Treatments

| Treatments | Adhesive | ZnO Nanoparticles (%) |
|------------|----------|-----------------------|
| T1 | UF | 0 |
| T2 | UF | 0.5 |
| T3 | UF | 1 |
| T4 | MF | 0 |
| T5 | MF | 0.5 |
| T6 | MF | 1 |

MDF Panels Production

Before panel production, the fibers were oven dried to a moisture content of 3 wt.%. For each panel, 1800 g of fibers were mixed with adhesive in a laboratory blender. A fiber mat was formed, and the material was cold pre-pressed *via* a manual process with a pressure of approximately 1 kgf/cm² for 5 min to reduce the volume of the fiber mat. Hot pressing with a pressure of 10 kgf/cm² and a temperature of 180 °C was carried out for 10 min, resulting in an MDF panel with a final thickness of approximately 13 mm. This process

was divided into three cycles of 3 min of hot-pressing with a 30-s break, according to Campos and Lahr (2004) method.

Tests and Results Analysis

The physical tests conducted included the determination of density, moisture content, and thickness swelling after a 24-h water immersion. Preparation of the specimens and the procedures for each test were developed according to the normative document ABNT NBR 15316-2 (2015). A semi analytical scale (0.01 g of precision), a digital caliper (0.01 mm of precision), and a micrometer (0.001 mm of precision) were used to perform the physical tests

Determination of apparent density

Density for each treatment was determined using ten square specimens of 50 mm side (see Eq. (1)). Width and length were measured with a caliper, thickness was measured in five different points – four corners and at the center – with a micrometer and mass was determined with a precision scale,

$$D = [m/(w/t)] * 1,000,000 \quad (1)$$

where D is the apparent density [$\text{kg} * \text{m}^{-3}$]; m is the mass of the specimen [g]; w is the width [mm]; l is the length [mm]; and t is the thickness [mm].

Determination of moisture content

Each treatment moisture content (see Eq. (2)) was determined using ten square specimens of 50 mm side with initial mass determined in a precision scale. Samples were dried in a laboratory oven at 103 ± 2 °C until reaching constant mass (*i.e.* fluctuation between mass measurements inferior of 0.1 %),

$$U = [(m_i - m_d)/m_i] * 100 \quad (2)$$

where U is the moisture content [%]; m_i is the initial mass of the specimen [g]; and m_d is the dried mass of the specimen [g].

Determination of thickness swelling

Ten square specimens with dimensions of 50 mm x 50 mm were completely submerged in water in order to determine treatments thickness swelling (see Eq. (3)). Thickness swelling was determined by the increase in the thickness dimension after the specimens were soaked in water for 24 hours, measured by a micrometer with precision of 0.001 mm. Water had a constant temperature of 25 °C and pH of 7 during the test,

$$TS = [(t_s - t_i)/t_i] * 100 \quad (3)$$

where TS is the thickness swelling [%]; t_s is the specimen thickness after water soaking [mm]; and t_i is the specimen initial thickness [mm].

The results of the physical tests were analyzed with analysis of variance and Tukey tests with significance levels of 5% using *R* software version 3.3.1 (<https://www.R-project.org/>).

RESULTS AND DISCUSSION

Table 2 presents the average results obtained for the physical tests of density, moisture content, and 24-h thickness swelling for all the treatments studied. The panels from treatments 1, 2, 4, and 5 presented density values in accordance with ABNT NBR 15316-2 (2015), which indicates the range of density from 651 kg/m³ to 800 kg/m³ for panels with thickness between 12 mm to 19 mm. Treatments 3 and 6 met the requirements of the ANSI A2008.2 (2016) standard.

According to ANSI A2008.2 (2016) medium density boards have values ranging from 500 to 1000 kg*m⁻³ for interior applications, so the panels of the T3 and T6 treatments fit into this group.

Table 2. Average Density, Moisture Content, and 24-h Thickness Swelling

| Treatment | Condition | Density (kg/m ³) | Moisture Content (%) | 24-h Thickness Swelling (%) | 24-h Thickness Swelling (mm) |
|-----------|---------------|---|-----------------------|-----------------------------|------------------------------|
| T1 | UF | 749.75 c ² (30.88) ¹ | 5.54 b (0.20) | 18.46 b (2.38) | 2.40 (0.41) |
| T2 | 0.5% ZnO + UF | 689.11 b (63.82) | 5.56 b (0.21) | 15.26 ab (2.41) | 2.22 (0.67) |
| T3 | 1.0% ZnO + UF | 588.49 a (36.03) | 7.29 c (0.19) | 36.70 c (2.91) | 5.11 (0.38) |
| T4 | MF | 779.67 c (35.65) | 4.77 ab (1.22) | 17.17 b (1.10) | 1.99 (0.29) |
| T5 | 0.5% ZnO + MF | 748.43 c (61.58) | 4.04 a (1.13) | 11.77 a (2.75) | 1.55 (0.39) |
| T6 | 1.0% ZnO + MF | 588.96 a (24.04) | 7.33 c (0.10) | 36.93 c (2.30) | 5.21 (0,36) |

¹ Means followed by equal letters present no statistical difference (Tukey, $\alpha = 0.05$)
² Standard deviation of the data

The moisture contents obtained from all treatments were more homogeneous than the density, even with the addition of nanoparticles. Treatments 1 and 2 (panels produced with UF) presented very similar moisture contents, with values of 5.54% and 5.56%, respectively. For treatments 4 and 5 (panels produced with MF), the values of moisture content were lower: 4.77% and 4.04%, respectively. The superior performance of the panels produced with MF occurred due to their greater resistance to water.

