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WATER-RELATED PROPERTIES OF *PINUS PINASTER* WOOD TREATED BY DIFFERENT METHODS

A study was made of water-related properties of Pinus pinaster wood impregnated with paraffin or modified by heat treatment or furfurylation. Treated woods were submerged in water for periods ranging from 2 to 1680 hours. Water absorption, swelling, and dimensional stability in the radial and tangential directions – expressed as Anti-Shrinking Efficiency (ASE) – were determined. Water absorption increased with time, reaching approximately 140% after 1680 h for untreated and heat-treated wood, and 60% for paraffinated and furfurylated wood. The rate of swelling differed between the first hours of soaking and after prolonged immersion. The final swelling was approximately 9% and 6% for untreated pine, 8% and 4% for paraffinated pine, 5.5% and 3% for heat-treated pine and 2.5% and 1% for furfurylated pine (in the tangential and radial directions respectively). At the end of the soaking test, furfurylated pine had the best ASE of approximately 80% and 70% in the tangential and radial directions respectively, followed by heat-treated pine with 44% and 34%, and paraffinated wood with 35% and 13%.

Keywords: ASE, furfurylation, heat treatment, modified wood, paraffin impregnation, swelling, water soaking

Introduction

Wood modification has been defined [Hill 2006] as a process that improves the properties of wood, producing a new material that at the end of its life cycle does not present an environmental hazard greater than that of untreated wood. There are three main types of processes: thermal, chemical and impregnation modifications.

Thermal modification is the most successful wood modification procedure, probably due to the low cost of the treatment and the fact that no chemicals are used in the process. Several commercial treatments are available, including ThermoWood®, Plato® and Perdure®. Thermal treatment decreases the equilibrium moisture content, and improves the stability and the durability of

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wood, increasing resistance to fungi and insects, except in ground contact, but has little effect on termite resistance. The wood becomes darker, with lower wetting properties and thermal conductivity [Esteves and Pereira 2009]. Chemical modification processes are based on the reaction of wood with chemicals that replace hydrophilic groups in the wood with hydrophobic substituents – as in the case of acetylation with acetic anhydride, where hydroxyl groups are replaced with acetyl groups, which reduce the ability of the wood to absorb water. This process, called Accoya®, is the most important commercially available chemical modification, but it still lags far behind thermal modification in terms of commercial success. Other compounds have been tested, such as maleic anhydride [Roussel et al. 2001; Li et al. 2012]. In addition to the improvements produced by thermal treatment, chemical modification also increases resistance to termites and ultraviolet radiation.

Modification by impregnation is based on non-biocidal chemicals impregnated in wood. There are several mechanisms, including impregnation with a monomer and subsequent polymerisation, introduction of a soluble material that becomes insoluble after treatment, or simple impregnation with a water-repellent material, although this last is not a genuine modification process, since these compounds usually have no ability to penetrate the cell wall. Furfurylation (Kebony®) is the best-known impregnation process, but several others have been tested with acceptable results; for example, treatment with wax [Scholz et al. 2010a; Scholz et al. 2010b], paraffin [Esteves et al. 2014], or silicon compounds such as inorganic silanes [Donath et al. 2007], silicones [Militz et al. 2008; Weigenand et al. 2008; Ghosh et al. 2012] and silicates [Chen et al. 2014]. Most methods of impregnation modification are based on reducing the accessibility of hydroxyl groups, which are chiefly responsible for the hygroscopy of wood. All of the treatments have demonstrated a reduction in equilibrium moisture content [Epmeier et al. 2004; Epmeier and Kliger 2005; Esteves et al. 2006]; however, these tests are usually conducted in air with relative humidity ranging from about 35% to 95%. When samples are submerged in water, usually a short soaking time is used. For instance, Baysal et al. [2004] soaked furfurylated wood until it submerged in water, and obtained a water absorption index of approximately 20% for the treated wood against 180% for untreated sugi (*Cryptomeria japonica* (L.f.) D. Don) wood. In water soaking tests performed by Kocaefe et al. [2008] with untreated and heat-treated jack pine (*Pinus banksiana* Lamb.) and aspen (*Populus tremuloides* Michx.) wood, the water absorption after immersion for 24 h was measured at 20% and 12% respectively for untreated and heat-treated jack pine and 30% and 26% for untreated and heat-treated aspen. Kartal et al. [2007], with untreated and heat-treated sugi, reported water absorption after soaking for 24 h of around 90% for the untreated wood and slightly lower for wood that had been heat-treated at 180°C for 2 h. Wood treated for a longer time (4 h) or at a higher temperature (220°C) exhibited lower water absorption, ranging from approximately 60% to

