Maleic Anhydride Treated Wood: Effects of Drying Time and Esterification Temperature on Properties

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To improve technical performance of wood siding, treatment with maleic anhydride was applied. The effects on technical performance of drying time and esterification temperature parameters were analyzed. Wood samples of lodgepole pine and white pine were treated and tested. Results indicated that treatment improves technical performance of wood (dimensional stability, fungal degradation resistance, and accelerated aging). FTIR spectroscopy analysis showed spectra with peaks at 1750 to 1730 cm^{-1}. These correspond to ester bonds formed between wood hydroxyl groups and MA carboxylic acid groups. SEM images indicate that the MA quantity in wood cavities was increased with decreasing esterification temperature. Weight percent gain (WPG) increased with decreasing time and temperature of esterification. Artificial aging and fungal degradation performances were monitored using FTIR analysis. Esterification temperature had no important effect on fungal degradation. Weight loss after fungal exposure of treated samples was not only due to fungal action but also due to evaporation of MA during the drying step. Regarding artificial aging, degradation of wood components and ester bonds were less for samples esterified at 180 °C than those esterified at 160 °C or 140 °C.

Keywords: Dimensional stabilization; Maleic anhydride; Esterification; Mono and di ester bonds; Wood siding

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INTRODUCTION

Used as a material for building and heating, wood is highly present in our societies. In buildings, wood siding is used for interior and exterior walls. Like other materials (synthetic polymers, wood polymers, stone, cement, concrete, bricks, *etc*.) solid wood exterior siding for residential and non-residential buildings is subjected to weathering (rain, wind, UV, *etc*.) and attack by decay agents. These factors cause wood to undergo physical and chemical changes that reduce its service life. It is thus important to improve the performance of solid wood exterior siding products. Exterior wood siding competes with other materials such as polymers (vinyl), wood polymer, stone, steel, concrete, brick, fiber cement panels, *etc*. There are a number of reasons to choose solid wood for siding: price, aesthetics, appearance, environmental friendliness, and insulation.

Nowadays, the increasing sensitivity of consumers to environmental concerns influences producer and political decisions. As a renewable resource, solid wood is a responsible, biodegradable, and environmentally friendly material compared to steel and concrete materials (Perez-Garcia *et al.* 2005). Over the last few decades, the siding industry has encountered various issues related to the intrinsic properties of wood material.

Dimensional variations, resistance to fungal attack, photo-degradation, and warping are some issues which the siding industry has to face (Siau 1984; Chang and Chang 2001; Teaca *et al.* 2013).

Several studies have already been undertaken in order to solve problems for the wood siding industry. One way is the impregnation of wood with a chemical solution. Three basic criteria must be satisfied to have good impregnation with monomer chemical solution (Stamm and Seborg 1936). The first is that the solution should be sufficiently polar to exhibit a high affinity with wood hydroxyl groups; second, molecules must be soluble in a polar solvent; and third, a molecule's weight should be small enough to facilitate the penetration into the wood cell wall structure. The sizes of wood micropores are especially important (Mantanis *et al.* 1994; Hill 2006). According to a study conducted by Hill (2006), the maximum size of wood cell wall micropores should be between 2 and 4 nanometers (nm). The apparent porosity of Canadian wood species (*Acer saccharum* Marshall, *Betula alleghaniensis* Britt., and *Picea glauca* Voss) presents a mean diameter between 1.27 and 1.61 nm, as calculated with the Gibbs-Thomson equation (Nguegang Nkeuwa 2010). The molecules sizes of the treatment solution are important for easy penetration in wood structure. When greater or equal to 0.63 nm, penetration is difficult (Mantanis *et al.* 1994).

Since the 1930's, different wood treatments by impregnation have been performed. Treatment with formaldehyde resins has been found to provide 70% higher dimensional stability, even after repeated treatments in aqueous solution containing 20 to 30% resin (Stamm and Seborg 1936). However, release of formaldehyde, a carcinogenic volatile organic compound (VOC), in the atmosphere is an environmental and human health issue. Treatments with dimethylol dihydroxy ethylene urea (DMDHEU), furfuryl alcohol, organo-silane, maleic acid, and glycerol have been the subject of several studies (Goldstein *et al.* 1959; Weaver *et al.* 1960; Inoue *et al.* 1993; Uraki *et al.* 1994; Van Acker *et al.* 1999; Sèbe and De Jéso 2000; Lukowsky 2002; Sèbe *et al.* 2004; Westin *et al.* 2004). Wood treatment with carboxylic acids is based on the same principle as that for the anhydrides, which is a nucleophilic substitution on the acyl carbon. The difference is only the low reactivity of the acyl carbon carboxylic acids compared to carboxylic anhydrides (Bender 1960). Wood treatment with maleic anhydride has been investigated by many authors. As a cyclic anhydride, wood reactions with maleic anhydride do not yield a by-product (Hill 2006). Molecule of maleic anhydride reacts with hydroxyl group of wood to forms ester bonds. For each ester bond formed, there is one water molecule produced. In this reaction, there are possibility to form monoester or diesters bonds. A monoesters bond is formed firstly because the energy required to open the anhydride cycle is less than that required to form the diester bonds (Hill 2006; Matsuda 1987; Matsuda *et al.* 1984). Generally, the proportion of monoester bonds is greater than diester at low esterification temperature. Otera and Nishikido (2010) indicate that at 90 °C, 95% of monoester bonds are formed.

Wood treatment with maleic anhydride has been performed in the vapor state. Improvements of technical performances (dimensional stability, fungal degradation) have been observed, but the cited studies used sapwood as samples (Yang *et al*. 2014; Iwamoto and Itoh 2005; Iwamoto and Itoh 2006; Iwamoto *et al*. 2005). Authors Chang and Chang (2001) also used sapwood samples, but they carried out extraction before treatment to remove extractible fraction and after to remove unreacted anhydride. In the siding industry, the use of sapwood is not the current practice, and solvent is less and less used. The process complexity, toxicity, and cost of the chemical products used for wood treatment are factors

that limit the industrial applicability of processes developed in laboratories. Wood treatment with conventional liquid phase of maleic anhydride was investigated in the years 1970 through 1980. However, very few studies have taken into account the reusing of reagent.

The objective of this study was to determine the technical performances of samples treated with a maleic anhydride liquid phase. The particularity of this work is the continuous reusing of maleic anhydride liquid phase and the analyses of the influence of two parameters on wood technical performances: drying time after impregnation and esterification temperature. Can these two parameters have an influence on the technical performance of treated wood?

Regarding technical performances, the work in this paper is divided into three parts. The aim of the first part is to demonstrate the improvement in dimensional stability. Many analyses are performed to evaluate effects of different parameters on dimensional stability, along with FTIR spectroscopy analysis and SEM analysis. Mono- and diester bonds formed between the hydroxyl groups of the wood structure and the carboxylic groups of maleic anhydride identified and quantified by titration. The unreacted quantity of maleic anhydride present in wood structure was determined by a leaching test. The aim of the second part was to evaluate the decay resistance to fungi through a biodegradation test. Sample degradation was analyzed by FTIR spectroscopy, and weight loss was calculated. In the third part, the chemical changes occurring on the surface of treated and untreated wood samples after artificial aging was evaluated. The progressive degradation was followed by FTIR spectroscopy analysis. All data were analyzed using the Statistical Analysis Software (SAS 9.3) program. Statistical analysis consisted of computing an analysis of variance (ANOVA) of ASE. Probability (P-value) was computed at the 0.01 confidence level. Multiple comparison tests were performed according to the Tukey method to determine significant differences between different treatments.

EXPERIMENTAL

Materials

Furan-2,5-dione ($C_4H_2O_3$), commonly named maleic anhydride (MA), with 99% purity was used to treat wood samples. The material was obtained from Sigma-Aldrich Co. (USA). Nitrogen (N_2) used to apply pressure at the impregnation step was obtained from Praxair Canada Inc., Canada. Malt and Agar were obtained from EMD chemical Inc., an affiliate of Merck KGaA (Germany).

Samples used were from two different wood species: white pine (*Pinus strobus* L.) and lodgepole pine (*Pinus contorta* Douglas). Wood species were firstly conditioned in a conditioning room at 20 ±2 °C and 40 ±4 % of relative humidity (RH). At constant mass, wood was planed, sawed, and cut to produce samples of different dimensions. Sample dimensions depend of the test to be performed. After cutting, all samples were placed in the room at 20±2 °C and 40±4 % of RH conditions until they reached the equilibrium moisture content around 8%. All samples were free of knots, visible resin, stain, or fungi. Table 1 shows the dimensions of all samples used for each test. For the decay test, fungi strains were obtained from the fungi collection of FPInnovations, Canada.

Treatment solution and wood used in this experience were labeled as follows: (MA) for maleic anhydride, (Lp) for lodgepole pine, and (Wp) for white pine. Fungal strains were *Irpex lacteus* (IL) and *Postia placenta* (PP). Weight loss was indicated by (WL).

Table 1. Sample Dimensions

Test	Length (mm)	Width (mm)	Thickness (mm)
Swelling and shrinkage	20	20	10
Infrared spectroscopy	25	25	10
Scanning electron microscopy	10	10	10
Mono- and di-esters determination	Mesh (40-60)		
Leaching	20	20	10
Biodegradation	25	25	10
Artificial aging	60	60	10

Methods

Impregnation parameters

Wood samples were impregnated with MA solution inside a pressure reactor (model 4522, Parr Instrument, USA). The reactor was connected to a vacuum pump and to N_2 to apply pressure. To determine the ideal parameters for impregnation of wood samples, different pressure values at different times were tested. A vacuum was applied (for less than 10 seconds at 720 mbar) to remove the air inside the reactor before applying pressure. Optimal parameters were determined for Wp and Lp impregnation (Table 2).

Table 2. Impregnation Parameters for White Pine and Lodgepole Pine Wood Samples

Dimensions (mm)	Pressure (Psi)	Impregnation times of White pine (h)	Impregnation times of Lodgepole pine (h)
20 x 20 x 10	200	2	3
25 x 25 x 10	200	2	3
60 x 60 x 10	300	3	4

Wood treatment

The dimensions of wood samples to be tested were selected according to the ASTM and AWPA standards of each test performed in this work. All samples were placed on the shell inside the reactor in fiber direction for impregnation. The inherent variability of the material was taken into account by carefully selecting (visually checking for no sapwood or apparent anomalies like nodes, pocket of resin, *etc.*) and matching the samples. All treatments were performed under the same conditions. The wood samples were first impregnated with MA solution using a vacuum/pressure process. MA solution after each impregnation was recovered and reused. A part (around 1/5 of the total volume of solution) of this was added to a new MA solution used for the next impregnation. Pressure was applied using N_2 (Fig. 1), using parameters listed in Table 2. After the impregnation step, the drying step was performed in an oven at 103 ±2 °C. During the oven drying step, the esterification reaction starts and some of the water evaporates (Otera and Nishikido 2010). Based on the entirely random experiment plan, impregnated samples were divided in three groups for three different drying times (12 h, 18 h, and 24 h). At the end of the oven drying step, each sample was wrapped in aluminum foil and placed in an oven for esterification at

three temperatures (140 °C, 160 °C, and 180 °C) for 2 h. The term *esterification temperature* indicates the oven temperature used for the third step.

