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POTENTIAL USAGE OF NANOTECHNOLOGY IN WOOD DRYING: TREATING POPLAR BOARDS WITH NANOMETALS AFFECTS THE DRYING BEHAVIOR

HOSSEIN LOTFIZADEH[a], MAHDI SHAHVERDI [b], HADI DASHTI [b], HAMID REZA TAGHIYARI [c *]

[a]*Department of Mechanical Engineering, Karaj Branch, Islamic Azad University, Karaj, Iran*

[b]*Department of Wood and Paper Science & Technology, Karaj Branch, Islamic Azad University, P. O. Box 31485-313, Karaj, Iran*

[c]*Wood Science and Technology Department, the Faculty of Civil Engineering, Shahid Rajaee Teacher Training University, Tehran, Iran*

Effects of silver and copper nanoparticles on wood drying of poplar boards were studied. The boards were cut by two patterns of flat-sawn and quarter-sawn, as well as three thicknesses of 2.5, 5 and 7.5 cm. They were divided in three groups of nanosilver-impregnated (NS), nanocopper-impregnated (NC), and control treatments. NS and NC boards were first impregnated with nanosilver and nanocopper suspensions, respectively; they were then dried in a laboratory convective kiln along with the control boards. The drying rate above and below the fiber saturation point (FSP), moisture content gradient slope, and drying residual stresses were measured. The results revealed higher drying rate both above and below the FSP in nanometal-impregnated boards. Also, less residual stress and moisture gradient slope were observed in NS and NC boards. It may then be concluded that nanometal particles may have the potentiality in improving the drying conditions and decreasing drying stresses in convective kilns.

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Keywords: Wood drying, Nanotechnology, Poplar, NanoSilver (Ag), NanoCopper (Cu)

1. Introduction

Many researches have been carried out with regard to the use of nanoparticles in different sciences (Abedini et al., 2012; Dashti et al., 2012a,b; Geoprincy et al., 2011; Gogoi & Deb, 2012; Korayem et al., 2012; Prodana et al. 2011; Heidarpour et al. 2011; Sima & Sima, 2012; Taghiyari, 2011a,b,c; Rassam et al., 2011; Taghiyari et al., 2011a; Taghiyari et al. 2012a,b,c,d; Taghiyari 2012; Teoh et al., 2010; Wei et al., 2012; Yu et al., 2012). Research in nano-science, given the size of particles in nano-scale, has led to progress of materials and structures in improvement of physical and chemical properties of wide range of materials (Wegner et al., 2005; Wegner and Jones 2006). In this connection, due to the alteration of wood quality by rotation period, mono- or mixed-species cultivation, light and soil, as well as interaction between clone-type and site (Ajala & Ogunsanwo, 2011), and the quality of wood can be affected by rotation period, mono- or mixed-species cultivation, light and soil, initial spacing, as well as interaction between clone-type and site (Addo-Danso et al., 2012; Barna, 2011; Girma & Mosandl, 2012; Jans et al., 2012; Luo et al., 2012; Oke et al., 2012; Taghiyari et al., 2010; Taghiyari & Sarvari Samadi, 2010; Taghiyari & Efhami, 2011; Taghiyari et al. 2011b; Tenorio et al. 2012), the advantage of composite-boards, as a homogeneous material without restrictions as to the shape and size (Uetimane & Ali, 2011), and the recent studies to find methods for limitation of formaldehyde emission (Valenzuela, 2012; Stockel et al. 2012) and their other shortcomings, is becoming more and more conspicuous to the industry.

*Corresponding author: htaghiyari@srttu.edu, htaghiyari@yahoo.com

In this way, wood fiber nano-composites with favorable properties have been extensively developed (Yeh and Gupta 2008; Nakagaito and Yano 2008). Lei et al. (2006) added nano SiO_2 into gypsum particleboard to improve the mechanical properties of the board. Jinshu et al. (2007) showed that a compound comprised of urea-formaldehyde (UF) resin and nano-SiO_2 improved general properties of poplar wood. In a research by Lei et al. (2006) on plywood, it was shown that adding the nanoclay NaMMT to UF resin results in increased water resistance. Leach and Zhang (2004) used nanoparticles of copper-carbonate and iron oxide inaqueous systems for preservative treatment of wood. Kartal et al. (2009) found that nanozinc possessed favorable properties for wood preservation, such as leach resistance, termite mortality, and inhibition of termite feeding and decay by white-rot fungus. Giorgi et al. (2006) investigated on nanotechnologies for the conservation of waterlogged wood. Wang et al. (2006) used nanoindentation as a tool for understanding nano-mechanical properties of wood cell wall and biocomposites. Henriksson et al. (2008) used wood nanofibrils to prepare porous cellulose nanopaper of remarkably high toughness. Clausen (2007) investigated the role of nano-technology in wood preservation and concluded that silver, zinc and copper nanoparticles have high transmittance and low viscosity which allow them to distribute uniformly. Shah et al. (2010) also investigated the effect of copper and iron nano-particles on production of destructive lignocellulosic enzymes by *Trametes versicolor*. Results indicated that these nanoparticles have significant effect on production of these enzymes in the white rot fungi. Matsunaga et al. (2007) reported that the amount of copper particles was more seen in middle lamella rather than in secondary cell wall. In addition, the large number of copper particles was seen in S_3 layer, as well as in cell pores which in presence of copper in cell walls extremely differed (entrance of silver nano-particles into secondary wall is almost infeasible).