80%. In a study by Temiz et al. [2006], Scots pine (*Pinus sylvestris* L.) sapwood specimens impregnated with two colloidal dispersions of silica and commercially available acetylated and heat-treated wood were soaked in water for times of 24-336 h. The water absorption of the untreated wood ranged between 62% (24 h) and 91% (336 h). All of the treatments reduced the water absorption; however, the decrease was small in the case of Silicon 15 (to 61% after 24 h and to 80% after 336 h). The best results (25% after 24 h and 79% after 336 h) were obtained for heat-treated wood. Bastani et al. [2015] studied the water uptake and wetting behaviour of furfurylated, N-methylol melamine – modified and heat-treated wood, and concluded that all of the modifications significantly reduced water absorption in the longitudinal, tangential and radial directions for short (24 h) and longer contact times (168, 336 h) with a saturated sponge. The best results were obtained for furfurylated wood.

This work is part of the ongoing project PPT-PROJ/CI&DETS/2017/026 and aims to study the long-term performance of soaked *Pinus pinaster* (Aiton) wood treated by different methods, since – as noted above – most of the currently available studies are based on tests in air or with short soaking times. Three different treatments were selected for testing of long-term effectiveness: heat treatment, furfurylation (impregnation followed by polymerisation) and paraffin treatment (impregnation with a water-repellent material).

Materials and methods

Softwood from *Pinus pinaster* (Aiton), important in the central region of Portugal, was used for the tests. Several treatment procedures were used: heat treatment, furfurylation and paraffin impregnation.

Heat treatment

Heat treatment of pine wood in an autoclave was carried out in an industrial prototype [Esteves et al. 2006] designed for the heat treatment of cork, installed in a plant for the production of black cork agglomerate located in Silves (Portugal). The equipment is heated by two different processes. The walls are heated by a shirt that contains a pipe with overheated steam. At the same time the interior of the autoclave is heated by a mixture of superheated and saturated steam that enters at the bottom of the autoclave. The tests were conducted at ambient pressure and 200°C for 6 hours. Heating was carried out slowly, through the shirt, up to 130°C; then between 130°C and the final treatment temperature heating was performed more rapidly by introducing a mixture of saturated and superheated steam into the autoclave. The treatment temperature was controlled by a thermocouple placed centrally in the autoclave. The treated samples had approximate dimensions of 20 × 20 × 360 mm.

Furfurylation

The furfurylation procedure was conducted in accordance with [Esteves et al. 2010]. Two boards of pine (*Pinus pinaster* Aiton) 2 m long, 20 mm thick and approximately 300 mm wide were cut from the same tree and dried to about 10% moisture content. Each board was cut into four panels with dimensions 1000 × 150 × 20 mm. The transitional zone between heartwood and sapwood was removed to obtain pure heartwood and sapwood parts. The panels were treated with a mixture of furfuryl alcohol (FA 70 mix, Kebony, Norway). The treatment was performed in an autoclave, beginning with a vacuum and pressure phase, and the panels were subsequently cured and dried in a vacuum-drying oven. After treatment, the samples were kept in a temperature-controlled chamber for three weeks, and the equilibrium moisture content was determined. Mass gain was calculated in relation to the dry wood.

Paraffin impregnation

Paraffin impregnation was carried out by a hot-and-cold process with 51-53°C paraffin from Panreac (melting point 53°C, density 0.9 g/cm^3 at 20°C). The treatment was performed using a hot bath (to 180°C) and a cold bath (to 70°C). The wood was placed in the hot bath for approximately 120 minutes, after which it was removed and introduced rapidly into the cold bath to promote the absorption of paraffin, remaining in that bath for 30 minutes. The mass gain was approximately 80% [Esteves et al. 2014]. The treated samples had approximate dimensions of 20 × 20 × 360 mm.

Water soaking test

Eight cubic samples with edge lengths of approximately 20 mm were cut from boards that had been treated by the different methods, and subjected to a soaking test.