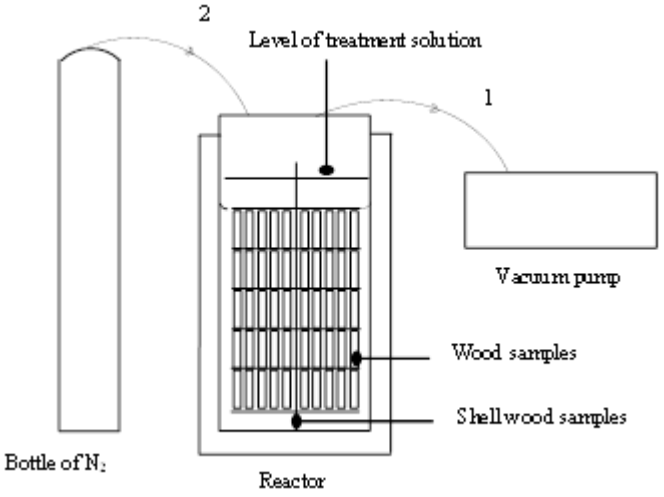


Fig. 1. Schematic representation of impregnation process

Impregnation increases the width and thickness of the treated samples. During the drying and esterification reaction in the oven, treated samples lost part of the solution absorbed, reducing their weight. After the esterification reaction, all samples were immediately placed in a desiccator containing phosphorus pentoxide (P_2O_5) for cooling. After 30 minutes, samples were unwrapped and put inside a conditioning room at 20 ±2 °C and 40 ±4 % RH. Exposed to these conditions, three treated and untreated samples were randomly chosen to monitor the weight. The samples were weighed every 6 h. The weighing was stopped when the sample weight was stable. Samples were weighed at the moisture content of 8% and weight percent gain (WPG) was calculated.

Swelling (α), shrinkage (β), anti-swelling efficiency and anti-shrinkage efficiency (ASE)

All impregnated samples were divided into two groups for two condition tests. Swelling and shrinkage tests on the first sample group was performed using 20 ±2 °C and 90 ±4 % RH, followed by 50 ±2 °C and 15 ±4 % RH. The second group was tested by water immersion for 10 days (water temperature was 20 ±2 °C), and then oven dried at 103 ±2 °C for 24 h. The swelling ($\boldsymbol{\alpha}$) of wood samples treated was measured in the radial and tangential directions, using a digital micrometer with a precision of 0.001 mm. The radial ($\boldsymbol{\alpha}_R$) and tangential swelling ($\boldsymbol{\alpha}_T$) were calculated following Eqs. 1 and 2 as defined ISO 4859 (1982). The swelling coefficient ($\boldsymbol{\alpha}$) of each sample was calculated by summing radial and tangential swellings as follows (Eq. 3):

$$\alpha_R\,(\%) = [(R_1\text{-}R_0)/R_0] \times 100 \quad (1)$$

$$\alpha_T\,(\%) = [(T_1\text{-}T_0)/T_0] \times 100 \quad (2)$$

$$\alpha\,(\%) = (\alpha_R + \alpha_T) \quad (3)$$

In these equations, R_1 and R_0 are the radial dimensions of the samples, respectively, after and before the swelling test, while T_1 and T_0 are the tangential dimensions after and before the swelling test.

Shrinkage (β) of samples was measured in radial and tangential directions. Radial (β_R) and tangential shrinkage (β_T) were measured with the same device and calculated following Eqs. 4 and 5 as defined ISO 4859 (1981). The shrinkage coefficient (β) of each sample was calculated by summing radial and tangential shrinkages as follows (Eq. 6):

$$\beta_R\,(\%) = [(R_1\text{-}R_0)/R_1] \text{ x } 100 \quad (4)$$

$$\beta_T\,(\%) = [(R_1\text{-}R_0)/R_1] \text{ x } 100 \quad (5)$$

$$\beta\,(\%) = (\beta_R + \beta_T) \quad (6)$$

Anti-swelling efficiency and anti-shrinkage efficiency (ASE) was calculated following Eqs. 7 and 8 as defined by different authors (Sèbe and De Jéso 2000; Hill 2006; Yong *et al.* 2010). In the literature, several authors confirm that longitudinal swelling and shrinkage can be neglected because it is small compared to that in that radial and tangential directions (Panshin *et al.* 1964; Norimoto *et al.* 1992; Sèbe and De Jéso 2000).

$$\text{ASE } (\%) = [(\alpha_{ut} - \alpha_t)/\alpha_{ut}] \text{ x } 100 \quad (7)$$

$$\text{ASE } (\%) = [(\beta_{ut} - \beta_t)/\beta_{ut}] \text{ x } 100 \quad (8)$$

In Eqs. 7 and 8, α_t/β_t is the swelling/shrinkage coefficient of treated wood sample and the quantity α_{ut}/β_{ut} is the swelling/shrinkage coefficient of untreated wood sample (control). Anti-shrinkage efficiency (ASE) was calculated in the same way.

Fourier transform-infrared (FTIR) spectroscopy

Qualitative analysis of treated wood samples compared to untreated samples was performed using a FTIR spectrophotometer. The objective was to illustrate the presence of ester bonds formed between the hydroxyl groups of the wood and maleic anhydride. The FTIR spectrophotometer used was the Spectrum 400 from Perkin Elmer, UK. An attenuated total reflection (ATR) crystal diamond accessory was used to record the spectra. 64 scans were taken at a 4 cm^{-1} resolution and the spectral range was 4000 to 500 cm^{-1}. Only the set of samples oven-dried for 24 h and esterified at 140 °C, 160 °C, and 180 °C were considered.

Scanning electron microscopy (SEM)

To investigate the cell wall structure morphology of treated wood samples in comparison with the cell wall structure of untreated wood samples, SEM analysis was performed. This technique illustrates the changes occurring in the cell wall and cell cavity of treated samples. The SEM equipment used was the JSML-6360LV model from JEOL Corporation, Japan. To make this test representative, four treated and untreated samples were chosen for each wood species. Samples of 10 mm x 10 mm x 10 mm (longitudinal-transversal-radial), treated and untreated, were analyzed. To soften wood samples, they

were immersed in distilled water for several days. Then, the surface was planed using a microtome (Leica SM 2400, Germany). At the end of this step, samples were dried and surface was metalized to render the surface electrons conductive. After this, the samples were placed inside a vacuum chamber until SEM analysis. SEM images were taken for each sample, at an accelerating voltage of 15 kV. These images were taken at a magnification between X 650 and X 300 in order to evaluate a large overview of the transversal section sample.

Determination of mono and di-ester concentration

The reaction between MA and the wood structure, catalyzed by temperature, can form two different types of ester bonds: mono-ester (I) and di-ester (II) bonds (Fig. 2). Determination of the proportions of each ester bond provides information about the dimensional stability results according to Matsuda *et al.* (1984). Sample sets considered for this test were the above-mentioned samples, which were oven-dried for 24 h, heated at three different temperatures (180 °C, 160 °C, and 140 °C) and samples oven-dried at 18 h and 12 h were heated at 180 °C. This was performed for each wood species. After conditioning at 20 ±2 °C and 40 ±4 % of RH, the test was subdivided in 3 steps.

The first step involves splitting up, crushing, and sieving (mesh 40 to 60) each set of samples. Each treatment constitutes a sample set. The aim of the second step consists in MA excess removal from the wood solids through an extraction operation. It consists of putting inside a glass beaker 7 g of wood powder and 150 mL of acetone. The mixture was stirred for a few minutes and then filtered. Each wood powder specimen was washed with acetone and subsequently washed with 1 L of distilled water. Further, washed wood powder was subjected to a Soxhlet extraction with 150 mL of acetone for 6 h. After extraction, each wood powder specimen was dried for 24 h at 20 ±2 °C under the hood. This process produces esterified wood mesh (Matsuda *et al.* 1984). The third step consisted of determining the acidity (*A*) and saponification (*S*) values of the wood powder (Eqs. 9 and 10). The same step includes the determination of mono-ester (*M*) and di-ester (*D*) concentration contained in the wood powder.

$$M\ (\%) = A_1 - [(A_0 \times Y)/1000] \times (100M_1/Y). \quad (9)$$

$$D\ (\%) = S_1 - 2A_1 - [((S_0 - 2\,A_0) \times Y)/1000] \times (50\,M_2/Y). \quad (10)$$

In these equations X (g) is the weight increase due to treatment; Y is the wood content (g) in 1000 g of esterified wood with carboxyl groups (calculated as follows: $Y = 1000 \times [100/(100 + X)]$); A_1 is the acid value of esterified wood mesh; A_0 is the acid value of original wood mesh; M_1 is the molecular weight of anhydride; S_1 is the saponification value of esterified wood powder; S_0 is the saponification value of original wood powder; and M_2 is the difference M_1 minus 18.01, where 18.01 is molecular weight of water.

Concentration of "M" and "D" are expressed in % of the quantity of MA that reacts with the wood structure. The whole process was performed four times for each of wood species for each sample set.

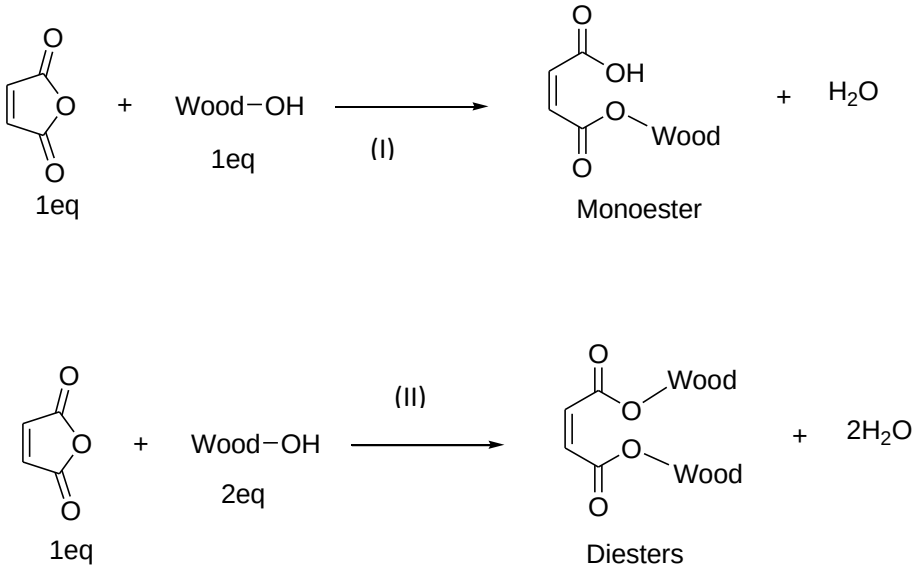


Fig. 2. Mono- (I) and di-ester (II) bonds formed between the wood structure and MA

Leaching medium test

The aim of this test was to evaluate the leaching of substances from the treated samples. Standard methods used to evaluate leaching preservative products generally require the use of ion-free, de-ionized, or distilled water (Terzi *et al.* 2012). In this study, distilled water was used at a temperature of 20 ±2 °C. Leaching procedures used for this test came from AWPA E11-12, "Standard Method for Accelerated Evaluation of Preservative Leaching" (AWPA 2014). For each wood species, all the sample sets were treated one time. Selected samples for each set had similar weight (± 0.01 g). The same criteria were used to select untreated samples for each species. All samples were conditioned at 20 ±4 °C and 65 ±5 % of RH until constant mass was reached before starting the leaching test. The most important parameter in this test is the quantity of water used for leaching preservative product. Accordingly to the preservative product employed, the high volume of distilled water used in wood/water ratio or insufficient replacement of leaching waters may inhibit the diffusion of molecules product into water (Goyette and Brooks 1997; Breslin and Adler-Ivanbrook 1998; Hingston *et al.* 2001). Several authors recommend a wood/water volume ratio of 1/5 (v/v) (Van Eetvelde *et al.* 1995a; Van Eetvelde *et al.* 1995b).

