

## APPLICATION OF NANO- AND MICRO-MATERIALS IN WOOD-BASED COMPOSITES IN IRAN

Hamid R. Taghiyari <sup>1\*</sup>, Elham Nadali<sup>2</sup>, Mahdi Arabi<sup>3</sup>, Reza Majidinajafabadi<sup>4</sup>

<sup>1</sup> *Wood Science and Technology Department, Faculty of Materials Engineering & Interdisciplinary Sciences, Shahid Rajaei Teacher Training University (SRTTU), Tehran 16788-15811, Iran; E-mail: htahghiyari@sru.ac.ir*

<sup>2</sup> *Ph.D. Graduate from the Department of Wood & Paper Science and Technology, Faculty of Natural Resources, University of Tehran, Karaj 77871-31587, Iran. Email: e.nadali@yahoo.com*

<sup>3</sup> *Department of Surveying and GIS Engineering, Faculty of Civil Engineering, Shahid Rajaei Teacher Training University (SRTTU), Tehran 16788-15811, Iran; E-mail: mahdi.a@sru.ac.ir*

<sup>4</sup> *Expert in the Conservation and Restoration of Historical and Museum Objects and Archaeometry of the University of Tehran Museums, The University of Tehran, Tehran, Iran. Email: r.majidi.n@gmail.com*

### ABSTRACT

Wood is a renewable raw material in different kinds, patterns, strengths, and varieties that nature has provided to be used in a myriad of applications since before history. With the rapid increase in population on earth, and the consequent growing need for wood, fast-growing wood species became of more importance every day though their properties of these species are considered rather poor. However, they can satisfactorily be used in wood-based composite panels, like particleboard, medium-density fiberboard (MDF), high-density fiberboard (HDF), flakeboard, plywood, oriented strand lumber (OSL), and wood-plastic composites (WPCs). Still, production and application of composite panels have some troublesome drawbacks, including vulnerability to water and high humidity, and hot-press as a bottleneck in the production process as well. Over the past two decades or so, many studies were carried out to overcome these drawbacks and to improve properties in composite panels from different aspects, using different materials at nano- and micro-scales, mostly as resin reinforcement, additives, and cross-bonding agents. The present article tries to briefly provide an outlook on the strengths and weaknesses of some of the above mentioned materials that have been used in Iran, with an aim of giving an idea to young researchers for their future studies.

**Key words:** Cellulose-based composites, Minerals, Nano- and Micro-materials, Natural fibers, Resin reinforcement, Wollastonite.

### INTRODUCTION

Wood-based composite panels are becoming more and more popular all over the world. Utilization of fast-growing wood species can be considered from two main perspectives. The first is that deforestation and over-cultivation of natural forests would eventually lead to climate change and global warming which is a universal concern. Therefore, governments have legislated restricting regulations on cutting down trees. The second reason is a technical one which is related to the compact ratio in panels, defining the original density of materials used in relation to the

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\* Corresponding author: Wood Science & Technology Department, Faculty of Materials Engineering & Interdisciplinary Technologies, Shahid Rajaei Teacher Training University; htahghiyari@sru.ac.ir & htahghiyari@yahoo.com; Cellphone: (+ 98) 930-2005235; Fax: (+ 98) 21-22970047.

density of the wood-based composites produced. As a general rule, composite panels with higher compact ratio provide with more suitable physical and mechanical properties from a technological point of view. This necessitates using raw materials with lower density to form the mats and furnish for composite panels. Low-density wood species can therefore be considered more suitable for production of wood-based composite panels. Eventually, fast-growing wood species provide not only a reliable source of raw materials for the composite manufacturing industry, but the end products would also be of higher quality. However, it is to be noted that there are many drawbacks in wood- and agroforestry-based composite panels that still have to be improved and attended to.

There are several aspects in production of wood-based composite panels that have been studied in Iran over the past two decades, two of which are of prime importance, namely the decreasing of hot-press time as a bottleneck in production of composite panels, and improving different physical and mechanical properties without increasing resin content. In the next sections, some of the achievements in this regards are summarized.

### **HOT-PRESS AS THE BOTTLENECK**

Wood flakes, particles, and fibers are stuck and fixed together by a kind of synthetic resin in a mat. The resins used in wood composite industry in Iran are usually amino resins (like urea-formaldehyde, and melamine-formaldehyde resins). These resins are categorized in thermosetting polymers which need to be heated for fast and effective polymerization so that desired physical and mechanical properties are achieved. The heating is carried out under hot-presses with multiple entries. The production rate at wood-based panel manufacturing factories is usually influenced by the number of hot-presses, and the number of openings in each. Therefore, lower hot-press times eventually results in faster production rate, lower energy consumption, and ultimately lower productions costs.