All of the samples were dried in an oven at 103°C until completely dry. Subsequently the samples were placed in a water bath at 20°C. After each soaking period the samples were taken out of the bath and the surface cleaned with a paper towel. The samples were then weighed and measured in the tangential, radial and axial directions with a calliper. After this the samples were again submerged in water. This procedure was repeated at 2, 6, 24, 48, 96, 168, 336, 672, 1008, 1344 and finally 1680 hours.

The water absorption was determined from the formula:

$$Wa(\%) = \frac{Wet\ mass - Dry\ mass}{Dry\ mass} \times 100 \quad (1)$$

where the wet mass is taken after each soaking period, and the dry mass is the mass of the original dried sample.

The swelling for each period was determined from the formula:

$$Swelling\,(\%) - \frac{Wett\ dimension - Dry\ dimension}{Dry\ dimension} \times 100 \qquad (2)$$

Dimensional stability (Anti-Shrinking Efficiency)

Dimensional stability was determined based on the ASE, which represents the percentage difference between the swelling of treated (T) and untreated wood (U). The swelling is calculated by equation (2), and the ASE by equation (3):

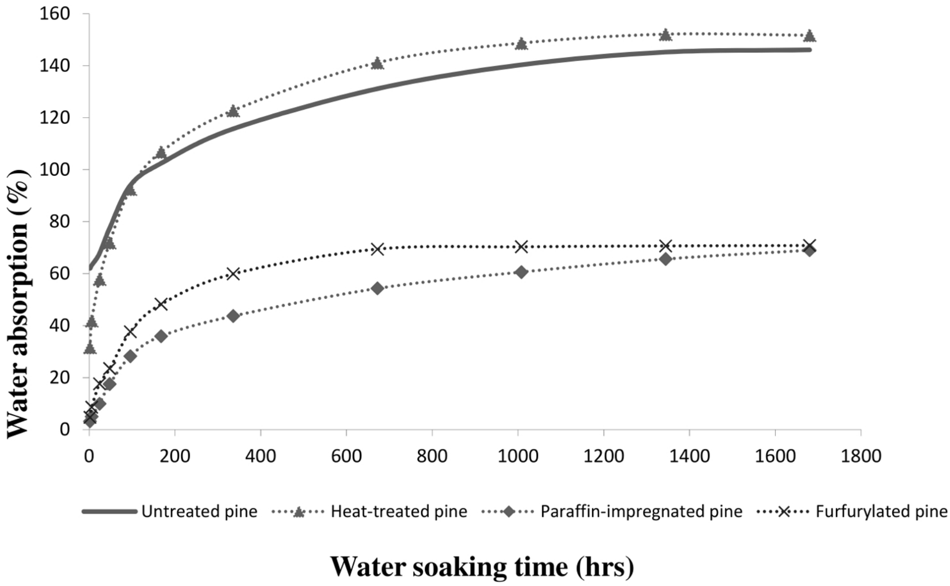
$$ASE\,(\%) = \frac{Swelling\ U - Swelling\ T}{Swelling\ U} \times 100 \qquad (3)$$

Results and discussion

Water absorption

Figure 1 shows the variation in water absorption during the time of the water soaking test, on decimal and logarithmic scales. In the first hours of the soaking test there is a more rapid increase in water absorption, as shown by the steeper slope. The logarithmised plot shows that there are three main stages in the absorption curve. The first stage, up to about 48 h, has a greater slope (on the decimal curve). Absorption is faster at this stage because there are still many voids available to be filled with water. The second stage lasts until about 672 h, with a shallower slope, due to the filling of most of the voids in the wood. In the final stage the curve is almost horizontal, meaning that the wood is saturated and incapable of absorbing more water.