Treatments 3 and 6 (1% addition of nanoparticles in panels produced with UF and MF, respectively) presented higher values of moisture content, namely 7.29% and 7.33%, respectively. The addition of nanoparticles accelerated the curing of the resin in the outermost regions of the mats and limited the heat transfer to the innermost regions, making it difficult for water vapor to escape, which may have caused an increase in the moisture content of the panel. The normative document used does not present reference values for this test.

The maximum 24-h thickness swelling value allowed by ABNT NBR 15316-2 (2015) is 12% for panels with nominal thicknesses between 12 mm and 19 mm. Treatments 1, 2, and 4 obtained higher swelling values of 18.46%, 15.26%, and 17.17%, respectively. Treatment 5 presented a thickness swelling within the established limits (11.77%). Notably, treatments 3 and 6 presented values much higher than the other treatments, which may indicate that the use of 1% of ZnO nanoparticles greatly accelerated the curing of the panels' outer layers and prevented uniform heat transfer over its thickness, impairing the performance of the panels in direct contact with water.

The standard ANSI A2008.2 (2016) states that the thickness difference before and after the test should be a maximum of 1.5 mm for panels with a thickness of less than or

equal to 15 mm. Treatments 1, 2, 4, and 5 showed thickness variations of 2.4 mm, 1.9 mm, 2.2 mm, and 1.5 mm, respectively. Thus, treatment 5 presented acceptable results according to the ANSI document in the same way that it did for the Brazilian standard. For treatments 3 and 6, the thickness variation was even higher: 2.91 mm and 2.30 mm, respectively.

None of the treatments presented values in accordance with the established standards except for treatment 5; however, the addition of nanoparticles caused a remarkable decrease of swelling percentages, for both panels with 0.5% UF and MF. The decreases observed were a 3.2% decrease of thickness between treatments 1 and 2 and a 5.4% decrease for treatments 4 and 5. Regarding the thickness of the panels from treatment 3, the panels from treatment 2 showed a 21.44% increase of thickness. The panels from treatment 6, with respect to those from treatment 5, presented a 25.16% increase in thickness.

Kumar *et al.* (2013) analyzed the possible changes in temperature inside MDF panels during pressing with the addition of aluminum oxide nanoparticles in a urea-formaldehyde resin. They compared the average 24-h thickness swelling results for panels without the addition of the nanoparticles with those from panels with 0.5%, 14.1%, and 13.5%. Their results also presented values higher than those mentioned in the normative documents, namely 12%. Nanoparticles of aluminum oxide, zinc oxide, positively influenced the decrease of the percentage of swelling in this percentage, although the panels were still unable to meet the normative specifications.

Mantanis and Papadopoulos (2010) evaluated the 24-h thickness swelling of three types of commercial wood panels with and without a surface application of a nanoparticle solution called SurfaPore W, which, according to the manufacturer, decreases water absorption and impregnation of oil stains on wood. The authors stated that MDF panels treated with the product showed a 13.6% decrease in thickness swelling. There was a smaller increase in panel thickness in the study cited than there was in the results obtained, which were 14.1% and 18.2% for the treatments with UF and MF, respectively. The panels produced in this work showed a percentage of 24-h thickness swelling that was higher when compared to panels treated with the commercial product SurfaPore W, except for the panels from treatment 5, which presented a better performance. Obtaining the best results from the panels from treatment 5 can be justified by the combination of MF resin already presenting a better performance in contact with water and the favorable effect on the observed heat transfer with the addition of ZnO nanoparticles.

The lower densities observed from treatments 3 and 6 are directly related to the greater percentages of swelling in thickness. This can be explained by the lower compaction of the panels due to accelerated curing from using higher percentage of ZnO nanoparticles. This accelerated cure also had a direct relationship with the moisture content of the panels from these treatments that were superior and statistically different from the others.

A further study of the panels' density profiles would allow better analysis and conclusions on the performance of the addition of nanomaterials in panel fabrication.

Regarding the use of two different resins, the best results were obtained for the panels produced with MF resin because of their better mechanical performance and their higher water resistance.

CONCLUSIONS

1. The addition of 0.5% ZnO nanoparticles presented better results for the medium density fiberboard, confirming what previous studies had already shown—the ideal percentage of addition must be found, and it may not necessarily be the greatest one.
2. Regarding the 24-hour thickness swelling, it was observed that the addition of 0.5% of nanoparticles presented the best results, indicating improvement in the performance of the panels in contact with water. However, an addition of 1% nanoparticles compromised the results.
3. The addition of 1% of ZnO nanoparticles, used for both UF and MF panel production, indicated a reduction in panel density and an increase in moisture content. These may have occurred due to the acceleration of heat transfer over the hot-pressing, making it difficult to thicken the panel, especially in the inner layer.

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