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Effects of fungal exposure on air and liquid permeability of nanosilver- and nanozincoxide-impregnated *Paulownia* wood

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ABSTRACT

Effects of aqueous dispersion of silver and zinc-oxide nano-particles on air and liquid permeability of *Paulownia* wood exposed to *Trametes versicolor* were studied in the present research project. Specimens were also heat-treated at 100 and 150 °C and compared with the control specimens. Permeability values were measured when the moisture content of the specimens was 12%. Results showed significant increase in air permeability after impregnation with either nanosilver or nanozinc. The increase in permeability was due to the breakage of tyloses under the high pressure in the impregnation vessel. However, significant decreases were observed in permeability in all treatments after the fungal exposure. The decrease was related to the growth and accumulation of hyphae along vessel lumens, blocking the path for fluid transfer. It was concluded that both heat-treatment at 150 °C and the impregnation with zinc-oxide significantly inhibited growth of the fungus, consequently decreasing wood mass loss. High and significant correlations were observed between air and liquid permeability only in specimens that were impregnated with either of the nano-suspensions.

1. Introduction

Different physical and mechanical properties in plants and solid woods are significantly influenced by growth conditions, including climate, chemicals present in the surrounding soil, daylight time, etc. (Mladenov and Pelovski, 2013). One of the decisive physical properties of wood and wood-composites, as porous media, is air and liquid permeability values, which can greatly affect many of their applications, such as impregnation with preservatives, wood drying, their potentiality to absorb glues and paints, etc (Shibata and Hirohashi, 2013; Taghiyari et al., 2014a, b). Existence or lack of significant correlation between air and liquid permeability values would provide an in-depth knowledge of the structural matrix of the porous materials, the likelihood of solids settling in the liquid suspension once they penetrate into wood pieces, liquid bonding with hydroxyl groups of the cell-wall components, etc.; all these data would provide wood-drying, wood preservation, and wood modification industries with a better insight for their decision-making processes.

Thermal modification is considered the most commercially-used wood modification process (Hill, 2006). It is a useful method to dimensionally stabilize wood; and some studies reported that it increases the biological resistance of wood towards different wood-deteriorating fungi (Rapp, 2001; Westin et al., 2006; Brischke et al., 2007; Hill, 2006; Abdolzadeh et al., 2015). Although thermal degradation of the polymers (mostly cellulose and hemi-cellulose) would result in a significant decrease in some of the mechanical properties, newly developed techniques have been reported to mitigate the negative effects of thermal degradation; for example, high thermal conductivity coefficient of metal and mineral nano-materials helped the transfer of heat to the inner parts of specimens, preventing from accumulation of heat on their surface layers and the consequent severe degradation of cell-wall polymers (Awoyemi, 2007; Taghiyari et al., 2013). Degradation of cellulose is predominant at about 270 °C, therefore, thermal modification of solid wood species are generally carried out at temperatures not higher than 220 °C. Lignin is also structurally modified when exposed to high temperatures (Repellin and Guyonnet, 2005).

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The decreased hygroscopicity caused by thermal modification was suggested to be not only due to mass loss, but also irreversible hydrogen bonding in the course of water movements within the pore system of the cell walls (Borrega and Karenlampi, 2010).

In a previous study, the thermal conductivity of nanofluids were significantly enhanced by the dispersion of metallic nanoparticles (Yu et al., 2010; Warrier and Teja, 2011; Li, 2012; Saber et al., 2013). Nanofluids were used to facilitate transfer of heat in solid wood species and wood-composites with very low thermal conductivity (Matsunaga et al., 2007; Akhtari et al., 2013; Taghiyari et al., 2014c). Some of these nanofluids, by transferring heat as well as demonstraging fungicidal properties. The fungicidal property of wollastonite nanofibers significantly improved the biological resistance against wood-deteriorating fungi. Likewise, it has been previously reported by Kartal et al. (2009) that nanoparticles of zinc, silver, and copper oxide impart resistance to *Trametes versicolor.*

Tyloses are outgrowths on parenchyma cells of xylem vessels of secondary heartwood; when some woody plants are stressed by drought or infection, tyloses will detach from the sides of the cells and penetrate the vascular tissue to prevent further damage to the plant. They act as a physical barrier towards the flow in gaseous and liquid fluids, and therefore, they significantly decrease the permeability (Taghiyari et al., 2014a,b). *Paulownia* is a woody species with an intense tyloses system (Ghorbani et al., 2012; Taghiyari et al., 2014a,b). Its low permeability makes impregnation with preservatives difficult because the preservatives cannot easily penetrate into the body of *Paulownia* wood. So, as a wood species vulnerable to fungal attack, finding new methods and techniques to lengthen the service life of this fast-growing wood species would be valuable. Nanosilver and nanozinc oxide successfully improved the biological resistance to a wood-deteriorating fungus (Ghorbani et al., 2012; Akhtari et al., 2013). They are both metal nanoparticles that can also improve the thermal conductivity in solid wood species. The present study was conducted to evaluate the effects of nanosilver and nanozinc oxide impregnation on the air and liquid permeability of *Paulownia* wood exposed to the white-rot decay fungus, *Trametes versicolor.*

