THE POTENTIAL USE OF ORGANOSILANE WATER SOLUBLE NANOMATERIALS AS WATER VAPOR DIFFUSION RETARDERS FOR WOOD

Hadi Gholamiyan[1], Asghar Tarmian[1♠], Kazem Doost Hosseini[1], Mohammad Azadfallah[1]

ABSTRACT

The retarding effect of organosilane water soluble nanomaterials (nano-zycosil and nano-zycofil) on water vapor diffusion through poplar wood (*P.nigra*) was evaluated in comparison with that of clear coatings (sealer and nitrocellulose lacquer and polyester lacquer) using cup and sorption methods. Two drying methods were applied to dry the nanomaterials -coated substrates: oven drying at temperature of 103 ± 2 ˚C for 24 h. and climatically drying at temperature of 25 ˚C and relative humidity of 65% for 20 minutes. The results showed that both coating materials decreased the water vapor diffusion rate through the wood. The sealer and nitrocellulose lacquer coating represented a stronger effect on the diffusion coefficient of wood compared to the other coatings. In this case, the nano-zycosil represented a better performance compared to the nano-zycofil. Furthermore, the drying method of the nanomaterials -coated substrates can impact the nanomaterials performance. The water vapor diffusion through the oven-dried substrates was faster than that through the climatically dried ones.

Keywords: Clear coating, nanomaterials, poplar wood, retarding effect, water vapor diffusion

INTRODUCTION

The study of moisture diffusion through wood is of great importance for many wood processing applications, such as drying, preservation, impregnation, moisture transfer through building wall systems, and packaging. Wood, as a hygroscopic material containing hydroxyl groups, is sensitive to humidity and temperature fluctuations in terms of moisture sorption. The surface checks develop due to moisture sorption stresses can enhance the weathering process of wood. Moisture diffusion into and out of wood can occur in response to a moisture gradient. In addition to the moisture sorption, water vapor diffusivity through wood increases its weathering process. The mass diffusivity refers to the ability of a porous medium to allow diffusion flow under a concentration gradient. Considerable research has been conducted relative to the moisture diffusion in porous media, proving the importance of this type of mass transfer (Nefzi and Jouini 2004, Zhelezny and Shapiro 2006, Nakashima and Kamiya 2010). Moisture diffusion in wood is governed by the vapor diffusion through the cell lumens and bound water diffusion through the cell wall. Many research efforts have been conducted to measure the diffusivity properties of wood by two main methods: the steady-state cup method and unsteady-state sorption method (Fick 1855, Martley 1926, Ping and Lianbai 2003, Burch *et al.* 1992, Absetz *et al.* 1993, Pang 1997, Mouchot and Zoulalian 2002).

Wood modification can be applied to alter its mass diffusivity properties. The modification can involve thermal modification (Rousset *et al.* 2004), surface coating (Cerny *et al.* 1996) and chemical

[1]Department of Wood and Paper Science & Technology, Faculty of Natural Resources, University of Tehran, Karaj, Iran, P.O.BOX 1585-4314
[♠]Corresponding author: tarmian@ut.ac.ir
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modification (Giorgi *et al.* 2009). Among the modification methods, surface coating is widely used to reduce the mass diffusivity through wood (Gholamiyan *et al.* 2010). The surface coating is basically used to improve the ultra violet (UV) stability of wood (Pai *et al.* 2008, Yu *et al.* 2007), to reduce water uptake (Grelier *et al.* 2007, Van *et al.* 2007), and to increase its attractive appearance. The measuring of diffusivity properties of a coated substrate can be useful to evaluate its water repellency. Gholamiyan *et al.* (2011) evaluated the water-proofing character of different coating materials by various methods.

Nanotechnology was one of the major fields of discovery of the twentieth century. Interest in nanotechnology and nanomaterials is stimulated by the fact that they demonstrate unique properties because of their small size and high surface to volume ratio. The potential use of nanomaterials for products based on natural materials, such as wood, has been investigated. The properties of wood and wood-based materials can be modified by the aid of nanotechnology (Lowry *et al.* 2008, Kaygin and Akgun 2009, Ashori and Nourbakhsh 2009, Lei *et al.* 2008). For example, the water absorption of wood can be modified through reinforcing of surface coating materials with nanoparticles (Gholamiyan *et al.* 2011). Giorgi *et al.* (2009) pointed out that the steaming of wood surface with nano-NAOH particles results in a substantial reduction in its gas and vapor diffusivity. This study is aimed at investigating the potential use of organosilane water soluble nanomaterials (nano-zycosil and nano-zycofil) as water vapor diffusion retarders for wood.