Wood is basically considered an insolent material. This is why the handles of many household and industrial utensils, where heat is not to be transferred to the other end, is made with wood. However, this is quite the opposite case; that is, heat is meant to be transferred from the hot plates of a press to the inner parts of the wood furnish. This concern can somehow be addresses to by increasing moisture content of the mat, although the increase results in not only higher energy consumption for evaporation of the extra water, but it also arises a much serious problem: occurrence of blows in the center of panels. Therefore, more practical solutions are to be found.

Addition of metal nanoparticles (silver and copper) helped the hot-press time to decrease by more than 10 percent (Figure 1). Enhanced transfer of heat resulted in improvement of physical and mechanical properties (Table 1).

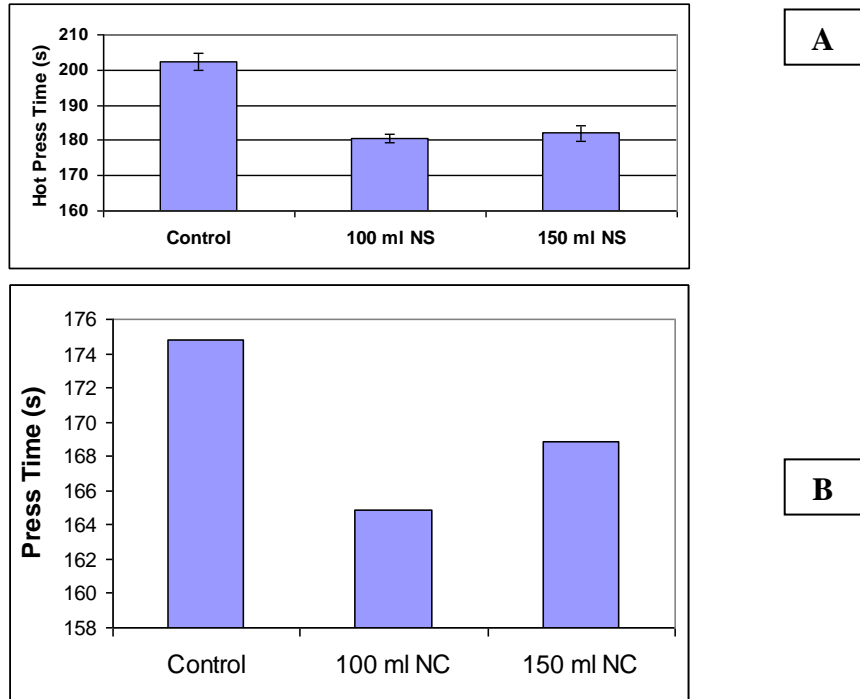


Figure 1: Duration of hot-press (second) in control and nanosilver-treated (A) and nanocopper-treated (B) particleboards (100 and 150 mL based on the dry weight of wood particles), (Taghiyari et al. 2011& 2013).

Table 1: Mechanical and Physical Properties of Control, 100 mL/kg, and 150 mL/kg Nano-silver Particle Boards.

Properties	Type of nanomaterial	Control specimens	100 mL/kg	150 mL/kg
Modulus of Rupture (kg/cm <sup>2</sup> )	Nanosilver	190 (B)*	204 (A)	205 (A)
	Nanocopper	116 (B)	118 (B)	124 (A)
Modulus of Elasticity (kg/cm <sup>2</sup> )	Nanosilver	23975 (B)	24048 (B)	27128 (A)
	Nanocopper	18309 (AB)	18809 (A)	17755 (B)
Internal Bond (kg/cm <sup>2</sup> )	Nanosilver	11 (B)	12 (A)	12 (AB)
	Nanocopper	5 (A)	4 (B)	5 (AB)
Water Absorption (2 h) (%)	Nanosilver	39 (A)	39 (A)	38 (AB)
	Nanocopper	32 (A)	31 (A)	28 (B)
Water Absorption (24 h) (%)	Nanosilver	63 (A)	62 (AB)	62 (AB)
	Nanocopper	62 (A)	60 (A)	53 (B)
Thickness Swelling (2 h) (%)	Nanosilver	16(A)	16 (AB)	16 (B)
	Nanocopper	18 (B)	18 (AB)	19 (A)
Thickness Swelling (24 h) (%)	Nanosilver	28 (A)	28 (A)	28 (A)
	Nanocopper	20 (B)	19 (C)	23 (A)

\* Grouping of treatments based on Duncan multiple range test, at 95% significant level.

