Developing Environmentally Friendly Wood Composite Panels by Nanotechnology

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Nanoscience and nanotechnology provide numerous opportunities for enhancing the properties of wood composites. Formaldehyde emissions from wood composites are of great importance because of their negative impact on human health. Developing low formaldehyde-emitting particleboard and plywood panels as environmentally friendly composites by nanotechnology was the object of this study. The urea formaldehyde and melamine urea formaldehyde resins that were used to produce particleboard and plywood panels, respectively, were reinforced with various nanomaterials at different loading levels. Formaldehyde emission tests were carried out according to standard TS 4894 EN 120. The results acquired in this work indicated that nanomaterial reinforcement significantly affected the formaldehyde emission properties of the particleboard and plywood panels. Formaldehyde emissions of the composite panels decreased after reinforcement with nanoSiO_2, nanoAl_2O_3, and nanoZnO materials at proper loading levels. Therefore, using nanotechnology, it is possible to produce environmentally friendly wood composite panels with low formaldehyde emissions.

Keywords: Nanotechnology; Nanomaterials; Formaldehyde emission; Environmentally friendly wood composite panels; Nanosilica; Nanoalumina; Nanozinc oxide

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INTRODUCTION

Particleboard and plywood panels are renewable bioresources that are made from wood particles and veneers. Particleboard panels are generally used in furniture and decoration, while plywood panels are mostly used for structural applications. The production capacity of these composite panels is increasing annually. Turkey is one of the biggest wood-based panel producers in Europe; particleboard panel production capacity was 5,771,100 cubic meters in 2012 with 28 production lines. The estimated plywood production capacity for 2013 is 247,000 cubic meters with 55 production lines (Candan 2012; Central Anatolian Exporters Union 2011; Turkish Wood Based Panels Association 2013; Yildirim *et al.* 2013).

The formaldehyde emissions of wood composite panels due to their formaldehyde-based resin content are a disadvantage in many applications. Formaldehyde emissions are a crucial property to consider for particleboard and plywood panels that will be used in residential applications. It is known that formaldehyde has a carcinogenic effect on human health (National Cancer Institute 2012; Roffael 2006; Salthammer *et al.* 2010). Thus, there has recently been increased interest, in developed countries, in the development of wood composites having low formaldehyde emissions.

Nanotechnology can be defined as the manipulation of materials measuring 100 nm or less in at least one dimension. It is expected to be a critical driver of global economic growth and development in this century because it is a multi-disciplinary field of research that is providing glimpses into exciting new capabilities, and enabling materials, devices, and systems that can be examined, engineered, and fabricated on a nanoscale. Producing nanomaterials with unique properties is expected to revolutionize technology and industry (Jones *et al.* 2005). Nanotechnology can be applied to many areas of research and development, from medicine to manufacturing to computing, and even textiles and cosmetics. Because of its potential for business development, nano-technology is of global interest. It is attracting more public funding than any other area of materials technology, estimated at around 6 billion dollars worldwide in 2010 (Shand 2010).

The National Science Foundation of the United States predicts that within a decade, nanotechnology will be a one trillion dollar market and provide two million new jobs (Jones *et al.* 2005). Nanotechnology has been identified as a technological revolution by scientists from all over the world. Nanoscience and nanotechnology also have numerous advantages for wood composite materials. The use of nanotechnology in the manufacture of particleboard and plywood panels is of great importance to overcome the formaldehyde emission issue (Candan 2012; Ciraci 2005; Jones *et al.* 2005; Roughley 2005). To decrease formaldehyde emissions, urea-formaldehyde adhesives have been modified with nanoaluminum oxide (Dudkin *et al.* 2006), nanosilica (Lin *et al.* 2005; Lin *et al.* 2005; Samarzija-Jovanovic *et al.* 2011), and nanocrystalline cellulose (Zhang *et al.* 2011).

There is limited data in the literature on formaldehyde emissions of particleboard and plywood panels reinforced with nanomaterials at different loading levels. In this work, environmentally friendly particleboard and plywood panels were developed using nanotechnology. The effects of the nanomaterial type and loading level on the formalde-hyde emission characteristics of both types of panels were also investigated.

EXPERIMENTAL

Materials

Urea formaldehyde resin, wood particles, hardener, and paraffin were supplied by Kastamonu Integrated Wood Industry and Trade Inc., located in Kastamonu, Turkey. The wood species used to manufacture particleboard panels in this study were *Pinus nigra*, *Populus tremula* L., *Fagus orientalis* Lipsky, and *Abies nordmanniana*. Melamine urea formaldehyde resin, wood veneers, and additives were supplied by Cag Forest Products Inc., also located in Kastamonu, Turkey. The wood species used to manufacture plywood panels in this work were *Tetraberlinia bifoliolata* and *Populus* × *canadensis* Moench. The nanosilica, nanoalumina, and nanozinc oxide particles used to modify both urea formaldehyde and melamine urea formaldehyde resin were provided by MKNano Corp. (Canada). The average particle size values (APS) of the nanoparticles ranged from 15 nm to 50 nm. The purity of the nanoparticles used to modify the thermosetting polymers was 99.9%. All of the nanomaterials were received as powder. The specific surface area, boiling point, and melting point values of the nanoSiO_2 were around over 600 m^2/g, 2200 °C, and 1600 °C, respectively.