MA reacts with water to produce maleic acid. To estimate the quantity of leaching MA, a pH-meter was used to measure the acidity of the leaching waters. For each treatment, three samples were chosen randomly to constitute one set of samples. Each set of samples was placed into a 200 mL beaker and held at the bottom by a piece of stainless steel mesh. A volume of distilled water corresponding to 5 times the volume of wood samples present in the beaker was added. Each beaker was closed with an aluminum sheet to limit water evaporation. All beakers were subjected to mild agitation (speed 100 rpm) with a Barnstead/Labline agitator (model number 4633, USA). Water was changed after 6 h, 24 h, and 48 h, followed by changes every 48 h for a total of 2 weeks (9 leachate collections). At the end of each period, the pH of leaching waters was measured. The beaker was rinsed

several times to remove all traces of acid and the same quantity of new distillate water was added. Three repetitions were performed for each sample set.

After 2 weeks, the test was stopped and all samples were conditioned at a temperature of 20 ±2 °C and a RH of 65 ±5 % until constant mass was reached. Sample weights were measured and the percentage of maleic anhydride leached was calculated for each sample set following Eq. 11. Each condition was evaluated with three repetitions, and the average is reported in this paper:

$$\text{Percentage of maleic anhydride leached} = [A/ (A+B)] \text{ x}100 \quad (11)$$

In Eq. 11, *A* is the total weight of maleic anhydride in leachate (mg) for each sample set, and *B* is the total weight of maleic anhydride in leached blocks (mg) for each sample set. "*A*" represents the difference of weight percent gain (WPG) of sample set, before and after the leaching test, whereas "*B*" is the WPG of sample set after leaching.

Biodegradation test

In wood, macromolecules (polysaccharide and lignin) act as nutrients and substrates for fungi. When conditions (favorable temperature, supply of oxygen, adequate amount of moisture and presence of suitable food supply) are favorable, they settle down and develop (Panshin *et al.* 1964). In wood attacked by fungi, the destruction of cell walls causes breakdown of the wood structure. In the present research, the goal of the decay test was to provide information about the effect of treatment on fungi decay resistance. This test was inspired by the AWPA E10-12 "Standard method of testing wood preservatives by laboratory soil-black cultures" (AWPA 2014).

The dimensions of white pine and lodgepole pine wood samples were 25 mm x 25 mm x 10 mm (longitudinal x tangential x radial). All samples were oven-dried for 24 h and esterified at different temperatures (180 °C, 160 °C, and 140 °C). The combination between oven-dry time and esterification temperature represents a treatment and constitutes a sample set. Each set was constituted of eight samples (six samples treated and two untreated). Basidiomycete class fungi were used for this test (*Irpex lacteus* and *Postia placenta*). Strain 103 A of *Irpex lacteus* was selected for white rot, and strain 120 AM of *Postia placenta* was selected for brown rot. Six repetitions were performed for each sample set per wood species and per fungi, in the same test conditions.

In this test, samples were weighed three times to obtain W_0, W_1, and W_2 values. For W_0, samples conditioned at 20 ±2 °C and 40 ±4 % of RH were dried in an oven under vacuum for 72 h at 40 °C, 30 in Hg of vacuum, and then weighted. At the end, samples were placed in a desiccator containing P_2O_5 until the sterilization and absorption step.

W_1 was obtained by weighting samples directly after fungal growth was removed from the sample surfaces. W_2 was obtained after the oven drying of these samples exposed to fungal decay. The W_1 weight provides sample humidity content, as it can be the reason for low or high fungal activity. Humidity % was calculated according to the following equation (12).

$$\text{Humidity (\%)} = [(W_1-W_2)/W_2]*100 \quad (12)$$

The weight loss caused by fungal activity is expressed in percentage and calculated according to Eq. 13:

$$\text{Weight loss (\%)} = [(W_0\text{-}W_2)/W_0]*100 \quad (13)$$

With the aim of analyzing the wood chemical compound changes, FTIR analysis was performed before and after exposure

Artificial aging test

Artificial aging is important when testing the suitability of wood for exterior wood products. The aim is to analyze the chemical composition of the wood (white pine and lodgepole pine samples) before and after the exposition to exterior conditions intensified in the laboratory by an artificial aging machine. This part of work was divided in two steps.

The first step consisted of exposing the surface of treated and untreated samples to exterior conditions (sunlight, moisture, heat, atmospheric pollution, biological attack, and saltwater exposure).

Considering the long amount of time that this test would take if performed in a real environment, we opted for an artificial accelerated aging process that offered similar conditions to exterior environment, and is free from any weather phenomena (atmospheric pollution, biological attack, and saltwater exposure). It was performed using a Ci65/Ci65A Xenon Weather-Ometer Atlas Material Testing Technology LLC (USA).

The artificial weathering test was performed according to ASTM G 155-13, "Standard Practice for Operating Xenon Arc Light Apparatus for Exposure of Non-Metallic Materials." Sample dimensions were 30 mm x 30 mm x 10 mm (longitudinal x tangential x thickness).

Treated and untreated samples were conditioned at 8% humidity (20 ±2 °C of temperature and 40 ±4 % of relative humidity) before artificial weathering exposure. The cycle number one of ASTM G 155-13 was used (Table 3). Three replications were prepared for both wood species. The samples tested were selected arbitrarily from a batch of samples of the same species.

Table 3. Parameters of Cycle 1 of ASTM G 155-13

Cycle	Filter	Irradiance (W/m^2. nm)	Wavelength (nm)	Exposure cycle	Time
1	Daylight	0.35	340	Step 1: 102 min light at 63± 3 °C black panel temperature Step 2: 18 min light and water spray	2000 h

In the second step, the chemical degradation of esterified samples (140 °C, 160 °C, and 180 °C) exposed to accelerated weathering was evaluated by FTIR spectroscopy. Spectra were obtained from the surface of the samples.

RESULTS AND DISCUSSION

Weight Percent Gain (WPG), Swelling (α), Shrinkage (β), Anti-Swelling Efficiency, and Anti-Shrinkage Efficiency (ASE) measurement

The interaction of drying time and esterification temperature influences the weight percent gain (WPG) and the dimensional stability (ASE) of treated wood. WPG of treated samples, after conditioning at 20 ±2 °C and 40 ±4% of RH, are represented in Fig. 3. WPG increased with the decrease of drying time and esterification temperature. For the ASE values, the opposite was observed. Average values of ASE decreased when drying time and esterification temperature decreased (Figs. 4.1-2 to 7.1-2).

Considering swelling and shrinkage, the treatment parameters (drying time, esterification temperature) that performed best in terms of dimensional stability were 24 h and 180 °C. This is confirmed for the two different exposure conditions (high RH and water immersion). For the test realized at high RH conditions (20 ±2 °C and 90 ±3% RH for swelling and 50 °C with 15% RH for shrinkage), the best average ASE values, for white pine and lodgepole pine wood samples, were found to be 47.63% and 33.29% respectively for the swelling test and 27.00% and 36.84% for the shrinkage test (Figs. 4.1-2 and 5.1-2). The best average ASE values at swelling test for the white pine and lodgepole pine wood samples were 73.92 % and 59.68 %, respectively, after 10 days of water immersion. However, they were 24.44 % and 43.65 %, respectively, after 24 h of oven-drying at 103 ±2 °C in the shrinkage test (Figs. 6.1-2 and 7.1-2). Statistical analysis was performed, and the difference between treatments is indicated by alphabetic letters placed in Figs. 4.1-2 to 7.1-2. This analysis indicates that in the higher relative humidity conditions test, significant differences between esterification temperatures are observed (Fig. 4.2). On the other hand, in Figs. 6.1-2, there are no significant differences with respect to swelling between drying time parameters and between esterification temperatures parameters in water immersion conditions tests.

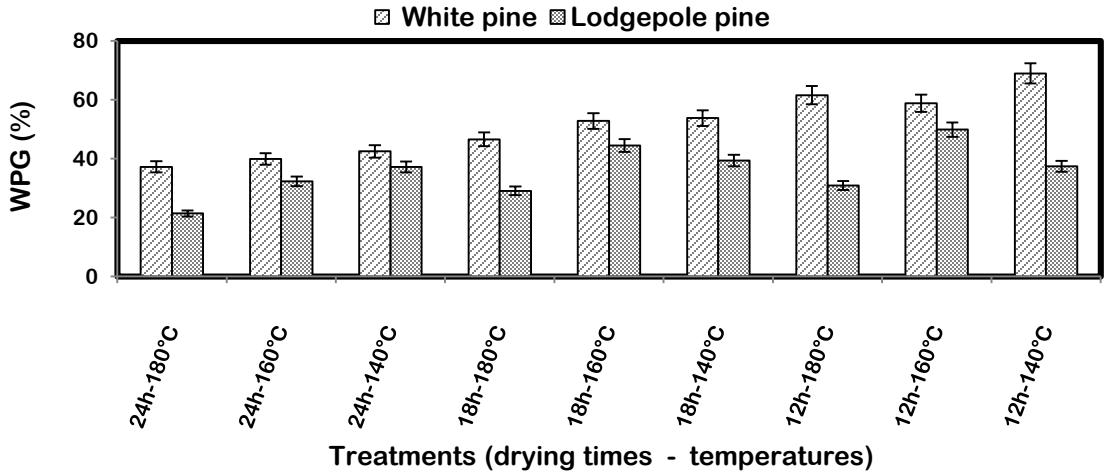


Fig. 3. WPG of white pine and lodgepole pine treated samples

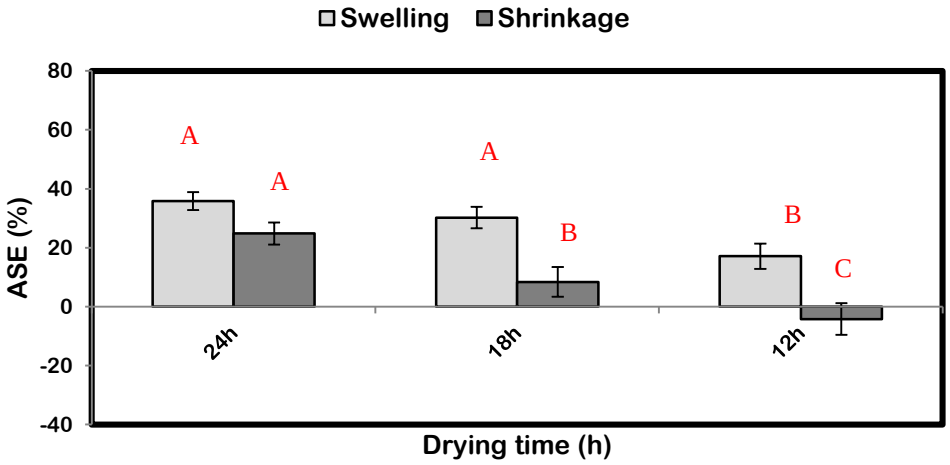


Fig. 4.1 Drying time effect on ASE averages values of white pine wood samples submitted to high Relative Humidity

