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THE EFFECT OF NANOCLAY ON THE MASS TRANSFER PROPERTIES OF PLYWOOD

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Effects of nanoclay as a filler was investigated in plywood in the present study. 15 plywood boards of 350 × 350 × 6 mm were made of hornbeam wood layers, using urea-formaldehyde (UF) resin. Clay nanoparticles were used at two levels of 3 and 5%; hot press time was also studied at two levels of 4 and 5 minutes. Mass transfer and gas permeability coefficients, as well as thickness swelling, were then measured. Results showed that moisture diffusion coefficient was significantly decreased with the increase in filler content. However, gas permeability was not significantly changed. Increase in press time caused better resin curing in the inner layers of the boards, resulting in reduction in permeability. Due to the hydrophobic property of clay nanoparticles, increase in the level of consumption of filler resulted in reduction in thickness swelling and diffusion coefficient.

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1. Introduction

Wood is frequently modified by engineering processes to give stiffness or homogeneous mechanical properties because few species offer radial and axial uniformity in their produced wood (Ajala & Ogunsanwo 2011); furthermore, the quality of wood would be affected by rotation period, mono- or mixed-species cultivation, light and soil, as well as interaction between clone-type and site (Oke, 2012; Addo-Danso, 2012; Girma & Mosandl, 2012; Jans et al.; 2012; Luo et al.; 2012). Composite-boards, however, offer the advantages of a homogeneous structure and the use of raw materials without restrictions as to the shape and size (Grace, 2005; Uetimane & Ali 2011). In this connection, the majority of humans world-wide depend upon wood products harvested from forests (Dykstra 2012); therefore, efficient use of wood is highly important. Nowadays, the use of wooden products particularly layered ones due to their special advantages as against raw wood is noticeably increasing all over the world. Furthermore, many changes in the production process of these products have been taken part with regard to the cost reduction and quality improvement. In the wood layered products manufacturing, for layers joint, mixture of adhesive and fillers is used. So far, many researches with regard to replacing wheat flour fillers by a variety of other materials have been carried out. The usage of nanoparticles as a filler has been recently increasing. With change in combination and structure of materials at nano scale, new materials are obtained which have unique properties. Nano-technology researches, given particles size at nano-scale, have led to development of materials and structures and consequently improvement in physical and chemical properties of materials (Wegner et al. 2005; Wegner and Jones, 2006). Nano-particles have a high specific surface so nanoparticles are equally distributed

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in adhesive. In this research, the effect of nanoclay as a filler on fluid transfer properties in plywood is investigated. As regards, there is little research concerning the effect of nanoclay on moisture transfer processes in the plywood. In a research conducted by Lei et al. (2008) showed that adding nanoclay NaMMT to urea-formaldehyde resin enhances water resistance in plywood. Doosthoseini and Zarea-Hosseinabadi (2010) mentioned that the usage of nanoclay at 5% level in UF and melamine-urea formaldehyde (MUF) resins for production of plywood improves its physical and mechanical properties. Moisture permeability and diffusion in wood and wood products are crucial factors for prediction of their performance in service conditions. Permeability degree of wooden composite panels is related to protection of wood products (Muin et al. 2003) and also adsorption and desorption of them (Beldi and Szabo, 1986; Sekino, 1994). Permeability has a great impact on the moisture and heat transfer processes during hot pressing (Zombori et al. 2003; Dai and Yu, 2004). A lot of researches have been carried out to investigate the fluid transfer characteristics (Sorz and Hietz, 2006; Straze and Gorisek, 2006; Tarmian and Perre, 2009). Moisture diffusion model based on Fick second law failed in evaluate moisture adsorption process in fiberboard and also fiber and polymer composites (Shi, 2007). In a study on the effect of nanoclay in epoxy resin, it was shown that presence of nanoparticles in composite reduces gas permeability compared to pure resin (Miller and Meador, 2007). In another research, the effect of nanoclay on gas permeability in nano-composite polypropylene was investigated (Pannirselvam et al. 2008). The results showed that gas permeability was reduced with increase of nanoclay. Ogasawara et al. (2006) in study of helium permeability on epoxy and nanoclay composite showed that presence of nanoparticles reduces permeability. Zhang and Smith (2010) in study of permeability of Oriented Strand Boards (OSB) found that nanoclay has not much effect on the permeability compared to control specimens. High correlation was also reported between gas and liquid permeability of nanosilver-impregnated solid wood specimens (Taghiyari, 2012).

2. Materials and methods

2.1Veneer preparation

Hornbeam veneers with the thickness of 2 mm were used for manufacturing of plywood. After cutting them to the dimensions of 50×50 cm, for equalizing moisture, they were dried in laboratory oven at 103ºC up to the humidity of 3%.