Methods

Composite manufacturing

Urea formaldehyde and melamine urea formaldehyde resin were reinforced with nanosilica, nanoalumina, and nanozinc oxide particles. The nanoparticles were added to each resin at loading levels of 1% and 3%. Urea formaldehyde, NH_4Cl, and paraffin were used as adhesive, hardener, and hydrophobic additive, respectively, in the manufacture of the particleboard panels. Melamine urea formaldehyde, $(NH_4)_2SO_4$, NH_3, and flour were used as adhesive, hardener, buffer, and filler, respectively, in the plywood panels. Control panels without nanoparticles were also produced for comparison. The composite manufacturing technique is shown in Fig. 1. Each type of panel (particleboard and plywood) was made with the three types of nanomaterials at the two tested loading levels. A set of control panels was also made. All panels were made in triplicate, giving a total of 42 panels for evaluation. The final thickness of the panels was 8 mm.

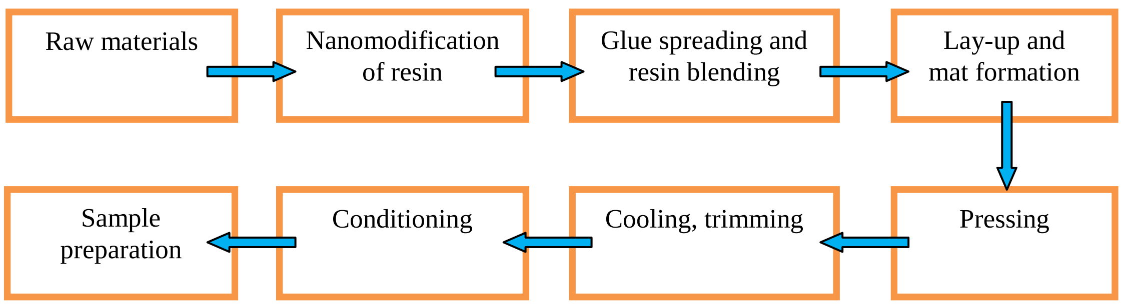

Fig. 1. Schematic diagram of the composite panel manufacturing process

Nanomaterial-reinforced particleboard and plywood panels were cut into test samples. In this study, the dimensions and density of the composite panels were determined according to TS EN 325:2012 (2012) and TS EN 323 (1999) standards, respectively.

Formaldehyde emission analysis

Formaldehyde emission tests were conducted on the particleboard and plywood panels according to standard TS 4894 EN 120 (1999). A perforator and spectrophotometer were used to determine the formaldehyde emission properties of the nanomaterial-reinforced composites. The test method states an extraction method, also known as the perforator method. The test specimens were randomly taken from the panels. The dimensions of the test pieces were 25 mm by 25 mm by panel thickness. The thickness of the particleboard and plywood panels used in this study was 8 mm. Moisture contents of the panels were also determined for formaldehyde emission analysis. TS EN 322 (1999) standard was used to calculate moisture content of the panels. Approximately 110 g panel samples were weighed with a precision of 1%, and then the samples were put into a flask. After that, 600 mL of toluene was added to the flask. The flask and the extraction system were connected, and then 1000 mL of distilled water was added into the extraction system. Afterwards, a Dimroth cooler, a double-bulbed tube, and a conical flask were connected to the system. The mantle heater was turned on. The extraction time was 2 h. When the first bubble passed through filter insert, the extraction time was started. The mantle heater was turned off after the extraction time completed. After the water in the extraction system cooled down to around 20 °C, the water was transferred into a flask with a volume of 2000 mL. Twice rinsing of the extraction system was performed with 200 mL of distilled water. The water (400 mL) from the rinsing process and the water (100 mL) in the conical flask were also added into the flask with a volume of 2000 mL. Then, 500 mL of distilled water was added into the flask to have 2000 mL of water containing formaldehyde. The formaldehyde content of this solution was determined by use of a spectrophotometer.

Statistical Analysis

To evaluate the formaldehyde emission characteristics of the particleboard and plywood panels reinforced with nanomaterials, all comparisons were first tested using an analysis of variance (two-way ANOVA) at $p < 0.05$. Significant differences between the mean values of treated and untreated groups were determined using Duncan's multiple range test.