In the first 24 h of immersion the untreated pine samples absorbed the greatest quantity of water, with a mass increase of almost 70%, compared with approximately 60% for the heat-treated pine. As the test progressed, the heat-treated pine samples began to absorb more water than the untreated wood, reaching an increase of approximately 150% after 1680 h (70 days), more than the untreated wood (140%). This shows that the heat treatment did not decrease the water absorption on soaking of the wood, but did slow down the process. This is probably because at the start of the soaking process the water enters the cell walls as bound water, which is present in lower quantities in heat-treated wood, but after some time the water fills all voids as free water, which is present in higher quantities. This is in agreement with Andersson et al. [2005], who reported that thermal modification of Scots pine (*Pinus sylvestris* L.) wood increased the porosity of the cell wall. According to Kekkonen et al. [2014] heat treatment reduces the quantity of bound water. The same authors report that for treatment temperatures above 200°C the quantity of free water decreases, demonstrating that heat treatment at higher temperatures closes the pits connecting the wood cells. The temperature used in this study was 200°C, which suggests that a higher temperature would be needed to ensure a decrease in free water, so as to achieve a greater reduction in water absorption.



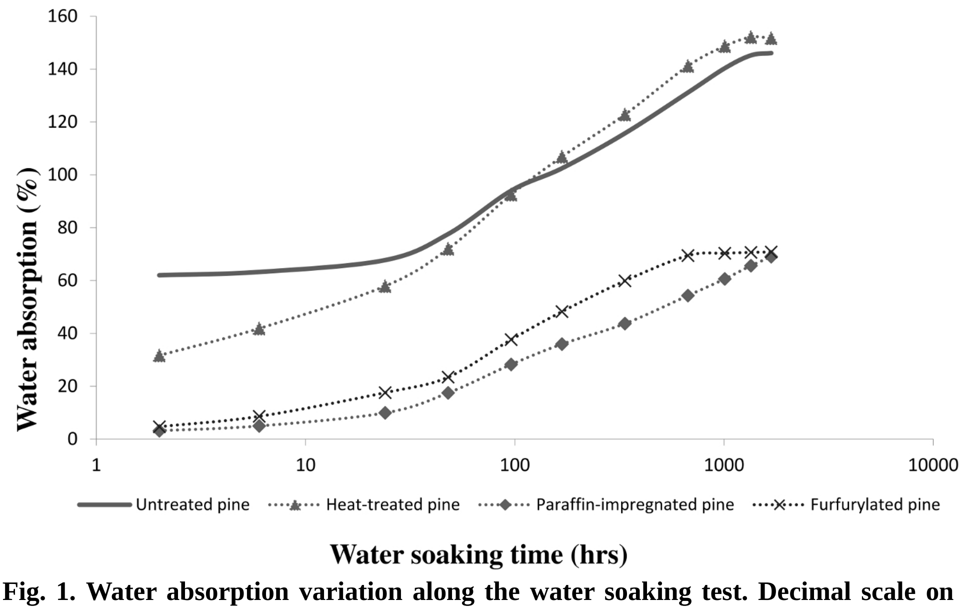


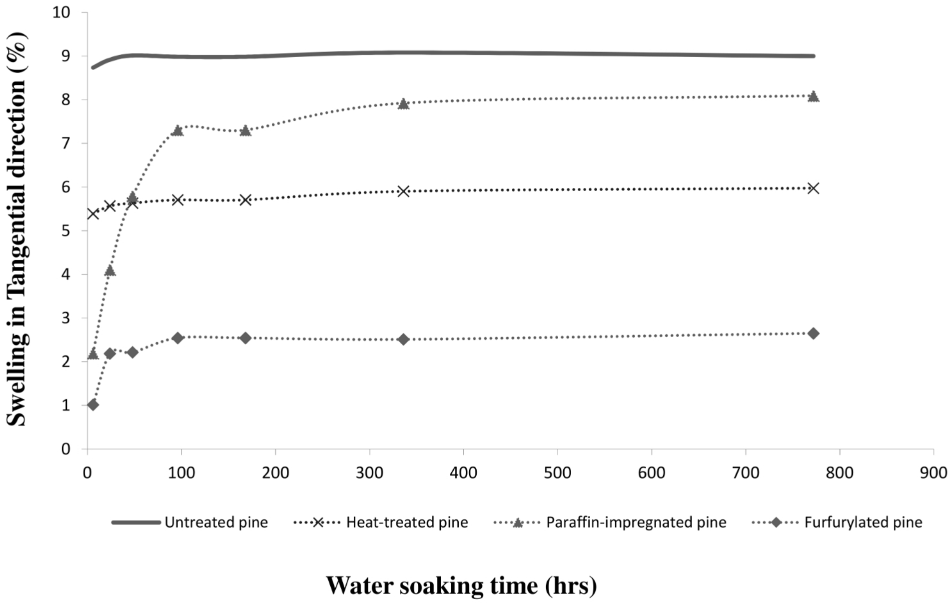
Fig. 1. Water absorption variation along the water soaking test. Decimal scale on the top and logarithmic scale on the bottom