2. Materials and methods

2.1. Specimen procurement and preparation

Three *Paulownia fortunei* trees were harvested from Mazandaran Province, located in the Northern part of Iran; the trees were 15 years old. Average densities of the first and last 7 rings were .35 and 0.37 g/cm^3 for the heartwood and sapwood at 12% moisture content, respectively. Average of the tree diameter at breast height was 17 cm. Permeability specimens were cut from disks cut from the breast height of the trees. The disks were conditioned at room temperature for two months. Cylindrical permeability specimens (30 mm long × 17.5 mm Diam.) were cut along the longitudinal direction of the disks. All specimens were free from defects (knots, checks, fissures, rots, or blue stain). A total of 180 specimens were randomly divided into three main groups: control (C), nanosilver-impregnated (NS), and nanozinc oxide-impregnated (NZ) specimens. Sixty specimens of each group were then divided into three subgroups: unheated (U), heated at 100 °C (HT100), and heated at 150 °C (HT150) with each subgroup containing 20 specimens. The cross-sections of the cylindrical specimens were trimmed by a sharp blade to the final length of 30 mm. The outer surrounding surface of the cylindrical specimens were covered with silicon adhesive to ensure the flow of air only in the longitudinal direction of the specimens.

Air permeability is a non-destructive test (NDT). The air permeability values of all specimens were then measured first. After treatment, the liquid permeability values of the control, NS-impregnated, and NZ-impregnated specimens were measured. In all groups and sub-groups, liquid permeability was measured after the specimens were exposed to the fungus. For the specimens that were heat-treated, the air permeability measurement was carried out in three stages: 1- pre heat treatment, 2- heated at 100 or 150 °C, and 3- exposed to the fungus. For nanoparticle-impregnated heat-treated specimens, air permeability measurements were carried out at four stages: 1- pre impregnation and heat treatment, 2 impregnated with nanosilver or nanozinc-oxide, 3- heated at 100 or 150 °C, and 4- exposed to the fungus. After the four stages of non-destructive air permeability measurements were carried out, the liquid permeability values were then measured.

2.2. Aqueous nanoparticle impregnation

Electrochemical technique was used to produce a 400 ppm aqueous dispersion of silver nanoparticles and 5000 ppm zinc-oxide nanoparticles. The size range of nanoparticles in both nanosuspensions was 10–80 nm; the formation and size of nanoparticles were monitored by transmission electron microscopy (TEM). In order to stabilize nanosuspensions, 1% of sodium bis(2-ethylhexyl)sulfoscuccinate (AOT), an anionic surfactant, was added. For the impregnation, the empty-cell process (Rueping) was carried out under 2.5 bar pressure. Empty-cell was used in the present study so that the cell cavities would be void of nanosuspension; this way, nanoparticles would primarily be stuck to the cell walls and the cell cavities would nearly be essentially void of nanoparticles. The impregnation process under pressure forced nanoparticle penetration deep into the specimens for two main purposes: first, heat would be easily transferred into the deepest part of the specimens (Taghiyari et al., 2013), and second, nanoparticles would be least likely to leach from surface water or be physically removed by abrasion. The intent was to make impregnation more environmentally friendly by forcing nanoparticles deep in the specimens, and maintaining a relatively low treatment retention. However, detailed study in this regard should be carried out to come to a firm conclusion. Specimens were weighted before and after the impregnation and retentions were calculated. Treated specimens were conditioned at 25 ± 2 °C, and 40 ± 3% relative humidity for three months. Permeability was measured again before the thermal treatment.

2.3. Air permeability measurement

Falling-water volume-displacement method was used to measure and calculate the specific air permeability (Taghiyari et al., 2014a,b,c) based on the microstructure porosity of wood (Taghiyari and Moradi Malek, 2014). For each treatment, twenty cylindrical specimens were cut with a hole-saw (a hollow-saw); they were cut at scattered locations from the disks to avoid similarity of position. The diameter and length of the specimens were 17.5 and 30 mm, respectively. Air permeability was measured at seven different water-column heights in a single run to provide seven different vacuum pressures for comparison. The vacuum pressure inside the tube of the apparatus was monitored with a milli-bar gauge in order to register the pressure difference (ΔP).

Each specimen was measured three times and the mean value was registered to calculate the superficial permeability coefficient by Siau's Equations (Siau, 1995) (Equations (1) and (2)). The superficial values were multiplied by the viscosity of air ($\mu = 1.81 \times 10^{-5}$ Pa s) to obtain the specific permeability values ($K=k_g\ \mu$).