Taghiyari (2011b) studied the effect of nano-silver on permeability of particleboard. Results showed that silver nanoparticles addition which added at two levels has significantly reduced permeability degree of particleboard. He considered the reduced permeability as a result of better polymerization of adhesive. Taghiyari et al. (2011) investigated the effect of silver nanoparticles on improvement of press time and mechanical properties of particleboard. Results indicated that heat-transfer properties of silver nanoparticles (Narashimha et al. 2011; Sadeghi & Rastgo, 2012) lead to reduction in press time. Besides, reduction of thermal gradient improves mechanical properties of particleboard as well. Despite numerous researches in usage of nano-technology in wood industry, few researches have been yet carried out with regard to this comprehensive science in the field of wood drying. In this research, application potential of copper and silver nanoparticles in the wood drying process is investigated.

2. Materials and methods

Specimen Preparation

Freshly-cut poplar (*Populus nigra*) logs belonging to a forest close to Taleghan city in Iran were studied. Boards were cut in two patterns: flat-sawn and quarter-sawn. For each sawing pattern, boards were cut in three thicknessesof 2.5, 5, and 7.5 cm while green. The width and length of boards were 10 and 15 cm, respectively.

Nanoparticles

200 ppm aqueous nanosilver (NS) and nanocopper (NC) suspension were produced using an electrochemical technique in cooperation with Iran Nanopooshesh Company. In nanoparticles manufacturing de-ionized water was used as a beginner, $NaBH_4$ as a reducing agent and TADDD as a stabilizer.

Impregnation of the boards

The impregnation of the boards with nanosilver (NS) and nanocopper (NC) suspensions was carried out by immersion method. Green Specimens were immersed in the suspensions for about 30 minutes. Immediately after the impregnation, the boards were coated on their four sides with epoxy resin to confine the moisture transfer only along the board thickness.

Drying Procedure

The boards were dried at aconstant dry-bulb temperature of 60^{o}C and relative humidity (RH) of 40% (EMC ≈ 8%) using a laboratory convective kiln. The drying process was terminated without any conditioning treatment. Table 1 illustrates the design of experiments and the number of replications.

Table 1. Design of experiments and the number of replications tested for each drying condition.

Board type	Thickness (mm)	Control	NS[1]-impregnated	NC[2]-impregnated
Flat-sawn board	25	3*	3	3
	50	3	3	3
	75	3	3	3
Quarter-sawn board	25	3	3	3
	50	3	3	3
	75	3	3	3

*replications
[1]NanoSilver
[2]NanoCopper

Residual stresses

Prong test was used to determine the degree of drying residual stresses (casehardening). Two U-shaped prongs were taken from each dried board to assess drying stresses. The stress prongs were cut in full thickness and width of the board and 20 mm along its length. Fig.1 shows a schematic picture of prong cutting for measurement of drying stresses. Prong response (PR) was calculated using the following Equation (Fuller 1995):

$$PR = \frac{x - x'}{l^2} \tag{1}$$

where: PR is prong response (mm^{-1}), x is distance between outerprong edges before the prong cut (mm), x' is distance between outer prong edges after the prong cut (mm), and *l* is the length of the sample's prong (mm). The prong tip distance was recorded before and after cutting. The influence of immediate change in surface moisture content of the prongs was neglected.

Drying rate and moisture content gradient

Drying rate was measured by weighing the boards during drying process. After drying, dried boards were sliced through the thickness to determine final MC profiles (Fig. 1).