Wood modified by paraffin impregnation and by furfurylation exhibited low water absorption, below 20% in the first 24 h of the soaking test. Although there was an increase in absorption as the test progressed, the water content of furfurylated and paraffinated wood after 1680 h was the lowest among the tested samples, with an increase of approximately 60%. Nevertheless, for paraffinated wood there was a higher increase for longer exposition times, probably due to some loss of paraffin during the test, since paraffin is not chemically bonded to the wood and there is no polymerisation reaction to ensure its retention as in the case of furfurylated wood. The lower water absorption is due to the bulk effect of furfuryl alcohol and paraffin, which fill the voids in the wood. Results previously reported by Wang and Cooper [2005] for wood treated with wax were comparable, with approximately 25% water absorption after soaking for 24 h and 50% after 192 h.

Similar results were reported by Kartal et al. [2007] for untreated and heat--treated sugi wood. They reported water absorption of around 90% for untreated wood after 24 h soaking, and a slightly lower value for wood that had been heat--treated at 180°C for 2 h. Wood treated for a longer time (4 h) or at a higher temperature (220°C) exhibited lower water absorption, ranging from approximately 80% to 60%. In water soaking tests performed by Kocaefe et al. [2008] with untreated and heat-treated jack pine and aspen wood the water absorption was considerably lower: 20% and 12% respectively for untreated and heat-treated jack pine, and 30% and 26% for untreated and heat-treated aspen. Nevertheless, the differences are most probably due to the size of the samples, since the samples used in this study had edge lengths of approximately 20 mm without sealed ends, while the test performed by Kocaefe et al. [2008] used boards and sealed ends. Temiz et al. [2006] presented surprising results, reporting 25% absorption for heat-treated wood and 48% for acetylated wood after soaking for 24 h; however, the only information given was that the maximum temperature of heat treatment was 240°C, which is higher than the normal treatment temperature, and no information was given on the degree of substitution in the acetylated wood.

Swelling

The rate of swelling of the soaked samples differed between the first hours of soaking and after prolonged immersion. Even after only 2 h of soaking, untreated pine samples swelled by around 9% in the tangential direction, but with an increase in the immersion time the swelling remained approximately the same. This means that the water absorbed at the beginning of the soaking tests not only filled voids in the wood (free water), but also rapidly entered the cell walls (bound water), leading to the observed dimensional changes. Very similar behaviour was observed for heat-treated wood, but with a significantly lower swelling of around 5-6%. These results indicate that the main effect of heat treatment is that, although the water absorption (fig. 1) is similar or even higher than in untreated wood, the swelling is considerably lower. This shows that there is a smaller quantity of bound water, which is responsible for the swelling; this may be due to the smaller number of accessible hydroxyl groups or to condensation reactions between lignin and polysaccharides, which prevent swelling. Kocaefe et al. [2008] reported 3.7% and 1.3% swelling in untreated and heat-treated jack pine wood.