MATERIALS AND METHODS

Sampling

Poplar wood (*Populus nigra*) from a forest near Taleghan in Iran was selected for the study. A tree with approximately 30 years of growth was felled. Several boards measuring 70 by 200 by 50 mm (T, R and L respectively) were cut. The average initial moisture content of the boards was 120%. The boards were conventionally dried in a laboratory kiln at a constant dry-bulb T of 60 ºC and RH of 40% to the final moisture content of about 12%. Then, cylindrical specimens with 18 mm in diameter were drilled in longitudinal direction. The thickness of specimens was 7 and 3 mm in longitudinal direction for the cup and sorption experiments, respectively. The diagram of sample preparation is illustrated in Fig. 1.

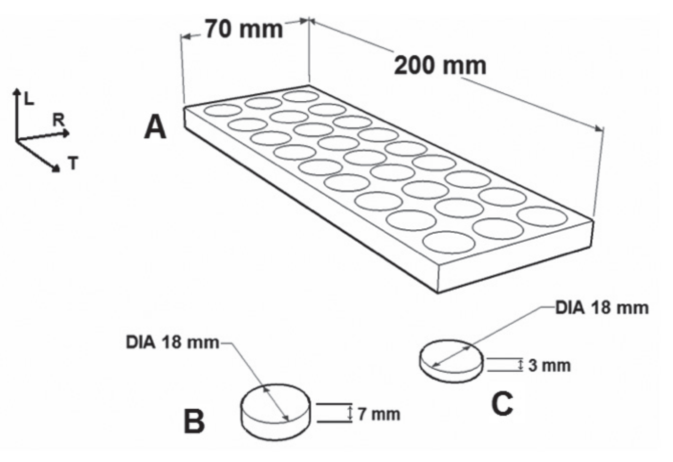

Figure 1. The diagram of sample preparation (A: A cross-cut board, B: cylindrical specimen for measuring diffusion coefficient with cup method, C: cylindrical specimen for measuring diffusion coefficient with sorption method) Coating materials

Sealer and nitrocellulose lacquer and polyester lacquer, which are commonly used in the wood furniture industry, were used as clear coatings. They were purchased from Dorsa Chemistry (Brilliant) Co. Nano-zycosil and nano-zycofil, which are organosilane water soluble nanomaterials, were purchased from Zydex Company. These nanomaterials have been mainly developed for waterproofing. For concrete, Nano-zycofilwith the size of 10-20 nm can enhance the waterproofing property of nano-zycosil treated surfaces by filling microcrackes and nano pores. However, based on some pre-testes conducted for wood in the present study, no enhancing effect was observed; thus, the mentioned nano-materials were applied, separately. The critical properties of nano-zycosil are summarized in table 1.

Table 1. Critical information of the employed nano-zycosil

Size	4-6 Nanometer
Color	Yellow
Density	1.7 (g/cm^3)(25°C)
Fire point	More than 100°C

Coating methods

First, the surface of samples was coated by epoxy resin to confine the water vapor diffusivity through the longitudinal direction. Then, one of the end sections was coated by the coating materials. After that, some nanomaterials-coated samples were oven dried at temperature of 103 ± 2 °C for 24 hrs, and the others were dried into a conditioning room (T = 25 °C and RH=65%) for about 20 minutes. All samples coated by the clear coatings were climatically dried inside the conditioning room. Table 2 shows the treatments. The sealer and nitrocellulose lacquer diluted by a lacquer thinner (1:2) were applied on the clear wood surfaces by brushing method. The clear polyester lacquer diluted by the lacquer thinner (1:2) and mixed by 10% catalyst (hardener) was brushed on the wood surfaces. Also, the nano-particles were applied on the surfaces by brushing. The mean coating weight for all treatments was 0.004 g/cm^2.