RESULTS AND DISCUSSION

The average density of the nanomaterial-reinforced particleboard and plywood panels is given in Table 1. The density values ranged between 0.55 and 0.64 g/cm^3 for the plywood panels. All of the plywood panels had similar density values, except the panels reinforced with 3% nanoAl_2O_3. The nanomaterial-reinforced particleboard panels had density values between 0.65 g/cm^3 and 0.69 g/cm^3. The results showed that the nanomaterial reinforcement did not affect the density values of these panels. It also revealed that the manufacturing processes for particleboard or plywood panels were meticulously carried out.

Table 1. Average Density of the Particleboard and Plywood Panels

Nanomaterial type	Nanomaterial loading level (%)	Particleboard panels (g/cm^3)	Plywood panels (g/cm^3)
Control	-	0.65 (0.035)	0.57 (0.045)
NanoSiO_2	1	0.67 (0.028)	0.58 (0.038)
NanoSiO_2	3	0.69 (0.027)	0.59 (0.032)
NanoAl_2O_3	1	0.65 (0.029)	0.59 (0.028)
NanoAl_2O_3	3	0.67 (0.021)	0.64 (0.019)
NanoZnO	1	0.67 (0.035)	0.56 (0.021)
NanoZnO	3	0.65 (0.036)	0.55 (0.020)

Standard deviation in parentheses

The formaldehyde emission results for the nanomaterial-reinforced plywood panels are shown in Table 2. The results indicated that the lowest formaldehyde emissions were obtained from the plywood panels reinforced with nanoZnO at a loading level of 1%, while the highest value was obtained from the plywood panels reinforced with nanoSiO_2 at a loading level of 1%. As shown in Table 2, the formaldehyde emission values of the plywood panels using 1% nanoZnO, 1% nanoAl_2O_3, and 3% nanoSiO_2 decreased by 50.66%, 30.66, and 20%, respectively. Table 2 also shows that the formaldehyde emission values from the plywood panels reinforced with 1% nanoSiO_2, 3% nanoAl_2O_3, and 3% nanoZnO were greater than those from the control panels.

Table 2. Formaldehyde Emission Values of the Nanomaterial-reinforced Plywood Panels

Nanomaterial type	Nanomaterial loading level (%)	Formaldehyde content (mg/100 g oven dry board)
Control	-	0.75
NanoSiO_2	1	1.68
NanoSiO_2	3	0.60
NanoAl_2O_3	1	0.52
NanoAl_2O_3	3	1.25
NanoZnO	1	0.37
NanoZnO	3	0.78

To investigate the effect of the nanoparticle type and nanoparticle loading level, a two-way ANOVA was carried out. The statistical analysis showed that the formaldehyde emission values of the plywood panels were significantly affected by the nanoparticle type, nanoparticle loading level, and the combined effect of these factors. The combined effect of the nanomaterial loading level and nanomaterial type was the greatest, with a partial eta squared value of 0.963. There was no significant difference in the formaldehyde emission values of the panels reinforced with 1% and 3% nanomaterials, but there were significant differences between the panels reinforced with nanoSiO_2, nanoAl_2O_3, and nanoZnO at a significance level of 0.05.

It is well known that nanomaterials have tremendous surface area. However, some nanoparticles are prone to aggregation in liquid. Increases in the loading level of the nanoparticles may have caused aggregation in the nanoreinforced resins, negatively affecting formaldehyde emission values. Salari *et al.* (2013) obtained similar results to this work. They modified urea-formaldehyde resin with nanoSiO_2 particles at different loading levels and produced oriented strandboard (OSB) panels. It was reported that addition of nanoSiO_2 particles affected the formaldehyde emission properties of the OSB panels. Formaldehyde emissions decreased when nanoSiO_2 loading level increased from 1% to 3%. But further increase in nanoSiO_2 level to 5% resulted in increased formaldehyde emission. NanoSiO_2 can react with active groups of urea formaldehyde. Consequently nanoSiO_2 can absorb free formaldehyde from adhesive. Hydrogen bonding is believed to be involved in the interaction between urea formaldehyde resin and nanoSiO_2 (Lin *et al.* 2006; Roumeli *et al.* 2012).

Dudkin *et al.* (2006) investigated interactions between urea formaldehyde resin and nanoAl_2O_3 particles. It was reported that the urea formaldehyde resin contains an equilibrium mixture on monomeric formaldehyde and polyoxymethylene glycols which can interact easily with OH groups of finely divided particles of alumina. This provides good compatibility of urea formaldehyde resin and alumina nanoparticles. Adsorption of formaldehyde on the nanoalumina surfaces involves acid-base interaction of the surface OH groups with formaldehyde oligomers on the pseudo liquid interface to form strong bonds (Dudkin *et al.* 2006).