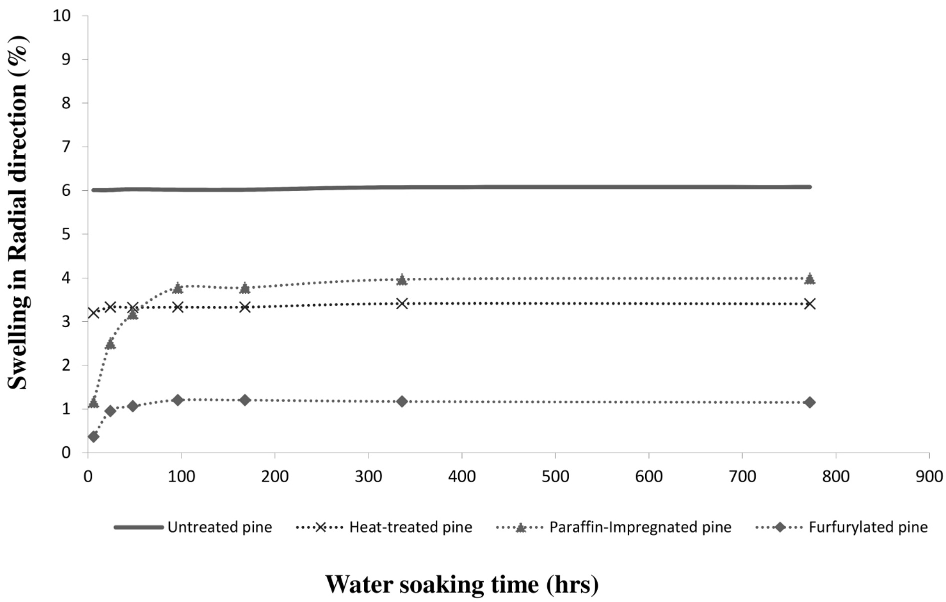


Fig. 2. Dimensional changes in tangential and radial directions along the water soaking test

Paraffin-impregnated pine underwent only slight swelling in the tangential direction, lower than 2% after 2 h soaking, but with prolonged immersion time the dimensional changes increased, reaching 8%, almost the same as the swelling in untreated pine wood, after 336 h of immersion. This may be due to the physical barrier created by paraffin wax, which at the beginning of the soaking process prevents water from reaching the cell walls, although with longer soaking the water finally reaches the cell walls, leading to swelling. This supports the hypothesis that paraffin only fills the voids in wood rather than impregnating the cell walls. Another reason might be the leaching of paraffin during the test, as indicated previously. Similar results were reported by Wang and Cooper [2005] for wood treated with wax, where the swelling ranged from 3% (24 h) to 10% (192 h).

In furfurylated wood there was a small increase in swelling in the first hours of the soaking test, but the swelling was found to be the smallest among all of the samples, remaining under 3% even after a longer time (fig. 2). This again confirms that furfuryl alcohol is capable of reaching the cell walls, reducing the number of available hydroxyl groups, and thus preventing swelling. These results show that the heat treatment is more efficient than paraffin at reducing swelling when the wood is soaked in water. There are differences between the degrees of swelling in the tangential and radial directions: the final swelling was approximately 9% and 6% for untreated pine, 8% and 4% for paraffinated pine, 5.5% and 3% for heat-treated pine and 2.5% and 1% for furfurylated pine in the tangential and radial directions respectively.

Dimensional stability

Dimensional stability was measured in terms of Anti-Shrinking Efficiency (ASE). Figure 3 presents the ASE in the tangential and radial directions over the course of the water soaking test. At the beginning of the test the tangential ASE value is highest for furfurylated pine (90%), followed by paraffinated pine (75%) and heat-treated pine (40%). Afterwards, the ASE decreases to approximately 75% for furfurylated wood, and for paraffinated wood exhibits a steep decline to about 10-20%. For heat-treated wood the ASE remains close to 40% throughout the test. Radial ASE behaves similarly, but with a smaller decrease for paraffinated wood. The final radial ASE was approximately 80% for furfurylated wood, 45% for heat-treated wood and 35% for paraffinated wood.

Most ASE values reported in the literature are determined between dry state and a state with relative humidity from 35% to 90%. Not many studies have been performed using the water soaking method. Temiz et al. [2006] reported the ASE of acetylated, heat-treated and silicon dioxide-treated wood soaked in water for between 24 and 336 h. The best ASE values were obtained for acetylated and heat-treated samples, while both silicon dioxide treatments produced very low ASE values. No substantial variation was observed along the soaking time for acetylated wood, with ASE ranging from 84.5% to 87.1%, although there was a slight decrease in the case of silicon-treated wood (from about 5.3% to 3.2%) and heat-treated wood (from 76.6% to 66.5%). The better dimensional stability reported in that study for heat-treated wood might be due to the higher temperature (240°C) used in the treatment, as reported previously [Kekkonen et al. 2014].