Table 2. Guide for treatments

Treatment code	Treatment
Control	None
CZ	nano-zycosil, coating conditioned
CZ Dry	nano-zycosil, oven dried
CZF	nano-zycofil, coating conditioned
CZF Dry	nano-zycofil, oven dried
CPS	polyester
CSC	sealer+ nitrocellulose lacquer+ polyester lacquer

Diffusion Coefficient Measurements

Cup method

The water vapor diffusivity of wood samples was measured under the steady-state condition (Agoua *et. al*. 2001; Avramidis 2007). Several cups were filled with a NaCl solution, providing a RH of 75%. The cups with attached 7 mm-thick samples were then placed in a conditioning chamber (RH=60%, T=20°C). The cups were weighed every 24 h until a constant weight was reached. After 21 days, when a steady-state condition was reached, the cup weight loss was plotted against the time. In fact, the steady-state condition was determined by the daily measurements of the cup weight. The dimensionless diffusion coefficient through the wood samples was calculated from equation 1 (Agoua *et al*. 2001)

$$q = -\rho_g D_{eff} \nabla \left[\frac{\rho_v}{\rho_g} \right] = -\rho_g f D_v \nabla \left[\frac{\rho_v}{\rho_g} \right] \cong -f D_v \nabla \left(\rho_v \right) \quad (1)$$

where q is water vapor flux through the wood sample (kg.s^{-1}m^{-2}), ρ_g is air density (kg.m^{-3}), ρ_v is water vapor density (kg.m^{-3}), D_{eff} is the effective diffusion coefficient of wood (m^{2}s-^{1}). In order to be more explicit, a dimensionless coefficient f was introduced (Agoua *et al*. 2001), which represents the ratio of mass diffusivity in the porous medium over what would have been obtained in a sample of air at rest. f is defined by the relation D_{eff} where D_v is the binary diffusion coefficient of vapor in air. D_v is calculated from equation 2:

$$D_v = 2.26 \times 10^{-5} \cdot \left(T \;/\; 273 \right)^{1.81} \cdot P_{atm} \;/\; P \quad (2)$$

Where T is temperature (K) and P is pressure. For a very diffusive material such as glass fibers of very low density, f is close to the unit whereas the f value of an impervious material equals zero. The dimensionless diffusivity f is calculated by the formula 3 (Agoua *et al*. 2001):

$$f = \frac{Q}{D_v A} \frac{l}{\left(RH_2 - RH_1 \right) P_{vs}(T)} \frac{RT}{M_v} \quad (3)$$

where Q is the measured mass flux (kg.s^{-1}), A is the cross section of sample (m^2), M_v is the molar weight of vapor (kg.mole^{-1}), RH_1 is the relative humidity inside the climatic chamber, RH_2 is the relative humidity inside the cup, R is the constant of perfect gas, l is the sample thickness (m), P_{vs} is the pressure of saturated water vapor in temperature of $T(K)$, and D_v is the water vapor diffusion coefficient in air.

Sorption method

For unsteady-state measurement of diffusion coefficient, using the sorption method, 3 mm-thick samples were first equilibrated at an initial RH of 20% in a conditioning chamber. Then, the relative humidity of the chamber was changed to the new RHs, 40, 60, and 80%, respectively. The temperature of conditioning chamber was kept at 30 ºC. The weight change of samples was monitored to the nearest 0.001 g at regular intervals. The dimensionless change of sample moisture content at equilibrium was plotted as a function of the square root of time. The diffusion coefficient was calculated from the initial linear part of the sorption curve using the following equations (Avramidis 2007) (Fig. 2):

$$X^* = \frac{X(t) - X_i}{X_e - X_i} \tag{4}$$

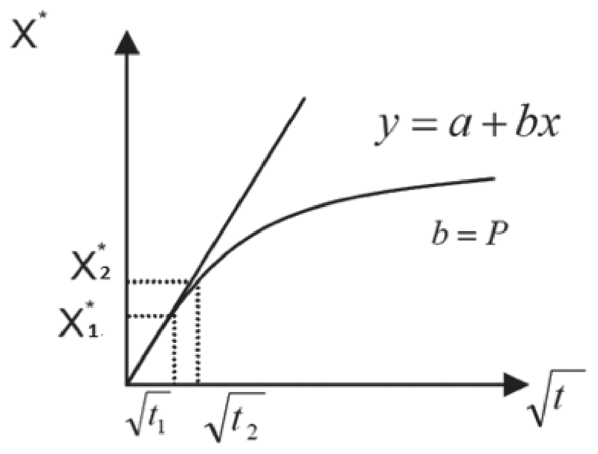

Figure 2. A sorption curve (moisture content vs. square root of time)