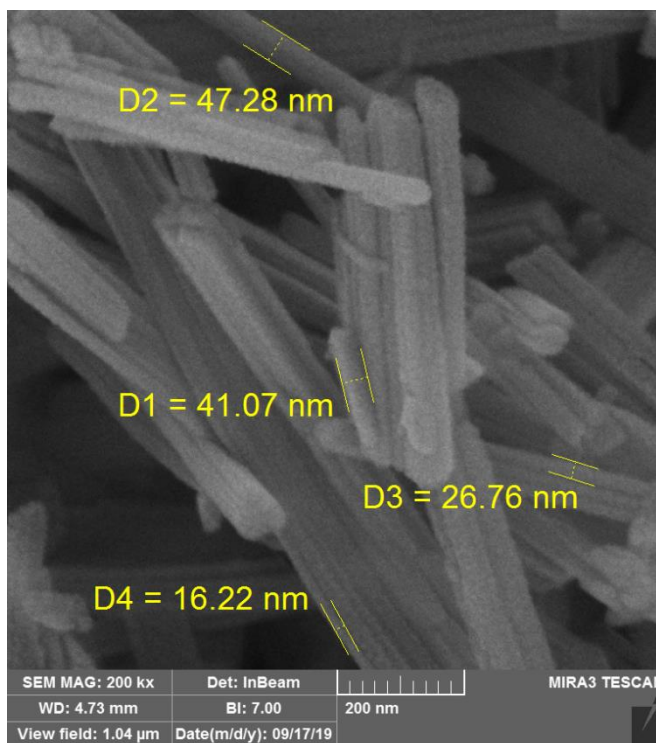
Sepiolite is a mineral material with thermal conductivity coefficient of  $3.90 \pm 0.31$  ( $W.m^{-1}.K^{-1}$ ) (Taghiyari et al. 2020a). It is a silicate mineral with more than 48% of SiO<sub>2</sub> (Table 2). In comparison to thermal conductivity coefficients of hardwoods (0.16 ) and softwoods (0.12 ) (Bergman et al. 2011), sepiolite can facilitate transfer of heat much more effectively. Addition of sepiolite nanostrands (Fig. 2) in UF-resin to produce oriented-strand lumber (OSL)

significantly increased thermal conductivity by 36% and 27% in the OSL panels produced with 8% and 10% UF-resin, respectively (Taghiyari et al. 2020a). Moreover, measurement of the core temperature of panels while in hot-press revealed significant increase in transfer of heat in panels with sepiolite content (Fig. 3). The accelerated heat transfer in panels with sepiolite content was reported to improve some mechanical properties, including hardness (Taghiyari et al. 2020a).

**Table 2: Sepiolite compounds based on XRF analysis of sample from Tanbo region (Iran), (Taghiyari et al. 2020a).**

Sepiolite compounds	Content (based on mass, wt. %)
SiO <sub>2</sub>	>48
Al <sub>2</sub> O <sub>3</sub>	>1
Fe <sub>2</sub> O <sub>3</sub>	>5.5
MgO	>15
SO <sub>3</sub>	≅0.6
CaO	≅8
Na <sub>2</sub> O	0
K <sub>2</sub> O	≅0.2
MnO	≅0.2
SrO	≅0.1
ZnO	≅0.2
BaO	0.5
L.O.I.*	>18

\*Loss caused by ignition of the specimen.



**Figure 2: Scanning electron microscope image of sepiolite nanostrands that were added in UF-resin, (Taghiyari et al. 2020a).**

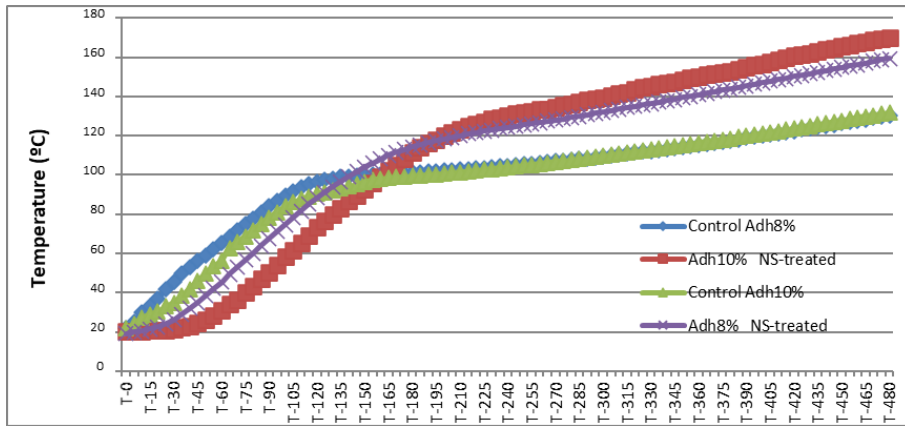
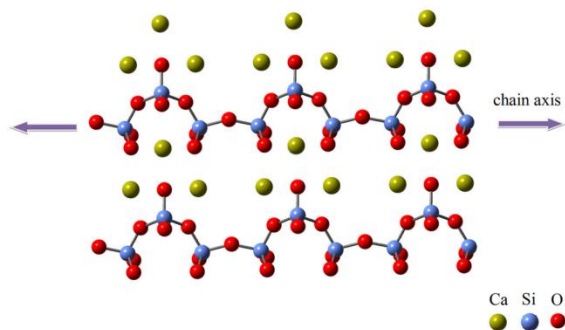