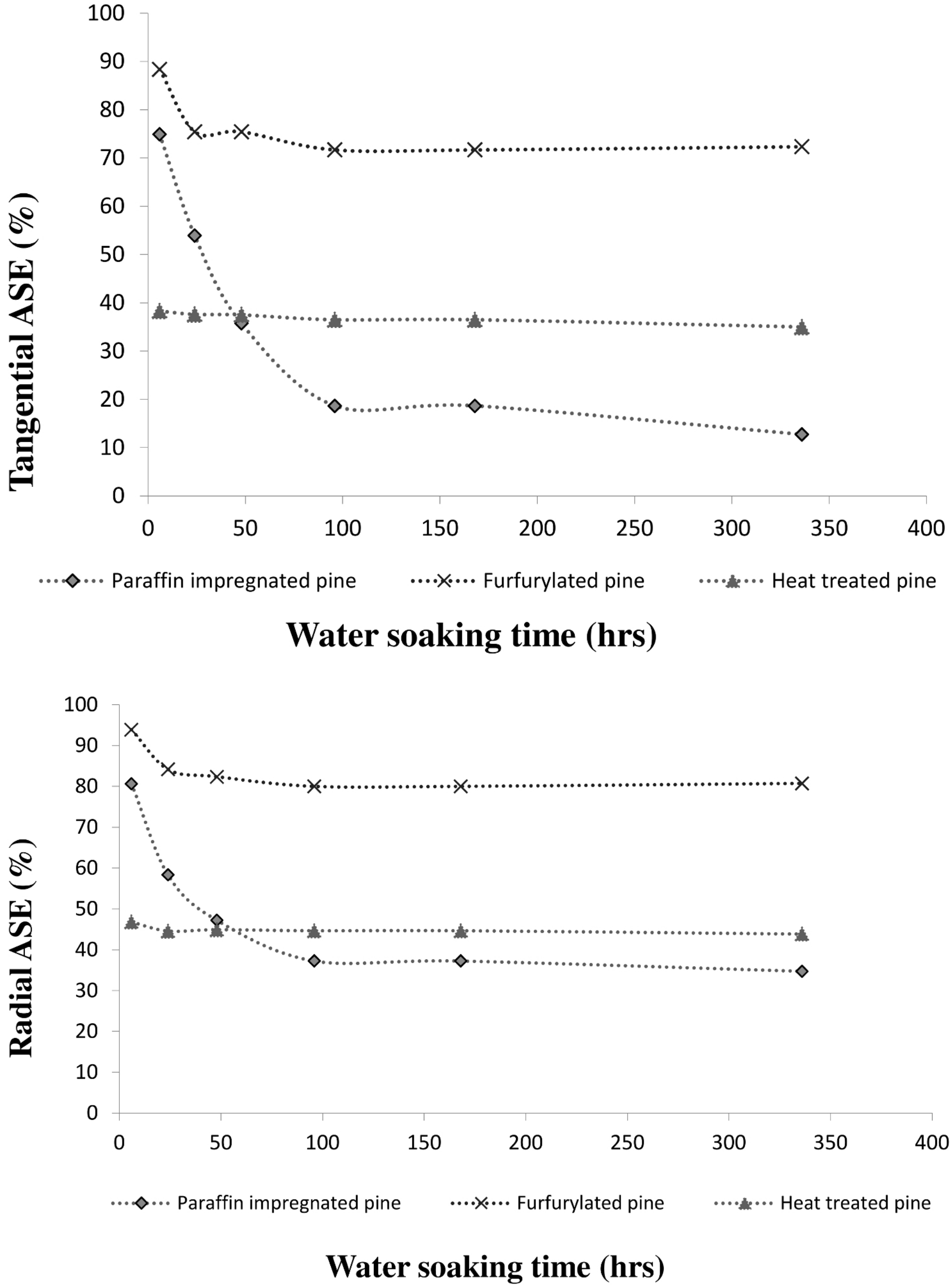


Fig. 3. Tangential and Radial ASE along the water soaking test

Conclusions

Water absorption increased as the test progressed, reaching approximately 140% for untreated and heat-treated wood, and 60% for paraffinated and furfurylated wood. The rate of swelling differed between the first hours of soaking and after prolonged immersion. The greatest difference was observed for paraffinated wood. Although heat-treated wood absorbs a similar quantity of water as untreated wood, the swelling is much lower, which indicates that heat-treated wood has more free water and less bound water than untreated wood. Water absorption is lower for paraffinated and furfurylated wood, but the results demonstrate that only furfuryl alcohol can penetrate the cell walls and reduce wood swelling. The small decrease in swelling for paraffinated wood is most likely due to the water-repellent effect of paraffin.

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