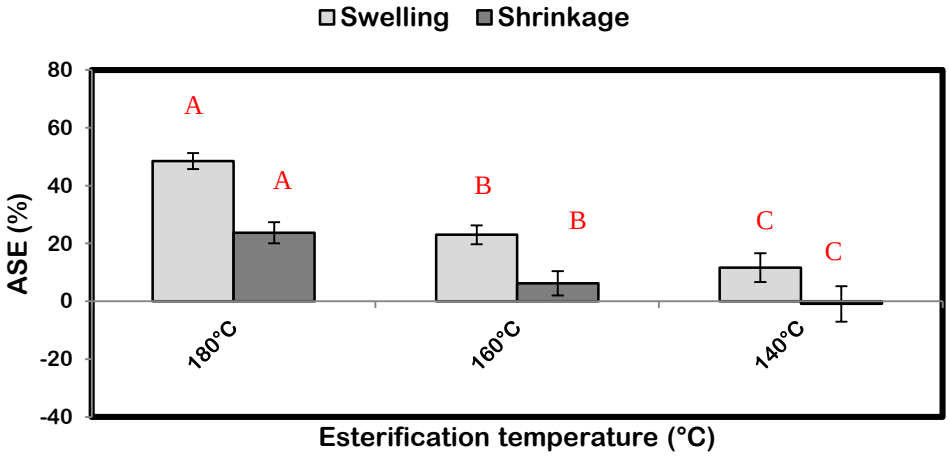


Fig. 4.2 Esterification temperature effect on ASE averages values of white pine wood samples submitted to high Relative Humidity

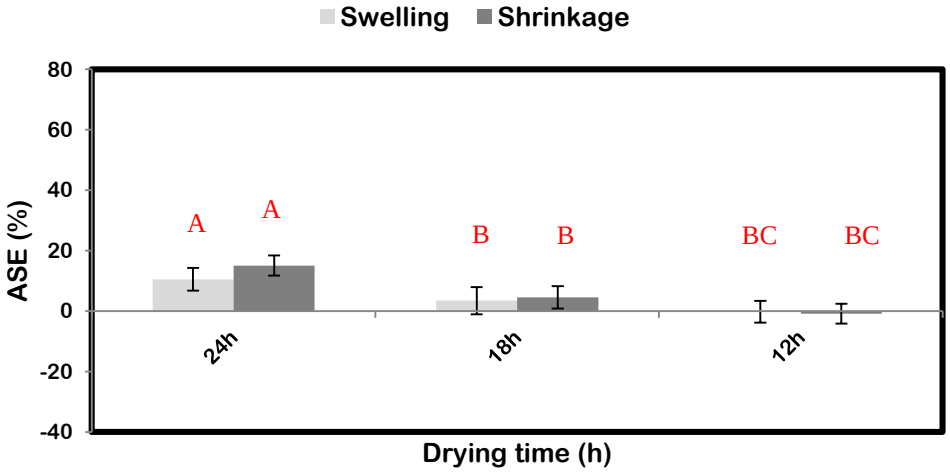


Fig. 5.1 Drying time effect on ASE averages values of lodgepole pine wood samples submitted to high Relative Humidity

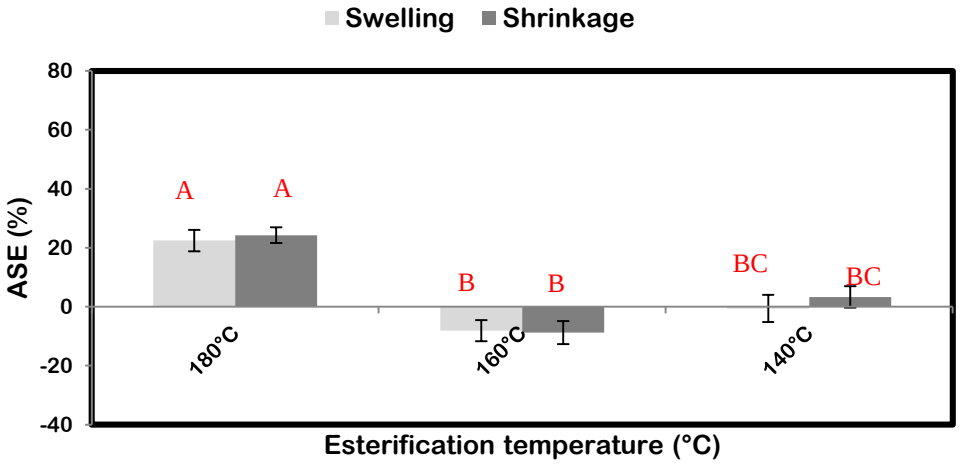


Fig. 5.2 Esterification temperature effect on ASE averages values of lodgepole pine wood samples submitted to high Relative Humidity

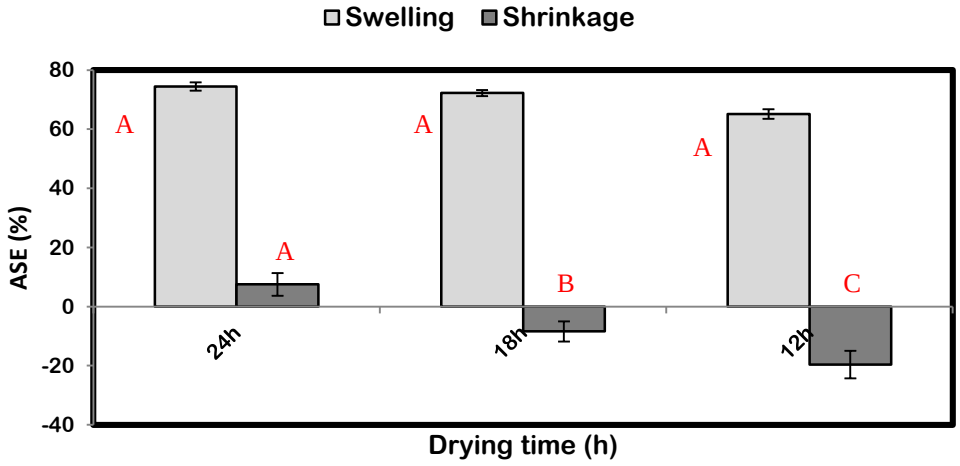


Fig. 6.1 Drying time effect on ASE averages values of white pine wood samples tested by water immersion

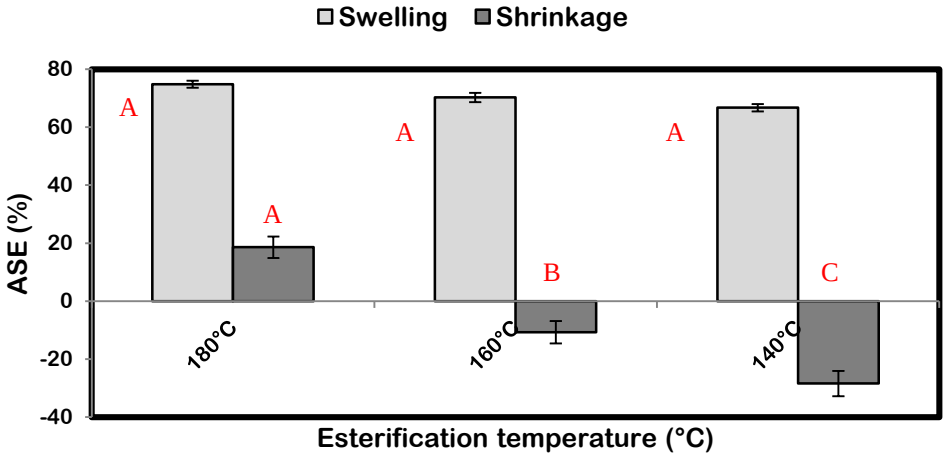


Fig. 6.2 Esterification temperature effect on ASE averages values of white pine wood samples tested by water immersion

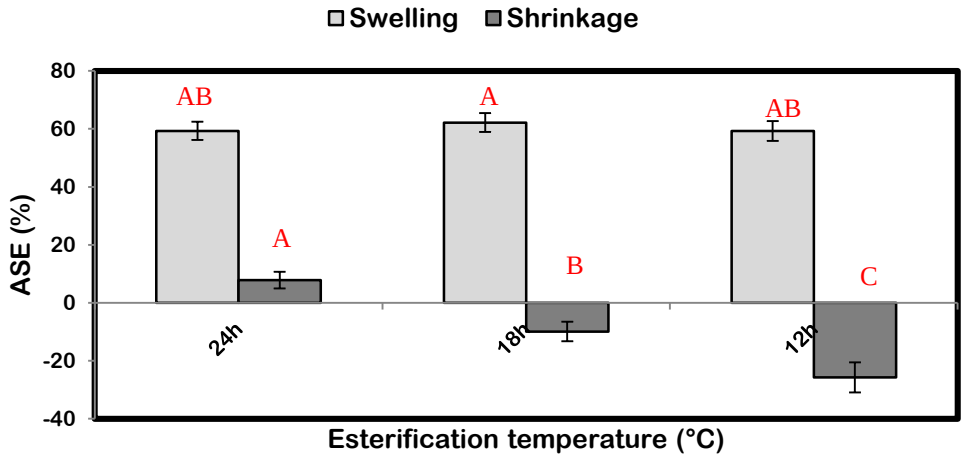


Fig. 7.1 Drying time effect on ASE averages values of lodgepole pine wood samples tested by water immersion

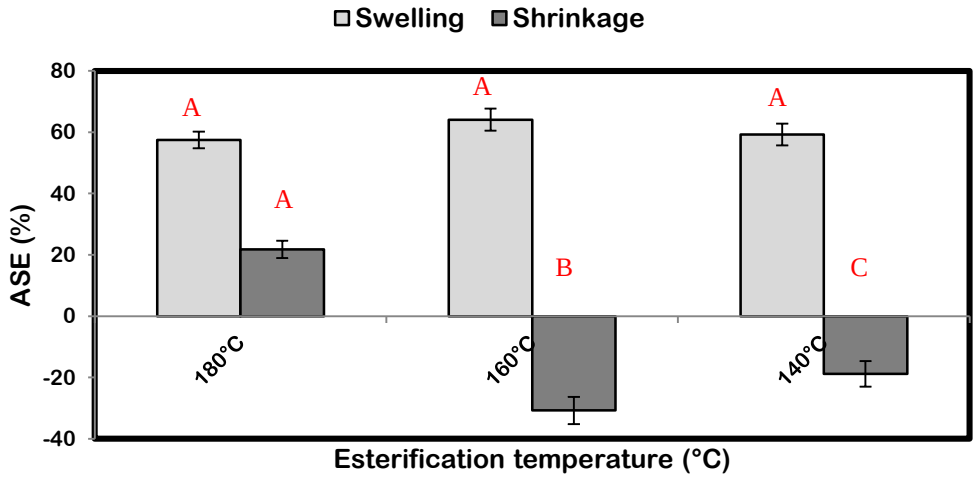


Fig. 7.2 Esterification temperature effect on ASE averages values of lodgepole pine wood samples tested by water immersion

To explain negative values of ASE obtained for both species at the test conditions 20 ±2 °C and 90 ±3 % RH, the equilibrium moisture content of treated and untreated samples was determined. All treatments were considered. Groups of 30 treated samples for each treatment were tested. Sample groups were first conditioned at 25 °C and 90% RH until weight equilibrium. Sample weight was measured and after, all samples were dried at 103 ±2 °C until weight was at equilibrium again. Sample weight was measured once more. Equilibrium moisture content was calculated following the Eq. 14, and values obtained are presented in Fig. 8. A significant difference was found between treatments for each species. Treatment with 24 h of drying time and 180 °C of esterification temperature presented lower equilibrium humidity than the one with 12 h of drying time and 140 °C of esterification temperature. Considering each drying time (24 h, 18 h, and 12 h), the same tendency was observed when esterification temperature decreases and this happens for both wood species.