2.2 Nanoclay filler preparation

The nanoclay used in this study was of Sodium montmorillonite (MMTNa) type produced by Iran's Persian Gulf Trade Company. According to the provided information by the producer company, the amount of its montmorillonite was between 95-98%. Its specifications are presented in Table (1).

Table 1. Montmorillonite physicochemical properties

Moisture content (%)	Average lamellar thickness	Density (g/cm^3)	Appearance	Color
Less than 3	Less than 5.3	89.1	Fine Powder	Milk white

2.3 Adhesive and layer gluing

UF resin was procured from Iranian Tiran Shimi Co. Features of this adhesive which has provided by the producer company are presented in table (2). In addition, chloride ammonium (1% of resin dry weight) was used as the hardener of UF resin. The amount of UF resin that was used for making of boards was 120 g/m^2.

Table 2. urea–formaldehyde (UF) Resin properties.

Gel time (s)	PH	Free formaldehyde (%)	Specific gravity (g/cm3)	viscosity (CP)	Solid content (%)
58	8.7	2.2	250.1	370	58

2.4 Variable factors

Given the preliminary test, the amount of nanoclay was selected at three levels of 0, 3 and 5%. Furthermore, 4 and 5 minutes press time was considered for construction of boards. In the control treatment boards, wheat flour was used as filler by 40% of resin dry weight.

2.5 Preparation and pressing

Layers gluing was conducted by observing equal glue diffusion over their surface and the layers were pressed after assembling. The press required temperature was 160ºC that it was constant for all the boards. The boards, for moisture equalization and also for balancing internal stresses, were kept under laboratorial condition for two weeks. Subsequently, after side-cutting and cutting of boards, the samples were transferred to a climatic chamber of 65% relative humidity (RH) and 20ºC temperature.

2.6 Water absorption and thickness swelling

Water absorption and thickness swelling was carried out using 100×100mm samples. Their amounts were measured at two different times of 2 and 24 hours according to ISO16983.

2.7 Gas Permeability Measurement

Longitudinal gas permeability measurement was carried out by an apparatus designed and built by the author (Taghiyari, 2011c; Taghiyari and Efhami, 2011; Taghiyari et al., 2012b) (Fig. 1) equipped with automatic-time-measurement device with milli-second precision. Falling-water volume-displacement method was used to calculate specific longitudinal gas permeability values based on the microstructure porosity of wood (Siau 1971, Taghiyari et al. 2010). 5 specimens were randomly cut at scattered locations from the boards of each treatment by a hole-saw. Diameter of specimens was 18 mm. For each specimen, gas permeability values were measured at 7 different water-column heights, that is 7 different vacuum pressures, in a single run. Internal diameter of the glass tube was 13 mm. Water level was 15 cm above the starting sensor of the first time-measurement device (Gas 1). Connection between the specimen and holder was made fully air-tight. A pressure gauge with milli-bar precision was connected to the whole structure to monitor pressure gradient (ΔP) and vacuum pressure at any particular time as well as height of water column. Vacuum pressures at starting and stopping points for each of the 7 different heights are listed in Table 1.

Three measurements were taken for each specimen. Superficial permeability coefficient was then calculated using Siau's equations (Siau, 1995) (equations 1 and 2). The superficial permeability coefficients were then multiplied by the viscosity of air (μ=1.81×10^{-5} Pa s) for the calculation of the specific permeability ($K=k_g\,\mu$).

$$k_g = \frac{V_d CL(P_{atm} - 0.074\bar{z})}{tA(0.074\bar{z})(P_{atm} - 0.037\bar{z})} \times \frac{0.760mHg}{1.013\times 10^6 Pa} \quad (1)$$

$$C = 1 + \frac{V_r(0.074\Delta z)}{V_d(P_{atm} - 0.074\bar{z})} \quad (2)$$

***Where*:**
k_g = longitudinal specific permeability (m^3 m^{-1})
$V_d = \pi r^2 \Delta z$ [r = radius of measuring tube (m)] (m^3)
C = correction factor for gas expansion as a result of change in static head and viscosity of water.
L = length of wood specimen (m)
P_{atm} = atmospheric pressure (m Hg)
$\bar{z}$ = average height of water over surface of reservoir during period of measurement (m)
t = time (s)
A = cross-sectional area of wood specimen (m^2)
Δz = change in height of water during time t (m)
V_r = total volume of apparatus above point 1 (including volume of hoses) (m^3)