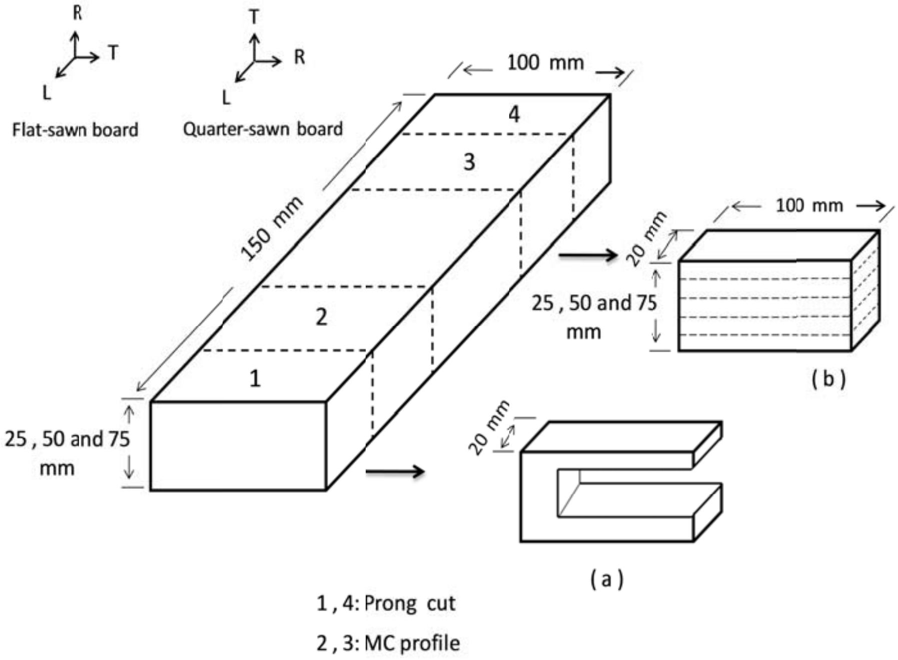

Fig. 1. A schematic of sample cut for measurements of drying stresses (a), and MC profiles (b) of the dried boards.

3. Results and discussion

Drying rate

Study of the drying rate was separately conducted within range of free water (higher than 35%) and bound water (lower than 30%). It can be drawn from Table 2 that with increase of the board thickness, drying rate within free water range has decreased. Drying rate within this domain was higher in flat-sawn boards than that in quarter-sawn ones. Shmulsky (2001) also indicated that drying rate above the fiber saturation point (FSP) is higher in flat-sawn boards than in quarter-sawn boards. Many factors affect difference in drying rate in tangential and radial directions in the free water range. Anatomical features, permeability (Choong et al. 1974), thermal conductivity coefficient (Griffiths & Kaye 1923) are among determinants of drying rate within this range (Simpson 1991). Free water does not affectas many wood properties as bound water, but does affect thermal conductivity and permeability (Simpson 1991). Results show that by emersion of samples in nanosilver and nanocopper, drying rate increases within range of free water in tangential and radial directions. Drying rate increase within this range took place in all boards with different thicknesses, but this increase was more observed at boards of 25 and 50 mm thicknesses. Increase in drying rate in the impregnated specimens by nanosilver and nanocopper are the result of high thermal conductivity coefficient of nanometals (Ghorbani et al. 2012; Shi, 2007; Wisitoraat et al., 2012; Wu et al., 2012). In fact, as a result of this treatment, heat has been transferred at a higher rate to the core of the boards and consequently quick heat transfer to the core leads to faster moisture reduction. One of the most important issues in drying of thick boards is providing sufficient heat to these boards core. In fact, a main reason for slower drying rate of thick boards is the slow moisture flux from the core of the boards to their surface layers. Given that the immersion method was used for treating of wooden samples, depth of particles' penetration compared to overall thickness is also an important factor in drying rate above the FSP. There is the possibility that with increase of concentration of nanoparticles suspension and use of a method for further increase of the particles penetration depth, drying rate increases as well.

Results of the increase in drying rate within hygroscopic range are presented in Table 3. The results indicate that with increase of boards' thickness, its drying rate within hygroscopic range decreases. Drying rate below the FSP was higher in quarter-sawn boards. Moreover, immersion in silver and copper suspensions resulted in increased drying rate within hygroscopic range at the all thicknesses. Treating samples by silver suspension was resulted in higher drying rate. Not many studies have been done with regard to effect of silver and copper nanoparticles on the drying rate. Taghiyari (2011a) investigated the effect of silver nanoparticles in thermal treatment on poplar (*populous nigra*). His findings revealed that silver nanoparticles have increased thermal conductivity in wood; consequently the results of heat-treatment were intensified. In another study, Taghiyari et al. (2011a) showed that addition of silver nano-particles has improved thermal conductivity in particleboards. The results indicated that properties of silver nanoparticles concerning their thermal conductivity may lead to reduced press time and improved physical and mechanical properties. The heat conductivity of silver nanoparticles is also reported to improve resin polymerization in the center of the mat, resulting in decrease in gas and liquid permeability (Taghiyari, 2011b).