Equilibrium moisture content = (M_H - M_0/M_0)*100 (14)

The equilibrium moisture content of treated samples was found to be greater than that of the untreated samples. This can explain why treated samples (12 h and 160 °C) were observed to swell much more than untreated ones. This produces negative ASE values (Figs. 4.1-2 and 5.1-2), caused by MA affinity for water molecules. The negative ASE values are also amplified by the presence of MA, which does not react with the wood structure.

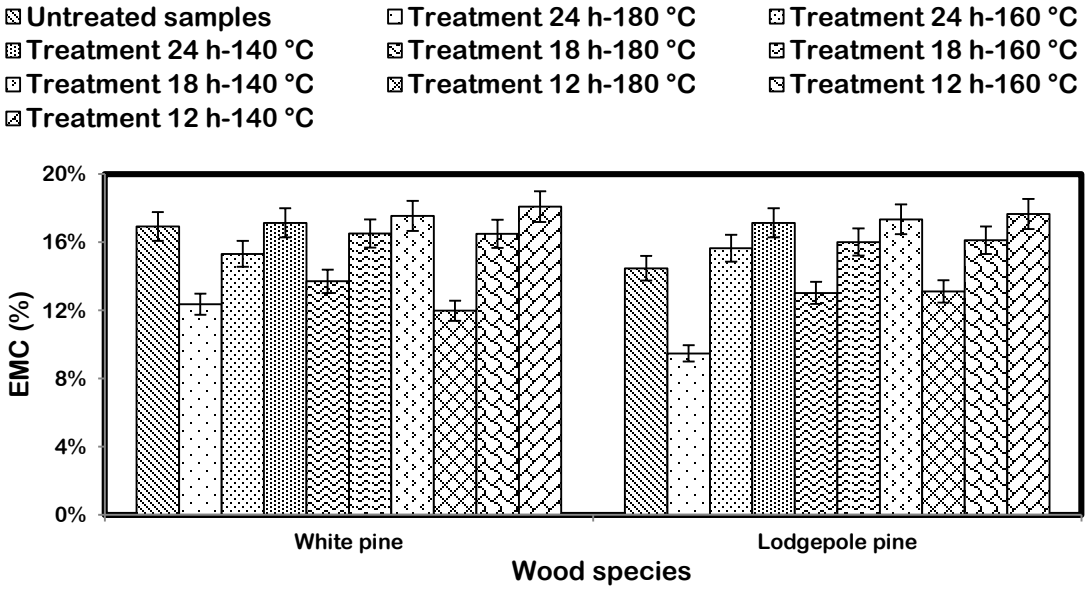


Fig. 8. Comparison of average values of equilibrium moisture content (EMC) of treated and untreated samples exposed in the same conditions.

Shrinkage in both test conditions (24 h oven-drying at 103 ±2 °C and 50 °C with 15% RH), showed negative values of ASE in several treatments. These negatives values were higher in the case of swelling in water immersion for 10 days than in samples conditioned at high RH (Figs. 4.1-2 to 7.1-2). This important loss of ASE indicates loss of sample material (wood macromolecules; principally, hemicellulose macromolecules). Liquid or steam water in contact with maleic anhydride forms maleic acid. When wood samples are treated with maleic anhydride, a percentage of MA was transformed in maleic acid. This loss of MA by hydrolysis is estimated to be around 5.7 % for each 1 % of water contained in wood (Bodîrlau and Teaca 2009).

The maleic acid action in the presence of high temperature can break down wood macromolecules. The instability, from weakest to strongest, starts with hemicelluloses (because of the presence of acetyl groups) followed by the amorphous parts of cellulose and lignin (Bodîrlau *et al.* 2008). According to a study realized by Chuan-Fu *et al.* (2007), a temperature of 101 °C corresponds to the beginning of the first stage of thermal degradation of the wood components. The degradation of hemicellulose to xylose (yield 80 and 90%) by maleic acid (0.2 M concentration) in the presence of temperature starts at

100 °C and finishes at 150 °C (Lu and Mosier 2008). This explains the sample mass loss, and is the reason of ASE loss in the shrinkage test considering that hemicellulose represents around 27 ± 2 % of the dry mass of Nord-American softwood (Stevanovic and Perrin 2009). Observing Figs. 9 and 10, it is possible to notice that generally, average values of ASE at shrinkage decreased with the increase of WPG, with the exception of treatments at 18 h and 12 h drying times at different esterification temperatures for lodgepole pine.

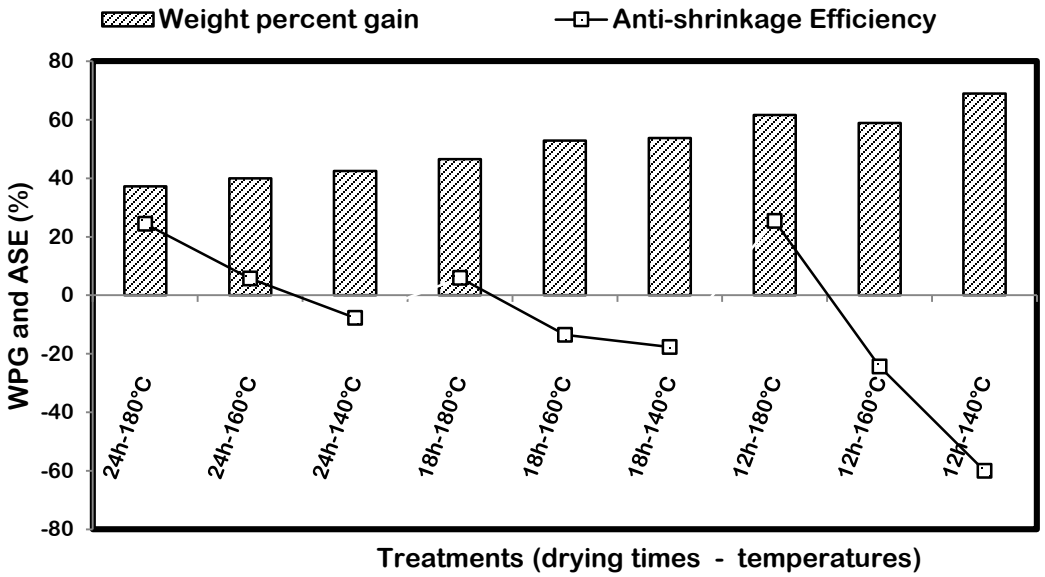


Fig. 9. Relation between WPG and ASE in white pine sample treated

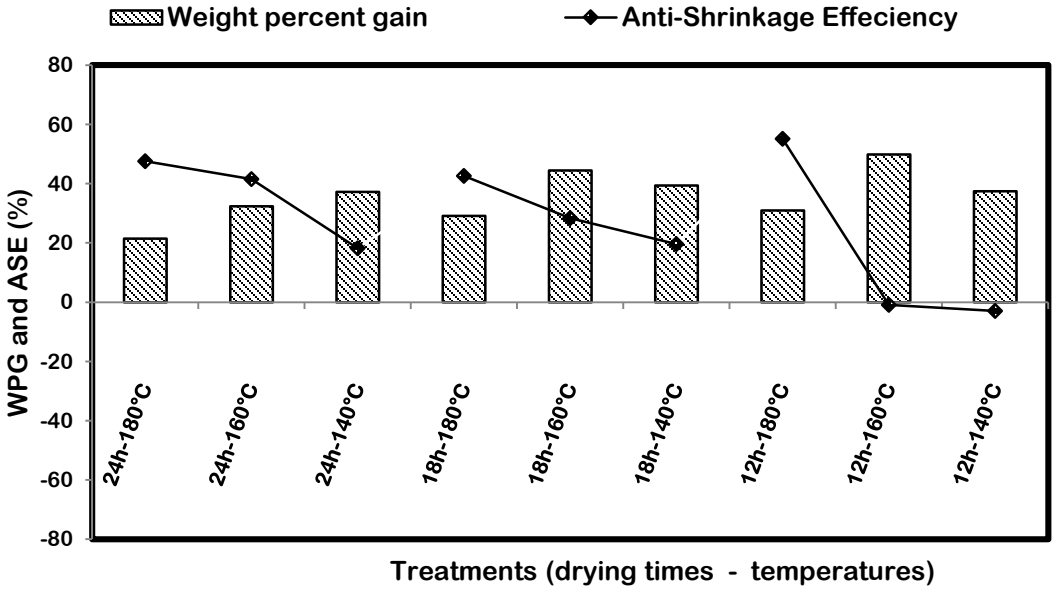


Fig. 10. Relation between WPG and ASE in lodgepole pine sample treated

Fourier Transform Infrared Spectroscopy Analysis (FTIR)

FTIR spectra taken with an attenuated total reflectance accessory in absorbance mode are presented in Fig. 11. They show a broad O-H absorption elongation band occurring in the 3500 to 2600 cm^{-1} region (Chang and Chang 2001). There was a clear difference between the spectra for treated and untreated samples in various regions. The absorbance band of hydroxyl groups (OH) in the region of 3340 to 3370 cm^{-1} presented a higher intensity for untreated samples than treated samples (Yong *et al.* 2010). The intensity of absorbance in this region increased with the decrease of esterification temperature (from 180 °C to 140 °C). All treated samples presented infrared bands between 1730 and 1750 cm^{-1}. This indicates reactions between MA molecules and wood hydroxyl groups to form ester bonds (monoester and/or diester bonds) (Paukszta *et al.* 2014). This contributes to the ASE values obtained. The low intensity band at 1780 cm^{-1} in treated samples confirms the presence of maleic anhydride in the wood structure. This increases when esterification temperature is decreased (De Roover *et al.* 1995). The band between 1627 and 1640 cm^{-1} corresponds to the -CH=CH- vibration of maleic acid or anhydride (Matsuda 1987). The intensity of this band also increased when esterification temperature decreased.