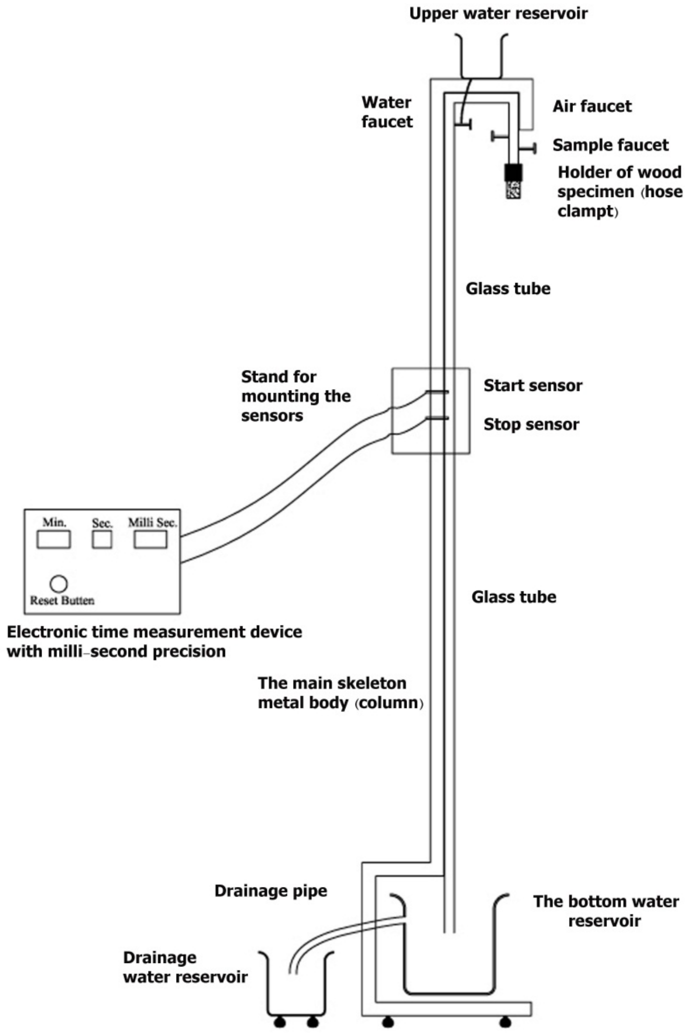

Fig. 1. The overview of the gas permeability apparatus (USPTO No. 8,079,249 B2; Pub. No. 2010/0281951 A1) equipped with single-storey milli-second precision electronic time measurement device (Taghiyari, 2011c; Taghiyari, 2012; Taghiyari et al., 2012b)

2.8 Moisture diffusion coefficient

The moisture diffusion coefficient was evaluated on the same specimens after the air permeability test. The cup method was used to measure the diffusion coefficient. The sample support comprises a 60-mm-long glass pipe and a 40-mm-long PVC pipe with external diameter of 22 mm. A rubber tube was applied between the PVC pipe and the wood sample. Thanks to a hole drilled in the PVC tube, partial vacuum may be applied for the rubber joint to temporarily stick to the internal part of the PVC tube to place the sample inside the cup without any damage to the rubber tube. The epoxy resin on the lateral face of the sample reduces strongly the roughness of this face and allows an air-tightness assembly of the sample and the cup along the rubber tube. Silicone-based grease (vacuum grease) was applied on the lateral surfaces of the specimen to avoid any flow in the microporosity layer formed between the sample and rubber surface. The saturated salt solution of sodium chloride (NaCl) was used to control the relative humidity inside the cup at about 75%. After preparation of the cups, they were placed inside a climatic chamber of 61% RH. Water vapor diffuses from inside the cup with a higher RH_1 (75%) to outside with a lower RH_2 (61%). In fact, a low RH difference was applied to reduce the MC gradient inside the sample. This precaution limits the sample warp due to differential shrinkage which could lead to measurement errors. The cups were weighed every 24 h until a constant weight was reached. Measurement of diffusion coefficient in cup method is done under stable condition.

$$f = \frac{Q}{\mathrm{D_{\nu}A}} \times \frac{L}{(\mathrm{RH_2} \times \mathrm{RH_1}) Pvs(T)} \times \frac{RT}{\mathrm{M}v} \tag{3}$$

The dimensionless diffusivity (f) is calculated according to the above formula: where Q is the measured mass flux (kg s^{-1}), A is the cross section of the sample (m^2), Mv 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), Pvs is the pressure of saturated water vapor at a temperature of T (K), and Dv is the binary diffusion coefficient of water vapor in air.