Figure 3: The average temperature (°C) measured at the core of OSB panels at 5-second intervals.

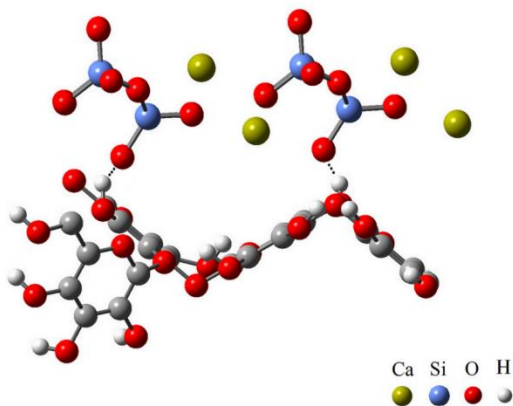
### ENFORCEMENT OF RESINS AND ADHESIVES

Resins and adhesives have always been considered as a main production cost at composite manufacturing plants. Over the past decades, two other global concerns intensified the necessity for researchers to find ways to decrease synthetic resin consumption in composite panels, namely the environmental and concern and health issues. These international concerns, in addition to other minor ones, gave way to investigate different types of resin reinforcement additives to modify resins and adhesives in order to decrease their content in wood-based composite panels.

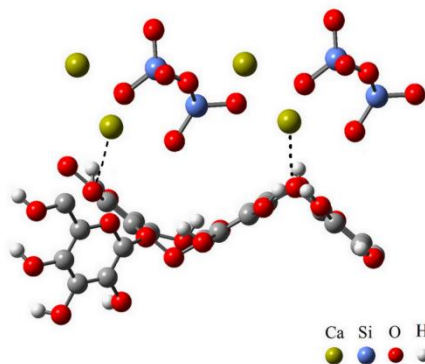
Addition of different fillers and enforcers in resins and adhesives is not a new technique to strengthen them. Different natural powders have been reported to improve physical and mechanical properties in wood- and lignocellulosic-based panels (Doosthoseini and Moezzi pour 2011). However, application of nano- and micro-additives in resins was introduced in the recent two decades. In terms of mineral materials, nanowollastonite was one of the first nanomaterials to be used in PVA and UF resins (Taghiyari and Nouri 2015; Taghiyari et al. 2020a,b). Wollastonite is a silicate mineral material which is mainly comprised of CaO (about 40%) and SiO<sub>2</sub> (about 47%) (Fig. 4). The silicate chain which is located along the central axis in the wollastonite crystals (Fig. 4a) are linked to a periodicity of three tetrahedra. Calcium molecules are in turn linked to six oxygen molecules by octahedral coordination (Buerger 1956; Richardson 1999; Giraud et al. 2015). This model was originally introduced by Kaith et al. (2011) and Pizzi and Tannins (2008, 2019). It was further more developed and elaborated to measure and calculate the potential adsorption of wollastonite on hemicellulose, and to compare adsorption of water molecules on hemicellulose as well.



(a)



(b)



(c)

**Figure 4: Predicted atomic structures of: (a) wollastonite, (b,c) side view of two models of the most stable configurations of wollastonite adsorbed on hemicellulose.**

Wollastonite was reported to improve different properties in wood-based composite panels both at nano- and micro-scales. Nanowollastonite improved physical and mechanical properties in medium-density fiberboard at 10% consumption level (based on dry weight of wood fibers) when used internally and on the surface of panels (Taghiyari and Nouri 2015). Higher

consumption of this mineral nanomaterial caused deteriorating of some properties because the nanoparticles absorbed part of the resin which did not let it to be actively involved in the process of sticking wood fibers together. Moreover, the density was kept constant; this decreased the wood fiber content in panels with higher wollastonite content which in turn led to lower integrity among wood fibers in the composite matrix (that is, MDF panels). It was also reported that surface application significantly improved fire properties in MDF panels at wollastonite content of up to 15%.