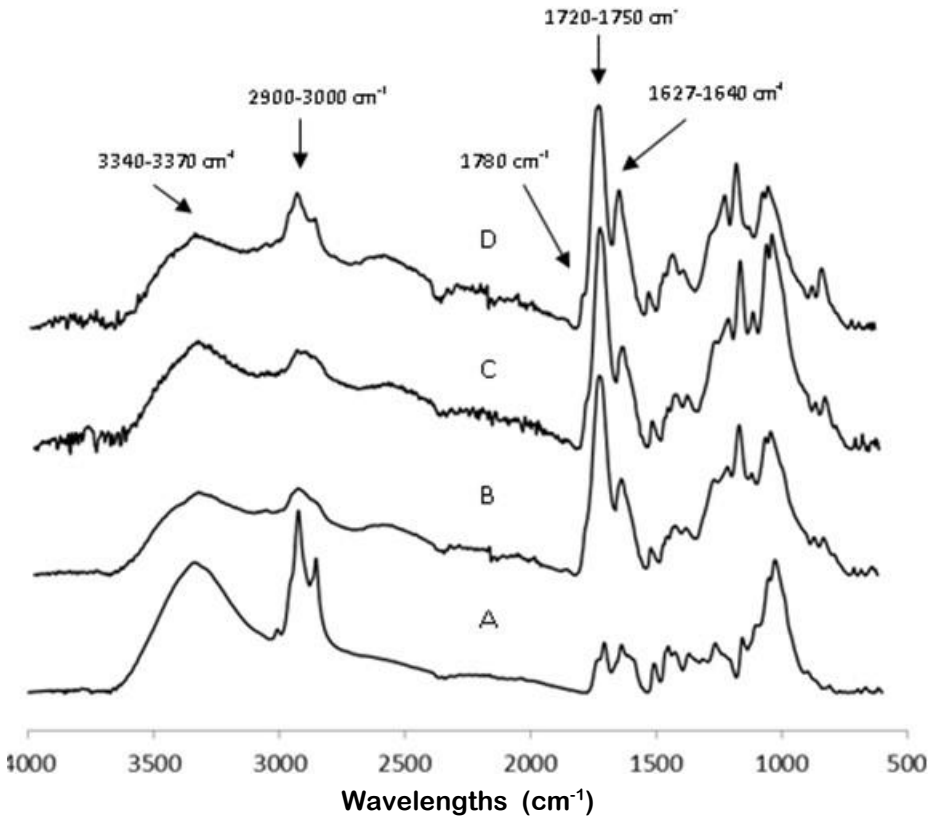


Fig. 11. FTIR spectra of untreated and treated samples (Wp and Lp) oven-dried for 24 h at 103±2 °C. (A) Untreated samples, (B) esterified at 180 °C, (C) esterified at 160 °C, and (D) esterified at 140 °C

Structure Characterization with SEM

After the swelling and the shrinkage tests, treated samples with the best dimensional stability were selected to perform SEM observations. The aim of this analysis was to highlight the temperature effect on the MA remaining in the ring-spaces of the cellular structure. All samples were oven dried for 24 h after impregnation, and esterified at different temperatures. SEM images present similar cell wall structure between untreated and treated samples (Yong *et al.* 2010); however, the images show an important difference between cell lumen spaces. The quantity of MA presents inside the ring-spaces of cellular structure decreased with the increase of esterification temperature at the same drying time (Fig. 12). This can explain why weight percent gain (WPG) of treated samples decreased when esterification temperature increased. This observation was the same for both wood species.

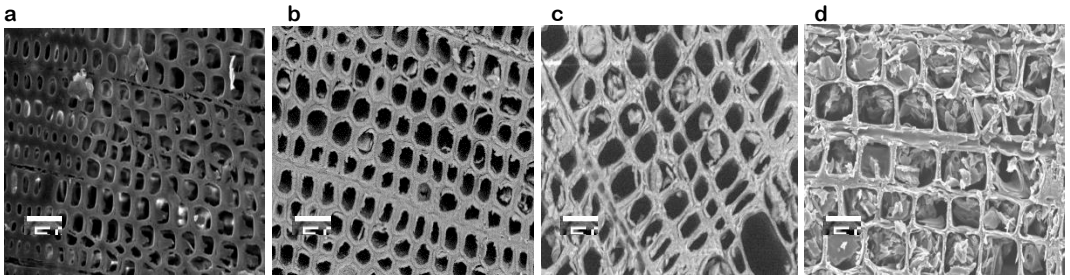


Fig. 12. (a) untreated sample (b) treated at 180 °C (c) treated at 160 °C and (d) treated at 140 °C

Mono and Diester Concentration

The proportions of mono and diesters calculated are presented in Table 4. The percentage of monoester was higher than the diester. This is because the formation of the monoester bonds starts at 90 °C (Otera and Nishikido 2010). A higher percentage of monoester in both wood species was observed following the treatment for 24 h at 140 °C. In the case of diester bonds, a higher percentage was found after treatment for 24 h at 180 °C which corresponds to the best ASE performance. For each drying time factor, at an esterification temperature of 180 °C, the sample presented less WPG, less percentage of monoester bonds, and higher percentage of diester bonds than samples esterified at 160 °C or 140 °C. For the better effect on dimensional stability, diester bonds are better than monoester. This is because the monoester presents a free carboxylic acid group, which can form a hydrogen bond with water molecules. So, the monoester bonds increases the weight of samples with less effect on dimensional stability. In fact, monoester bonds increase the complexity of the wood network structure.

Table 4. Results for Percentage of Mono and Diester Bonds

Wood species	Treatment		WPG (%)	Monoester (%)	Diester (%)
	Drying time (h)	T. (°C)			
Lodgepole pine	24	180	21.41	6.55	6.59
		160	32.31	15.77	3.24
		140	37.24	18.09	2.33
	18	180	29.08	16.52	2.56
	12	180	30.91	10.99	4.41
White pine	24	180	37.25	12.11	3.26
		160	39.91	15.40	2.28
		140	42.49	21.64	1.79
	18	180	46.58	16.29	1.15
	12	180	61.58	20.14	1.14

Leaching Medium Test

The results from the leaching test are presented in Table 5. The MA leaching medium is expressed in percent of the sample's WPG. It was found that MA loss increased with the decrease of the esterification temperature in the case of Lp wood samples. For the Wp wood samples, higher leaching was obtained from samples esterified at 160 °C than those at 180 °C and 140 °C. For the first pH values of leaching waters of all samples, there was a clear difference between samples of both species, esterified at different temperatures. This can be explained by two reasons. The first is that the loss of MA solution during the esterification process increased with temperature. The second one is that the minor leaching of MA indicated that MA formed more ester bonds with the wood structure. After the sixth day of immersion, the pH of leaching waters of all samples started to become more similar (Fig. 13).

Table 5. Average Percentage Values of MA Leached in Water

Species	White pine			Lodgepole pine		
Esterification temperature (°C)	180°C	160°C	140°C	180°C	160°C	140°C
Leaching medium of MA (%)	31.36	44.53	40.92	7.86	39.85	59.77

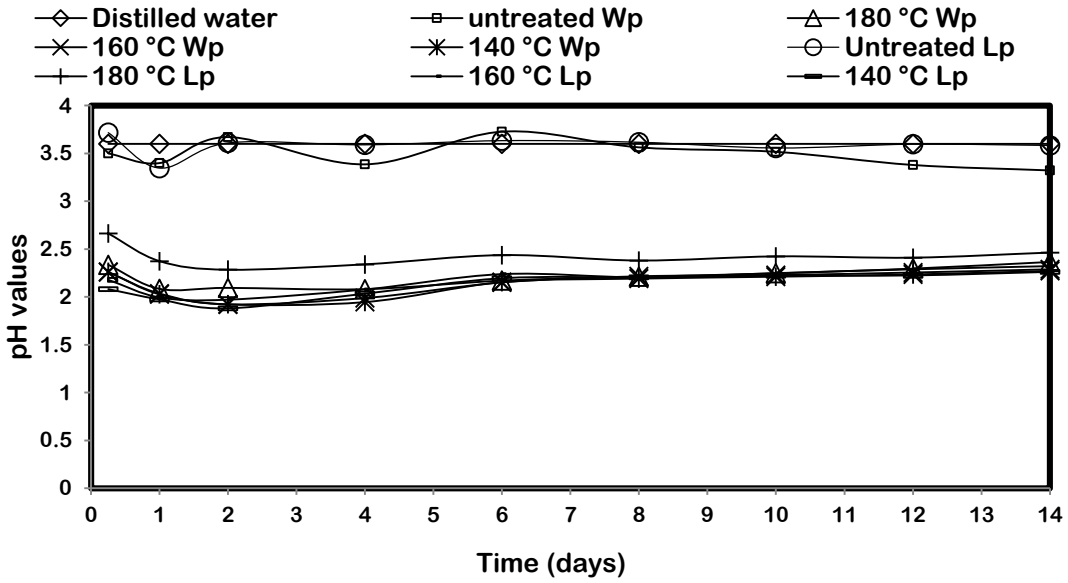


Fig. 13. Average values of leaching water pH

Decay Test

At the end of the incubation period, treated and untreated samples were removed from the culture bottles. Mycelium present on the surface of samples was carefully removed. Untreated samples were completely covered with mycelium, whereas the treated samples were lightly covered or not covered at all by mycelium. At the end of fungi exposition, treated samples exhibited a high percentage of moisture content, as shown in Table 6. This high moisture content influences and reduces fungal action.

After the drying and the weighing step, the samples were submitted to a visual evaluation. Untreated samples of both wood species presented deformations. The treated samples were free of visual degradation.

A representation of WL versus WPG is presented in Fig. 14. The results indicate that, when esterification temperature decreased, WPG and WL increased. These results were valid for both wood species and fungi used. The WL observed was not caused only by the fungal action but also by the loss of MA in wood samples structure during the drying step.

Table 6. Average Weight Loss Values for Fungi and Wood Species per Treatment

Fungi	Treatment	WPG (%)		Humidity (%)		Weight loss (%)	
		LP	PB	LP	PB	LP	PB
Irpex lacteus	untreated	-	-	53.02	73.50	6.43	-3.29
	24h-180°C	27.36	38.17	102.59	108.00	1.60	1.89
	24h-160°C	36.76	42.14	120.52	119.09	9.78	2.66
	24h-140°C	52.36	52.94	130.09	128.00	17.55	7.03
Postia placenta	untreated	-	-	53.02	51.37	32.49	33.44
	24h-180°C	20.65	37.82	96.82	114.79	1.09	3.84
	24h-160°C	35.53	42.27	114.04	121.78	9.32	8.20
	24h-140°C	46.49	48.99	125.89	127.26	15.74	9.51

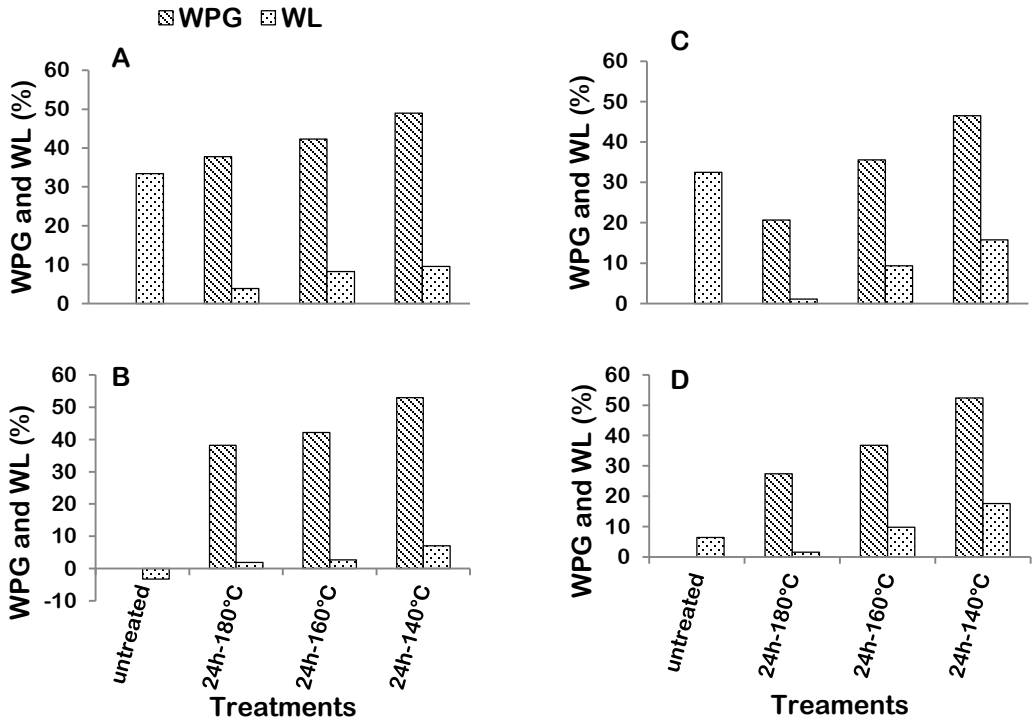


Fig. 14. Effects of WPG average values on WL average values for each treatment. Graphics (A), (B), (C), and (D) represent, fungi strain PP in WP samples, fungi strain IL in WP samples, fungi strain PP in LP samples, and fungi strain IL in LP, respectively.