3. Results and discussion

3.1 Effect of nanoclay on diffusion coefficient

In Table (3), the value of diffusion coefficient in the five treatments is presented. Statistical analysis showed that at 99% probability, there is a significant difference between nanoclay and control treatments. Surprisingly, by adding nanoclay, a significant reduction in diffusion coefficient compared to the control treatment took place. Consequently, nanoclay enhances plywood resistance against moisture. In fact, hydrophobic property of nanoclay results in improvement of resistance against moisture (Low et al. 2004). The value of diffusion coefficient was among 0.003 to 0.006 m^2/s. Minimum amount of diffusion coefficient was observed in press time of 4 minutes. With increase of nanoclay from 3% to 5%, diffusion coefficient at both press times increased. Value of diffusion coefficient in control treatment decreased about 50% as against nanoclay treatments. Increase of press time from 4 to 5 minutes in nanoclay treatments has led to increase of diffusion coefficient. Given that clay nanoparticles were injected inside the adhesive, dispersion of glue into wood tissue will cause that clay nano-particles disperse into wood texture as a consequence and prevent moisture adsorption by wood cell walls. On the other hand, given that clay particles are at nano scale and this surface increase, created by nanoclay in UF resin, leads to better linkage of the resin with wood fibers and eventually decrease of diffusion coefficient.

3.2 Effect of nanoclay on permeability coefficient

Although the mean values of nanoclay treatments were increased by adding nanoclay, statistical analysis showed no significant difference between nanoclay and control treatments at the 99% level of confidence (Table 3). Results suggest that press time had significant effect on permeability coefficient of nanoclay treatments. Increased press time leads to the increase of temperature degree in inner parts of board and resin consequently will cure completely (Lehman, 1972). Similar heat-transferring property was reported when using silver nanoparticles in particleboard and solid woods (Taghiyari et al., 2011c; Taghiyari, 2011a,b,c; Taghiyari et al. 2012a). In researches that has been done on the effect of nano-clay on diffusion coefficient, varying results have been obtained. Results obtained by Ogasawara et al. (2006) show that by adding nano-clay in epoxy resin, permeability degree decreases. Zhang and Smith (2010) indicated that clay nanoparticles have not caused any special changes in permeability degree of OSL boards. Also results by Zahedsheijani et al. (2011) demonstrated that with increase of nanoclay amount in UF resin, permeability coefficient of fiberboard decreases.

Table 3. Results of nanoclay content and press time on the diffusion and permeability coefficients

Press time	4 minutes			5 minutes	
Nanoclay content	0%	3%	5%	3%	5%
Diffusion coefficient (10^{-3} m^2/s)	6.1	3	3.8	3.2	4.2
Permeability coefficient (10^{-6} m^2)	3.8	12.6	11.8	7.7	5.8

3.3 Effect of nanoclay on thickness swelling

In Table (4), values of diffusion coefficient and thickness swelling are compared. Results show that with increase of nanoclay in plywood, the amount of thickness swelling has decreased at the correspond times of 2 and 24 hours. Doosthoseini and Zarea-Hosseinabadi (2010) pointed out that with increase of the amount of nano-clay in plywood, the value of thickness swelling and water adsorption have decreased. Furthermore, Cai et al. (2007) reported that the use of nanoclay resulted in increased resistance against moisture adsorption. They used MUF resin in their research and amount of water adsorption in 24 hours by adding nanoclay decreased from 38.5% to 22%. With increase of nano-clay, the amount of diffusion coefficient and thickness swelling decreased. Hydrophobic property of nanoclay particles has made moisture transmission in plywood difficult. On the other hand, usage of nanoclay has improved adhesion property of the resin with wood fibers.

Table 4. Changes in diffusion coefficient compared to thickness swelling in 2 and 24-hour immersions.

Press time	4 minutes			5 minutes	
Nanoclay content	0%	3%	5%	3%	5%
Diffusion coefficient (10^{-3} m^2/s)	6.1	3	3.8	3.2	4.2
Thickness swelling after 2- hour (%)	6.53	4.51	3.92	4.94	4.47
Thickness swelling after 24-hour (%)	8.57	6.29	7.08	5.95	8.04

4. Conclusion

Results showed that the increase in clay nanoparticles, diffusion coefficient significantly decreases. Hydrophobic property of nanoclay particles leads to increased moisture resistance in plywood. Higher specific surface of nano-clay particles has improved UF resin diffusion in wood layers and adhesion quality. On the other hand, results indicated that nanoclay particles didn't have much effect on the permeability coefficient. Increased press time in nano treatments due to improvement of UF resin curing in inner parts of the boards resulted in the decreased permeability coefficient. Moreover, results showed that increase of nanoclay in plywood has led to reduced thickness swelling. Given the diffusion coefficient is under influence of fibers' hydrophilic property, with the increase in nanoclay consumption level, resistance against moisture increased and amount of diffusion coefficient and thickness swelling noticeably decreased.

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