Wollastonite was also used to produce panels with no synthetic resins in which micro-wollastonite acted as a binder between wood fibers (Taghiyari et al. 2020). The cited authors reported rather high adsorption energy and short adsorption distance between wollastonite compounds with wood cell-wall polymers (mainly cellulose and hemicellulose). The calculations were carried out using density functional theory (DFT) analysis (Peymanirad et al. 2024). The calculated adsorption distance of 1.7 Å, along with the rather high adsorption energy of -6.6 eV, provided strong enough bonding between wollastonite nanoparticles to be fixed in wood cell-wall polymers (cellulose and hemicellulose) so that panels with acceptable strength were produced. However, immersion in water caused a serious problem. In the presence of abundant water molecules, the bonds between wollastonite and cell-wall polymers tended to break, ending up in losing the mechanical properties.

Graphene is a nano-sheet (one-atom-thick planar sheet) material that is comprised of carbon atoms. The sheets are generally arranged in a honeycomb structure to form a crystal lattice. This nanomaterial has gained considerable attention in the recent decades in terms of its outstanding properties (Majidi 2017ab; Dul et al. 2020; Salom et al. 2018; Papadopoulos et al. 2019; Jojibabu et al. 2020; Yang et al. 2020). It is used in different industries, including sensors, energy saving devices, electronic materials and utensils, a variety of modern composites and emerging materials. In another study, graphene was used in polyvinyl acetate (PVA) resin to investigate its shear strength in normal and thermally-modified beech wood (Taghiyari et al. 2022). It was reported that graphene acted as a reinforcing filler, and shear strength of PVA resin was improved in the preliminary phase of the study by 17%, in specimens prepared according to ASTM D143-14 (2014) standard specification. Other carbon-based compounds (like carbon black) was previously studied with improving effects on mechanical properties in wood-plastic composites (WPC) (Hyvärinen 2014). It is to be noted that solid contents play a vital role in resins and adhesives, and any alteration in the ratio (solvent versus solid contents) has significant influence on the final results. It was reported that graphene powder was more effective in improving shear strength in PVA resin in comparison to graphene gel. The higher improving effect was attributed to the dilution of PVA resin in the extra of graphene gel (with 60% solid content).

## BIOLOGICAL ASPECTS

In addition to the above-mentioned aspects, improvement in the biological resistance of composite panels by nano- and micro-materials against wood-deteriorating organisms (including wood-decay fungi, different insects and termite species) is another aspect of equal importance. Nanowollastonite (NW) and nanoclay significantly decreased the weight loss in wood and wood-based composite panels caused by exposure to different wood-decay fungi species, including white-rot fungi *Physisporinus vitreus*, *Trametes versicolor*, and *Pleurotus ostreatus*, and brown-rot fungi *Antrodia vaillantii*, and *Coniophora puteana*. The important point in using the above

mentioned two minerals is that they are considered of no health hazard to either human or livestock (Huuskonen et al. 1983ab; Seaton et al. 2010). In fact, they can improve growth potentials of some plants, too. Therefore, it can be used in composite panels that are to be used at home and offices with no health concerns for people who use the cabinet and furniture. Moreover, abundant sources of this mineral are available in many countries, including Iran, the US, and China, leading to its low-cost production and utilization. It also decreases formaldehyde emission which is common in composite panels produced by UF-resin.

## CONCLUSIONS

Based on the brief review above, it can be concluded that different metals and minerals have potentiality to be used at nano- and micro-scales to improve different properties in wood-based composite panels. Apart from the improving effects they are proved to have on different physical and mechanical properties of the panels, and to decrease vulnerability to biological organisms as well, they can remove other concerns that are of great importance in today's world. Two of the main concerns are the environmental and health concerns. Many metals and minerals (including silver and wollastonite) are not considered toxic to the environment and human, and even livestock. Therefore, they can freely be used with no particular anxiety as to pollution of the environment, or putting people's health at risk. Moreover, many of the minerals are available at large quantities around the world, making the production costs quite low in comparison to the chemicals that are used in forms of resins and preservatives. Cultivation of fast-growing trees may have extra benefits as well, like urban design, and absorption of carbon dioxide of the atmosphere. In this connections, many research studies have been carried out in the last two decades; still, a lot more are to be done by young researchers to find practical ways to introduce the above mentioned metals and minerals to be used at industrial scales, and to investigate on their possible negative side-effects on devices, especially cutting blades and abrasive tools and instruments.

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