As shown in Fig. 15 and Table 7, the relative intensities of holocellulose and lignin bands show an important change between exposed and unexposed samples. These changes were observed for both species and both fungi. For the lodgepole pine wood samples, the relative intensities of holocellulose bands decreased with fungal exposure. For the lignin components, the intensity of bands between 1515 and 1504 cm^{-1} increased, while the intensity of the band between 1260 and 1234 cm^{-1} decreased with exposure to fungi. For Wp samples, the intensity of the holocellulose bands (1740 to 1730 cm^{-1} and 1170 to 1153 cm^{-1}) decreases while that of the lignin band at 1510 cm^{-1} increased with fungal exposure. The relative intensity of holocellulose bands between 1740 and 1730 cm^{-1} presented a rapid reduction for treated samples when compared to the other peaks (Li *et al.* 2011). In the case of Lp, the band between 1260 and 1234 cm^{-1} increased for unexposed samples and decreased for all esterified samples. In Wp samples, lignin components presented an increasing absorbance with fungi exposition, which is in accordance with what was found by Li *et al.* (2011).

Regarding fungi aggressiveness on wood compounds, the strain of *Irpex lacteus* (IL) was more aggressive on the lignin component than *Postia placenta* (PP) at lignin band 1260 to 1234 cm^{-1} for Lp samples (Koyani and Rajput 2014). This was verified for Wp samples in the case of untreated samples only (Niemenmaa *et al.* 2008; Yelle *et al.* 2008;

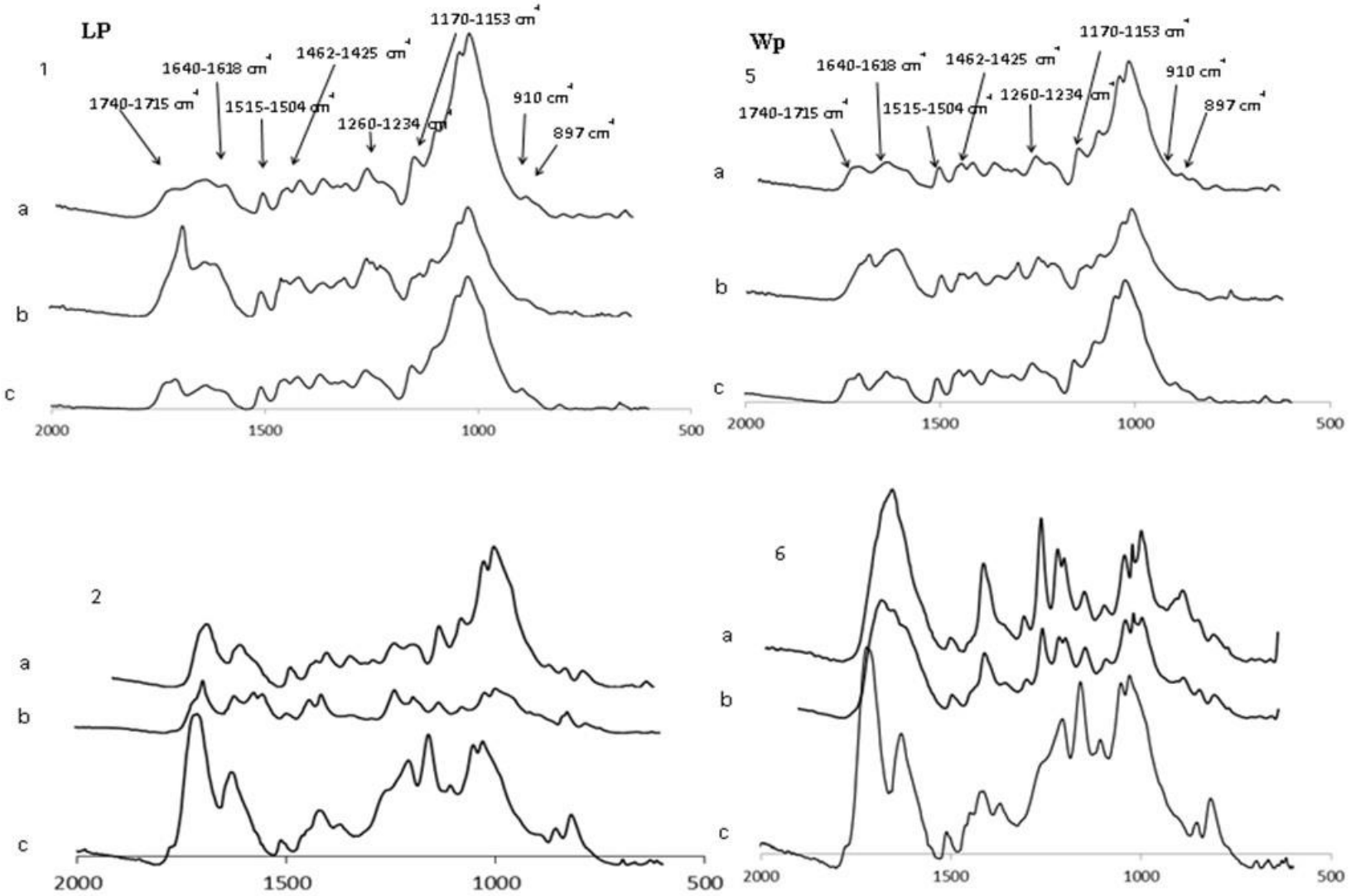
Wymelenberg *et al.* 2010). On holocellulose, fungus actions were shared (Wymelenberg *et al.* 2010). In the case of holocellulose for both wood species, the fungi strain of PP was more active on untreated samples and samples esterified at 140 °C compared to the other esterification temperatures (160 °C and 180 °C). Absorbance values increase with esterification temperature (140 °C, 160 °C, and 180 °C) in the case of Lp for peaks at 1740 to 1730 cm^{-1} and 910 cm^{-1} and for both fungi strains. For Wp, this was not observed.

Artificial Aging Test

Before and after exposure for 2000 h, the chemical composition of the exposed surface was analyzed by FTIR. Two different scales of absorbance were used to exhibit the peaks of the spectra. Spectra in Fig. 11 present an absorbance axis with 1.2 as the maximum value, whereas spectra in Figs. 14 and 15 present an absorbance axes with the maximum value at 10. The FTIR spectra of all treated samples exhibited an increasing intensity absorption in the region of O–H stretching after 2000 h, when compared with spectra of the same samples before exposition. This indicates that treated samples absorbed water molecules, which are represented generally by a band around 1647 to 1600 cm^{-1}. All treated samples presented bands in the range of 1700 to 1750 cm^{-1}. The presence of bands in this wavenumber range indicates an esterification reaction occurring through ester bonds between MA and the wood hydroxyl groups (Carlborn and Matuana 2005). This range corresponds to carbonyl groups absorption. The range near 1725 to 1750 cm^{-1} is related to ester carbonyl absorption and suggests the formation of diester bonds (Matuana *et al.* 2001). This test indicates that the absorption intensity decreased in the region of 1725 to 1750 cm^{-1} when the esterification temperature decreased (Fig. 16 and 17). This highlights the effect of high esterification temperature on the quantity of ester bonds formed. These spectra indicate that the surface degradation of esterified samples is more important at 140 °C than 180 °C (esterification temperatures). Treatment improves resistance to ageing and this was better when treatment resulted in a higher quantity of ester bonds.

Table 7. Wavenumber and Absorbance Values of Holocellulose and Lignin for Untreated and Treated Samples of Both Wood Species (Lp and Wp)

Wood samples	Incubation time (weeks)	Samples treated and untreated	Fungal strains	Holocellulose							Lignin	
				Wavelengths (cm^{-1})								
				1740-1730	1462-1425	1384-1346	1170-1153	897	1640-1618	910	1515-1504	1260-1234
				Absorbance (a.u)								
Lodgepole pine	0	untreated	-	-	1.670	1.802	2.246	1.062	1.146	0.999	1.128	1.973
	10	untreated	IL	-	1.870	1.913	3.132	1.031	1.821	0.999	1.195	2.489
	10	untreated	PP	-	1.768	1.486	1.768	0.757	2.396	0.766	1.110	2.524
	0	140°C	-	8.109	2.814	1.983	7.491	1.351	5.211	1.419	0.839	3.873
	10	140°C	IL	2.759	1.877	1.652	3.358	1.180	2.295	1.107	0.951	2.348
	10	140°C	PP	1.558	1.710	0.876	1.571	0.584	1.900	0.706	0.953	1.989
	0	160°C	-	10.197	2.456	1.959	8.343	1.777	5.003	1.961	0.748	4.828
	10	160°C	IL	3.926	1.717	1.514	3.471	1.196	2.383	1.212	0.890	2.633
	10	160°C	PP	4.186	2.478	1.641	3.773	1.435	3.096	1.541	0.970	3.468
	0	180°C	-	8.988	2.071	2.055	7.609	2.153	3.371	2.328	0.854	4.538
	10	180°C	IL	4.083	1.512	1.427	3.731	1.166	2.093	1.271	0.942	2.819
	10	180°C	PP	5.357	1.891	1.644	4.489	1.639	2.698	1.785	0.900	3.773
White pine	0	untreated	-	-	1.576	1.565	2.098	0.972	1.389	0.941	1.170	1.882
	10	untreated	IL	-	1.374	1.347	2.113	0.821	1.330	0.782	1.139	1.634
	10	untreated	PP	-	1.276	1.109	1.507	0.450	2.440	0.441	1.162	1.975
	0	140°C	-	9.168	2.939	2.414	8.261	1.607	5.805	1.730	0.900	4.116
	10	140°C	IL	3.230	4.663	1.658	3.241	3.262	5.636	3.006	0.934	5.990
	10	140°C	PP	3.750	3.033	1.590	3.276	1.787	4.169	1.692	0.973	3.816
	0	160°C	-	12.414	2.418	2.388	9.805	2.097	5.327	2.167	0.840	5.532
	10	160°C	IL	4.970	2.020	1.722	4.208	1.145	3.350	1.180	0.916	3.225
	10	160°C	PP	4.075	1.839	1.576	3.530	1.078	3.596	1.113	0.892	2.694
	0	180°C	-	9.451	1.836	1.661	7.583	1.582	4.646	1.715	0.840	4.313
	10	180°C	IL	3.616	5.671	1.909	3.327	3.524	5.902	3.389	1.040	7.066
	10	180°C	PP	5.692	1.879	1.690	4.699	1.256	3.172	1.331	0.963	3.568