Table 2. Drying rate above FSP in control and treated samples.

Treatment		Thickness		
		25 mm	50 mm	75mm
Flat-sawn	Control	1.991 (0.198)*	1.054 (0.318)	0.811 (0.221)
	NS	2.945 (0.937)	1.182 (0.273)	0.877 (0.046)
	NC	1.935 (0.203)	1.355 (0.044)	0.847 (0.041)
Quarter-sawn	Control	1.577 (0.265)	0.837 (0.163)	0.550 (0.254)
	NS	2.180 (0.098)	1.124 (0.122)	0.577 (0.019)
	NC	2.052 (0.076)	0.998 (0.110)	0.585 (0.254)

*standard deviation

Table 3. Drying rate below FSP in control and treated samples

Treatment		Thickness		
		25 mm	50 mm	75mm
Flat-sawn	Control	0.668 (0.139)*	0.375 (0.023)	0.293 (0.033)
	NS	0.810 (0.101)	0.362 (0.109)	0.396 (0.094)
	NC	0.680 (0.141)	0.299 (0.081)	0.292 (0.010)
Quarter-sawn	Control	0.253 (0.055)	0.343 (0.068)	0.154 (0.037)
	NS	0.550 (0.121)	0.517 (0.130)	0.336 (0.008)
	NC	0.400 (0.097)	0.396 (0.044)	0.240 (0.017)

*standard deviation

Moisture content gradient and residual stresses

Results indicated that with increase in board thickness, MC gradient slope becomes more intensive (Table 4). The boards impregnated with nanosilver had more homogeneous MC gradient along the thickness compared to that of control boards. Nanoparticles speeded up the heat transfer to the core of the board and further increased the temperature in these layers against the control specimens. In wood drying process, greater homogeneity of MC gradient in the dried boards is of high importance. Presence of extreme MC gradient in dried boards in addition to aggravation of wood drying stresses, leads to occurrence of various deformations in them during machining. Slower moisture flux from inner partsin the thick boards leads to occurrence of grave MC gradient in the dried boards. Therefore, as a result of nanosilver treatment and quicker transfer of moisture from the boards' inner parts to their surface layers, more homogenous MC gradient is developed in the dried boards.

Results of internal stresses are presented in Table 5. The results indicate reduced internal stresses in the boards treated by nanoparticles. Since MC gradient slope is one of the determinants of internal stresses, MC gradient improvement has led to reduced internal stresses in the treated samples compared to the control samples. The main reason for creation of the internal stresses was the difference in the shrinkage times of superficial and internal layers during the drying process.

Differential shrinkage between the shell and core of board also causes drying defects. Early in the drying process, the fibers in the shell (the outer portion of the board) dry first and begin to shrink. However, the core has not yet begun to dry and shrink, and consequently the core prevents the shell from shrinking. Thus, the shell goes into tension and the core into compression (Simpson 1991). As regards, addition of silver nanoparticles and more speedy transfer of heat to the inner parts lead to the reduced difference in shrinkage time between superficial and internal layers and consequently resulted in the decrease in the internal stresses in the dried boards.

Table 4. MC gradient slope through the thickness of control and treated samples (% mm^{-1})

Treatment		Thickness		
		25 mm	50 mm	75mm
Flat-sawn	Control	0.063 (0.009)*	0.092 (0.060)	0.105 (0.013)
	NS	0.052 (0.011)	0.060 (0.003)	0.069 (0.036)
	NC	0.025 (0.008)	0.051 (0.020)	0.073 (0.012)
Quarter-sawn	Control	0.040 (0.008)	0.105 (0.039)	0.322 (0.079)
	NS	0.039 (0.017)	0.089 (0.023)	0.147 (0.007)
	NC	0.015 (0.004)	0.098 (0.027)	0.092 (0.016)

*standard deviation

Table 5. Drying stress values in control and treated samples.