where X* is dimensionless moisture content, X*i* is initial moisture content, X*e* is final moisture content, and X*(t)* is the wood moisture content at the time of *t.* is normalized curve slope that can be calculated from equation 5:

$$P = \frac{x^*2 - x^*1}{\sqrt{t2} - \sqrt{t1}} \tag{5}$$

Then, the diffusion coefficient can be calculated from equation 6:

$$D_c = \frac{\pi \times P^2 \times l^2}{16} \tag{6}$$

Where *Dc* is the diffusion coefficient ($m^2.s^{-1}$) and *l* is sample thickness (m). Five replications were considered for each treatment to measure diffusion coefficient.

Statistical analysis

The statistical analysis was conducted using SPSS software. Analysis of variance (ANOVA) was sued to test for significant differences between means. Duncan's Test at the 95% confidence level was also applied to statically compare the mean values.

RESULTS AND DISCUSSION

Diffusion Coefficient Measured by Cup Method

The diffusion coefficients obtained for control specimens were greater than those obtained for all coated specimens, i.e., the clear coating and nanoparticles had a positive effect to decrease the water vapor diffusivity (Table 3). The diffusion coefficient of specimens ranged from 66.13×10^{-9} m^2 s^{-1} for sealer and nitrocellulose lacquer-coated specimen to 93.71×10^{-9} m^2 s^{-1} for uncoated (control) specimen. The D Uncoated sample / D Coated sample ratio ranged from 1.02 for sample coated by nanozycofil and oven dried (CZ dry) to 1.42 for sealer and nitrocellulose lacquer-coated sample (CSC). The sealer and nitrocellulose lacquer coating represented a stronger effect on the diffusion coefficient of wood compared to the other coatings and nano-particles. Nevertheless, the mean coating weight is the same for the other coating and nano particles. This may be due to rigid film formation on the wood surface (Gholamiyan *et al.* 2011). Cerny *et al.* (1996) also found different degrees of waterproofing for various coating materials. Based on diffusion modeling from simulated porous structures, Laudone *et al.* (2008) pointed out that the diffusion rate is small for tiny porous media. The nanozycosil-coated specimen had a higher resistance to water vapor diffusion than the nanozycofil-coated one, resulting from special properties of each nano-particle. The smaller size of nano-zycosil particles (4-6 nm) compared to nano-zycofil (10-20 nm) particles may play an important role in better reaction of the particles with OH groups of wood. Diffusion through the oven-dried specimens was faster than that through the climatically dried ones. This is probably attributed to crack formation in the coating nanomaterials (Oosterbroek *et al.* 1991).

Table 3. Diffusion coefficients measured by cup method

Treatment code	Specific gravity g/cm^3	SD*	Dimensionless diffusion coefficient (f) (10^{-3})	SD (10^{-8})	Diffusion coefficient $D\times10^9$ m^2 s^{-1}	Grouping by Duncan test
CSC	0.382	0.003	4.13	0.39	66.13	a**
CPS	0.381	0.0028	5.10	0.66	81.55	b
CZ	0.382	0.0041	5.23	0.17	83.76	b
CZ dry	0.382	0.002	5.84	0.15	93.41	c
CZF	0.381	0.0033	5.72	0.20	91.53	c
CZF dry	0.382	0.0022	5.77	0.22	92.29	c
control sample	0.382	0.0025	5.86	0.07	93.71	c

* Standard deviation
**a, b and c indicate the grouping by Duncan test ($p<0.05$). The values with the same alphabet have no difference between their means.