LP
1
1740-1715 cm⁻¹
1640-1618 cm⁻¹
1515-1504 cm⁻¹
1462-1425 cm⁻¹
1260-1234 cm⁻¹
1170-1153 cm⁻¹
910 cm⁻¹
897 cm⁻¹
a
b
c
2000
1500
1000
500
Wp
5
1740-1715 cm⁻¹
1640-1618 cm⁻¹
1515-1504 cm⁻¹
1462-1425 cm⁻¹
1260-1234 cm⁻¹
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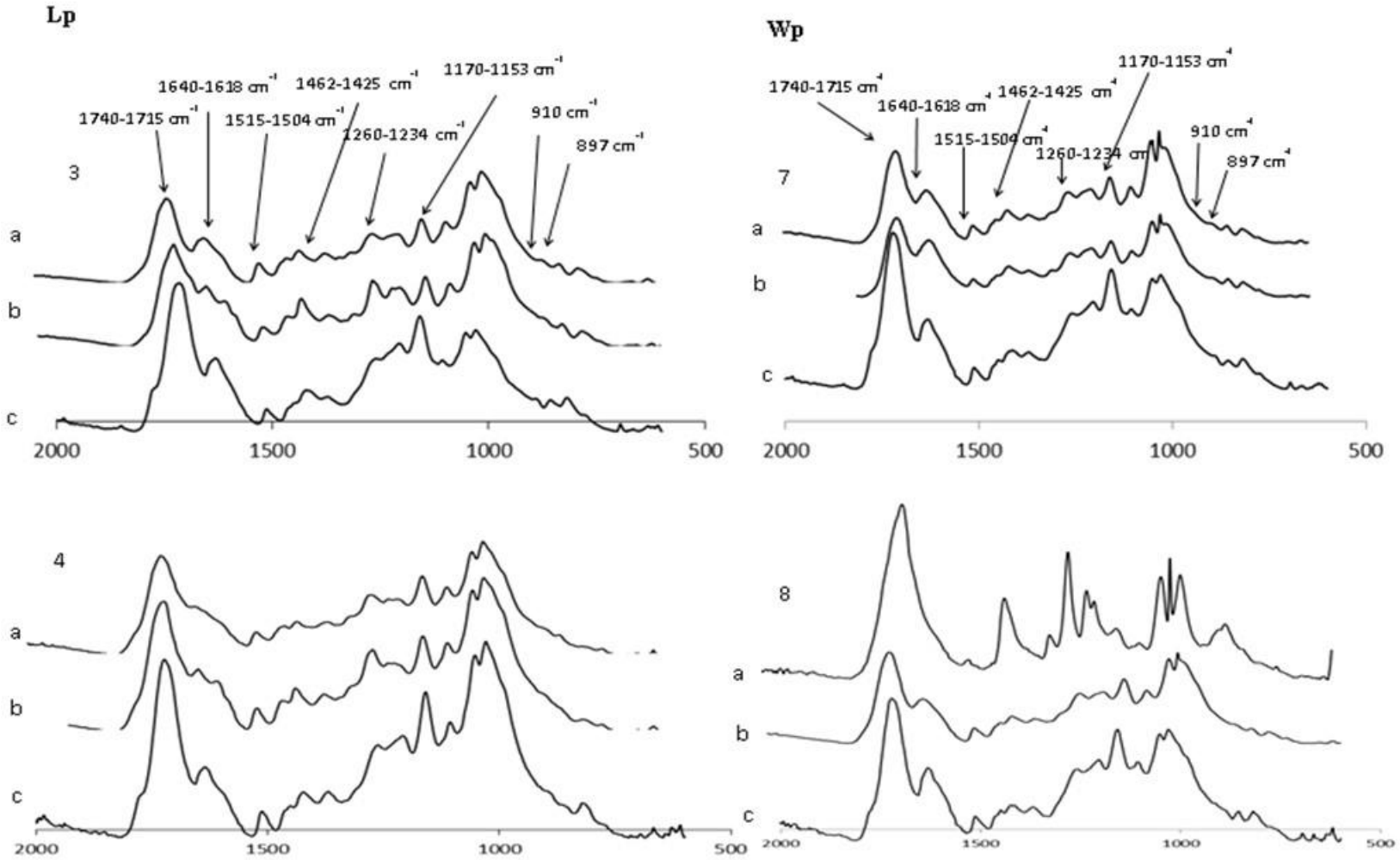

Fig. 15. FTIR of unexposed and exposed samples treated and untreated

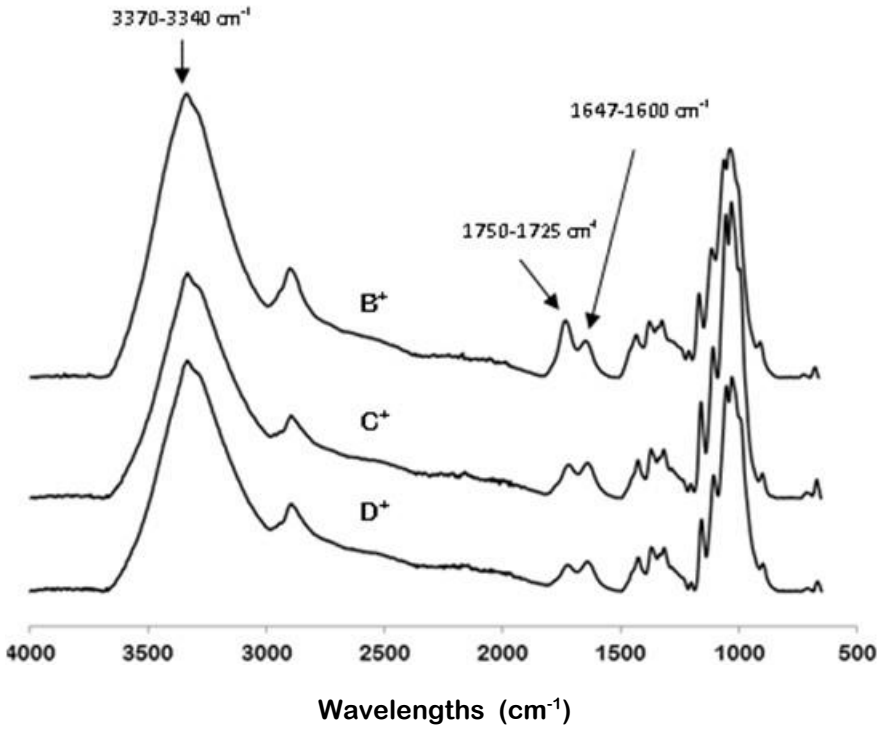

Fig. 16. FTIR spectra of lodgepole pine wood-MA after 2000 h of artificial aging exposition. (D^+) esterification at 140 °C, (C^+) esterification at 160 °C, and (B^+) esterification at 180 °C

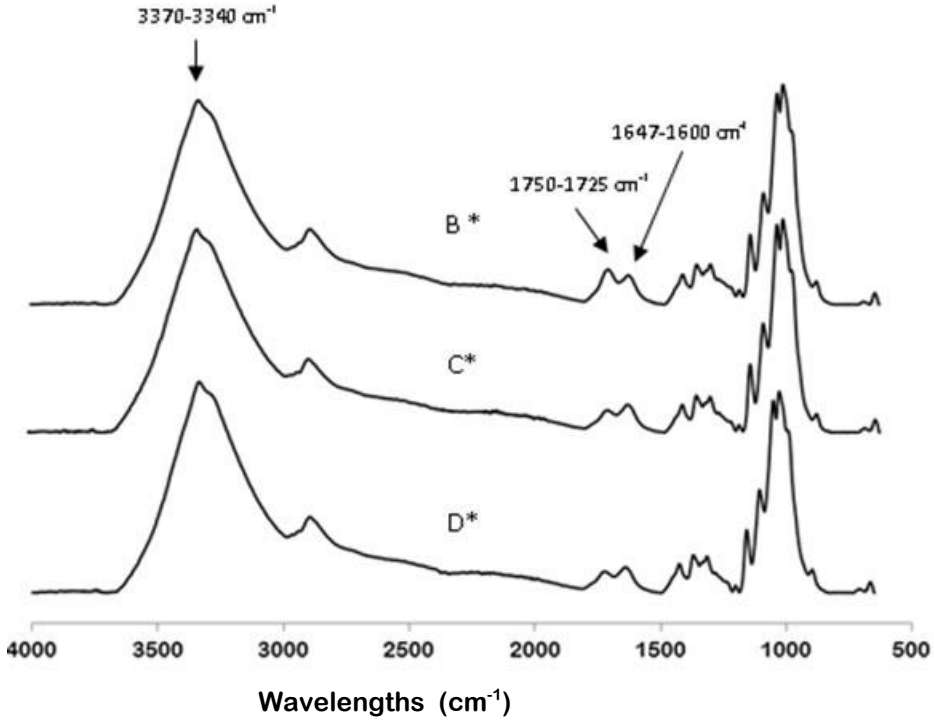

Fig. 17. FTIR spectra of white pine wood-MA after 2000 h of artificial aging. (D*) esterification at 140 °C, (C*) esterification at 160 °C and (B*) esterification at 180 °C

CONCLUSIONS

1. The esterification treatment was found to improve the technical performance of wood (dimensional stability, fungal degradation, and artificial aging). For the dimensional stability, the two parameters studied presented a clear general trend. For the treated samples, weight percent gain decreased with the increase of esterification temperature and drying time. Anti-swelling efficiency and anti-shrinkage efficiency (ASE), values were higher for samples esterified at 180 °C than the one esterified at 160 °C and 140 °C. This was the same for the drying time parameter and for both wood species.
2. Fourier transform infrared spectroscopy confirmed the formation of ester bonds between maleic anhydride (MA) and the wood structure. This explains the dimensional stability observed in the case of treated samples compared to untreated samples. This performance was higher when the percentage of diester bonds increased. Image obtained by SEM analysis showed the presence of free MA in the wood structure. It was observed that, at the same drying time (24 h), samples esterified at 180 °C presented less free MA in the cell lumen than samples esterified at 140 °C. This free MA contributed to water moisture uptake in comparison to untreated wood.
3. Regarding the decay test, the MA treatment improved the fungal resistance in comparison to untreated wood. With FTIR spectroscopy analysis, the effect of esterification temperature on wood resistance was not clearly present. However, the weight loss analysis indicated that the weight loss increased with the decreases of esterification temperature. Observation of weight percent gain and weight loss of treated samples presented the same trend. Weight percent gain and weight loss both increased when esterification temperature was decreased. The weight loss obtained after the decay test was the result of fungal action and MA convert to maleic acid. Part of this acid was loosened during the last drying step. This step was performed at the end of the fungal exposure.
4. Treatment improved the resistance to aging action. A higher quantity of diester bonds was present in wood after treatment at high esterification temperatures, which imparted higher resistance to aging.
5. Esterification temperature and drying time parameters showed an influence on wood's physical and chemical performance. This performance can be attributed to the complementarity of two reaction mechanisms: bulking cell cavities and the formation of ester bonds. The bulking cell cavities was due to free MA in the wood structure, which decreased the pH of the wood and reduced the uptake of water. Bulking also limited the fungal action. Diester bonds, formed between wood hydroxyl groups and carboxylic group of MA, reduced the availability of wood hydroxyl groups to uptake of water molecules. In future work, it would be interesting to see the effects on wood performance after the reduction of free MA in wood structure after impregnation through more than 24 h of oven drying time.

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