Treatment		Thickness		
		25 mm	50 mm	75mm
Flat-sawn	Control	0.0092 (0.0037)*	0.0258 (0.01392)	0.0035 (0.0028)
	NS	0.0121 (0.0061)	0.0174 (0.0069)	0.0036 (0.0012)
	NC	0.0124 (0.0053)	0.0139 (0.0088)	0.0032 (0.0054)
Quarter-sawn	Control	0.0042 (0.0023)	0.0191 (0.0092)	0.0195 (0.0084)
	NS	0.0074 (0.0021)	0.0196 (0.0102)	0.0142 (0.0091)
	NC	0.0052 (0.0013)	0.0152 (0.0096)	0.0153 (0.0103)

*standard deviation

Cluster analysis of the six treatments of 25-mm-boards based on the four criteria measured in the present study (drying rate above FSP, drying rate below FSP, MC gradient slope, and drying stress) showed that quarter-sawn (QS) nanosilver-impregnated boards were closely clustered with flat-sawn (FS) control boards (Fig. 2). This may indicate the potentiality of silver nanoparticles in improving the drying conditions of QS boards. However, QS-NC-impregnated specimens are clustered closely to QS-control specimens. As to the less heat conductivity of copper in comparison to silver, it may be concluded that copper nanoparticles did not have the potentiality in improving the drying conditions of QS-boards to be clustered to FS-boards in 25-mm thickness.

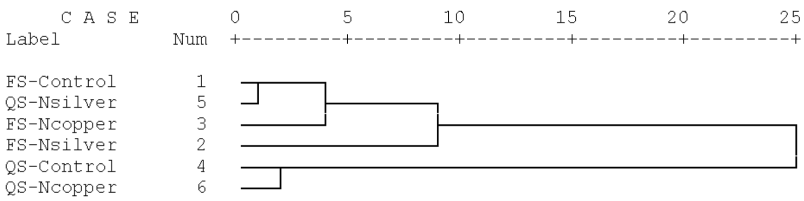

Fig. 2. Cluster analysis of 25-mm-boards based on drying rate above FSP, drying rate below FSP, MC gradient slope, and drying stress (FS=Flat-sawn; QS=Quarter-sawn)

In 50-mm-boards, the same overall increase in drying conditions is seen (Fig. 3); that is, QS-NS-boards are clustered with FS-control specimens, and also QS-NC-boards are clustered with QS-Control boards.

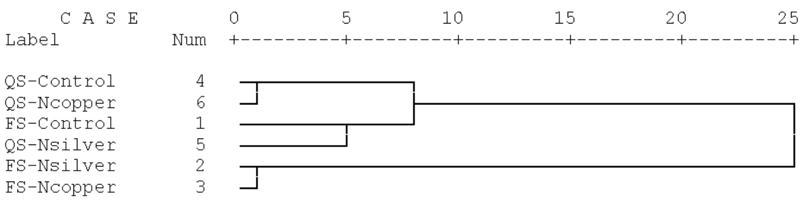

Fig. 3. Cluster analysis of 50-mm-boards based on drying rate above FSP, drying rate below FSP, MC gradient slope, and drying stress (FS=Flat-sawn; QS=Quarter-sawn)

In 75-mm boards (Fig. 4), QS-NS and NC boards are clustered rather differently with QS-control specimens; but not much dissimilarity is seen in FS-treatments. This may show that the effect of nanometals may be more significant in quarter-sawn boards.

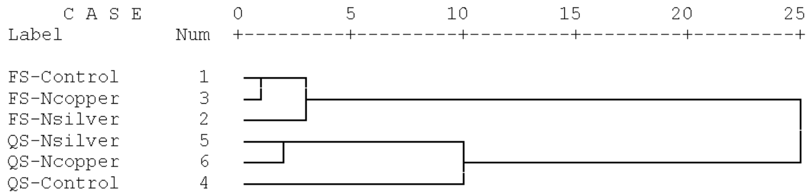

Fig. 4. Cluster analysis of 75-mm-boards based on drying rate above FSP, drying rate below FSP, MC gradient slope, and drying stress (FS=Flat-sawn; QS=Quarter-sawn)

4. Conclusions

The obtained results revealed that silver and copper nanoparticles, due to their high thermal conductivity coefficients, lead to more speedy transfer of ambient temperature of kiln to the board's inner parts and consequently to the improvement of wood drying process. Impregnation with nanosilver and nanocopper resulted in the increased drying rate of boards within free water and bound water range. Perhaps, the high thermal conductivity of the nanoparticles has led to an increase in the temperature of the inner layers of the impregnated boards, resulting in the reduction of MC gradient slope. Furthermore, the decrease in MC gradient slope led to the reduced internal stresses in the dried boards. In general, the decrease in MC gradient slope and internal stresses had positive effects and improved the quality of the dried boards. It may then be concluded that silver and copper nanoparticles may have the potentiality in improving the drying quality in convective wood-drying kilns.

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