Diffusion Coefficient Measured by Sorption Method

Figure 3 shows dimensionless weight change of samples versus the square root of time. The same trend of mass variation against RH-steps was observed for all coated and uncoated specimens. The water vapor diffusivities calculated from absorption cycle are presented in table 4. Similar to what was obtained from the cup method, the diffusion coefficient for all coated- specimens were lower than that for uncoated specimens. The sealer and nitrocellulose lacquer coating had a dominant effect on the mass diffusivity behavior of wood. The measured diffusion coefficient was in the range of 0.9×10^{-9} to 3.05×10^{-9} m^2 s^{-1}. In the RH-step of 20-40%, the $D_{Uncoated\ sample}$ / $D_{\text{Coated sample}}$ ratio ranged from 1.12 for the sample coated by nano-zycofil and oven dried (CZ dry) to 3.35 for the sealer and nitrocellulose lacquer-coated sample (CSC). For the RH-step of 40-60%, the ratio was in the range of 0.97-2.84 for the mentioned coated samples, respectively and similarly, for the RH-step of 60-80%, it ranged from 0.89 to 2.31. Indeed, the $D_{\text{Uncoated sample}}$ / $D_{\text{Coated sample}}$ ratio was lower when the sorption measurements made with a higher RH-step. As expected, the mass diffusivities measured by the two techniques for the same specimen did not coincide numerically. It can be interesting that there is a significant difference between the diffusion coefficients obtained by the cup and sorption methods. In addition, the $D_{\text{Uncoated sample}}$ / $D_{\text{Coatedsample}}$ ratio obtained in steady-state condition and transient sorption was different. Overall, a higher ratio was observed for sorption measurements. Furthermore, the sorption measurements made with the higher RH-steps resulted in lower diffusion coefficient. Houngan *et al.* (2006) also reported the same result for longitudinal and tangential diffusion coefficient of beech (*Fagus sylvatica*) wood calculated by the sorption method.

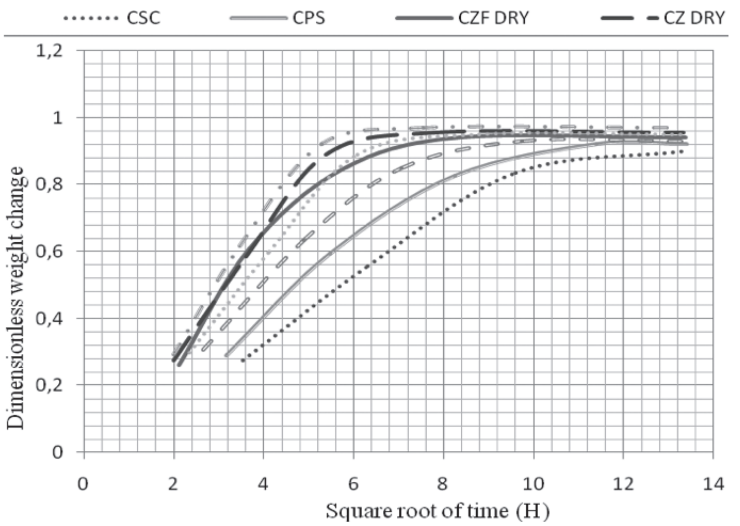

Fig. 3. Dimensionless weight change of samples versus the square root of time in sorption method

Table 4. Diffusion coefficients measured by sorption method

Treatment code	RH (%)		
	20-40	40-60	60-80
	Diffusion coefficient $D \times 10^9$ m^2 s^{-1}		
CSC	0.91	0.90	0.90
CPS	1.31	1.21	1.11
CZ	1.72	1.51	1.41
CZ dry	2.71	2.63	2.32
CZF	2.29	2.21	1.58
CZF dry	2.11	1.95	1.91
Control sample	3.05	2.56	2.08

CONCLUSION

The present study evaluated the potential use of nanotechnology in addition to clear coatings to modify the mass diffusivity properties of wood. The surface coating of wood by both clear coatings (sealer and nitrocellulose lacquers and polyester lacquer) and nanoparticles (nano-zycosil and nano-zycofil) can reduce the rate of water vapor diffusivity through the wood. Among all coating materials and nanoparticles used in this study, sealer and mitrocellulose lacquer had a pronounced effect on the mass diffusion coefficient of wood. In this case, the nano-zycosil represented a better performance compared to the nano-zycofil. Although both nano-zycosil and nano-zycofil particles were found to be effective nano-particles in decreasing water vapor diffusivity through wood, attention should be focused on the coating condition and drying method of coated substrate. Our study showed that the drying method of the nanoparticles-coated substrate can impact the nanoparticles performance. The potential effect of other nano-particles on the moisture diffusivity of the surface coated wood is recommended for further work.

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