Table 3. Formaldehyde Emission Values of the Nanomaterial-reinforced Particleboard Panels

Nanomaterial type	Nanomaterial loading level (%)	Formaldehyde content (mg/100 g oven dry board)
Control	-	4.07
NanoSiO_2	1	2.48
NanoSiO_2	3	3.82
NanoAl_2O_3	1	0.73
NanoAl_2O_3	3	4.97
NanoZnO	1	1.08
NanoZnO	3	0.74

The formaldehyde emission values of the particleboard panels are shown in Table 3. The results of this study revealed that all of the nanomaterial-reinforced particleboard panels had lower formaldehyde emission values than the control particleboard panels, except for the particleboard panels reinforced with 3% nanoAl_2O_3. It was also shown that the particleboard panels reinforced with nanoZnO had the lowest overall formaldehyde emission values. The formaldehyde emission values of the particleboard panels increased when the nanoSiO_2 and nanoAl_2O_3 loading levels were increased. As shown in Table 3, the particleboard panels reinforced with 1% nanoAl_2O_3 or 3% nanoZnO had the lowest formaldehyde emission values. The maximum decrease in formaldehyde emissions of the particleboard panels was 82%.

A two-way ANOVA was carried out to determine the effect of nanoparticle type and nanoparticle loading level on the formaldehyde emissions of the particleboard panels. The results showed that the nanoparticle type, nanoparticle loading level, and their combined effect significantly influenced the formaldehyde emission values of the particleboard panels. The nanoparticle loading level had the greatest impact on formaldehyde emission values, followed by the combined effect of the two variables, and finally the nanoparticle loading level. There was no significant difference in the formaldehyde emission values of the panels reinforced with 1% and 3% nanomaterial, but there were significant differences between the panels reinforced with nanoSiO_2, nanoAl_2O_3, and nanoZnO at a significance level of 0.05.

It was also observed that the plywood panels and particleboard panels behaved slightly differently in the presence of nanoparticles. When the loading level of nanoAl_2O_3 particles increased from 1% to 3%, the increase in the formaldehyde emission of the plywood panels was lower than those of the particleboard panels. The addition level of nanoZnO particles affected differently the formaldehyde emission values of the plywood panels and particleboard panels. This could be attributed to the resins used in the manufacture of the panels. The plywood panels were produced with melamine urea-formaldehyde resin, while the particleboard panels were produced with urea-formaldehyde resin. The results might have been influenced by interactions between the resins and nanomaterials.

Nanomaterials have unique characteristics such as excellent chemical activity, physical properties, and large specific surface area (SSA). These properties could be used to enhance performance of thermosetting resins and composite materials so that new opportunities could be achieved. The decrease in the formaldehyde emission of the nanoreinforced particleboard and plywood panels could be attributed to strong absorbability of the nanoparticles used (Xu *et al.* 2011). Barrier properties of the nanoparticles also affected the formaldehyde emission characteristics of the composite panels. NanoSiO_2 particles have been shown to reduce the formaldehyde emissions of the panels because of their shielding effect (Arafa *et al.* 2004; Roumeli *et al.* 2012).

The results obtained in this study are supported by a previous work by Dudkin *et al.* (2006). That work investigated the influences of nanoaluminum oxide on the free formaldehyde content of urea formaldehyde resin. It was concluded that nanoaluminum oxide decreased the free formaldehyde content of urea formaldehyde resin. Both of Lin *et al.*'s works (2005a, b) stated that nanosilica decreased the formaldehyde emissions of urea formaldehyde resin. Samarzija-Jovanovic *et al.* (2011) modified urea formaldehyde resin with nanoSiO_2 particles and hexamethylenetetramine (HMTA). It was stated that the formaldehyde content of the urea-formaldehyde resin decreased after using nanoSiO_2. Candan and Akbulut (2012) modified laminate flooring with nanoSiO_2, nanoAl_2O_3, and ZnO particles at different loading levels. It was reported that the nanoparticle type and loading levels significantly affected the formaldehyde emission values of the laminate flooring. The lowest formaldehyde emission value was determined from the laminate flooring reinforced with 1% nanoAl_2O_3. Xu *et al.* (2011) reinforced soy protein adhesive with nanoSiO_2 particles and then manufactured plywood panels with the resin. It was stated that an optimal loading level of nanoSiO_2 particles was 1% for dry strength.

CONCLUSIONS

1. In this work, urea formaldehyde and melamine urea formaldehyde resins were modified with various nanomaterials at different loading levels. The findings revealed that the nanomaterial type and nanomaterial loading level significantly affected the formaldehyde emission values of the particleboard and plywood panels.
2. The use of nanoparticle reinforcement on thermosetting resins can help develop novel particleboard and plywood panels that are environmentally friendly.
3. It can be concluded that nanoscience and nanotechnology offer important opportunities for the forest products industry. The formaldehyde emission values of particleboard and plywood panels can be decreased using the proper nanomaterial type and loading level.

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